Unusual Reactivity of Bent Acenes: Reactions of [6](1,4)Naphthalenophane and [6](1,4)Anthracenophane with Electrophiles

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Abstract: The unusual reactivity of [6](1,4)naphthalenophane (**2**) and [6](1,4)anthracenophane (**3**), the smallest-bridged acenophanes hitherto known, in electrophilic reactions has been disclosed. These reactions include (i) acid-catalyzed telomerization, (ii) peracid oxidation, and (iii) addition with dienophiles. Semi-empirical molecular orbital calculations (MNDO and MNDO/PM3) were performed in order to compare the geometries, energies, and bonding characters of **2** and **3** with those of [6]paracyclophane (**1**). The calculations predict that the deformation of the bridged aromatic ring increases in the order of **1** < **2** < **3**. On the other hand, the strain energy decreases in this order. Also, the calculations predict the following structural features (i–iii) in the deformed aromatic rings of **1–3**, although these predictions should be viewed with appropriate caution. (i) The π bond order of the bridgehead bond a of [6]paracyclophane (**1**) is smaller than that of the reference compound **4**. (ii) On the other hand, the corresponding π bond orders of **2** and **3** are larger than those of the planar molecules **5** and **6**, respectively, despite the fact that an overlap of the π orbitals is less favorable because the aromatic ring is bent into a boat shape. (iii) Moreover, inspection of the π bond orders and the bond lengths of the unbridged aromatic rings of **2** and **3** suggests that the bridged rings of **2** and **3** are disconnected as 4π systems from the unbridged rings which have more 6π and 10π character than **5** and **6**, respectively. Treatment of **1** with an acid (H_2SO_4 or trifluoroacetic acid) afforded the isomers **7** and **8**. When the reaction was performed under concentrated conditions, the dimer **9** formed along with **7** and **8**. On the other hand, naphthalenophane **2** afforded the dimers **10** and **11** predominantly, along with a small amount of the trimers **12** and **13**. In the case of anthracenophane **3**, only the trimers **14** and **15** were obtained even when the reaction was undertaken under dilute conditions. The structure of **14** was elucidated by X-ray crystallographic analysis. The stabilities of the arenium ion intermediates **21–23**, formed by ipso protonation of **1–3**, and those of **24–26**, derived by the 1,2-shift of the bridge of **21–23**, respectively, and the proton affinities of **1–3** were estimated by PM3 calculations. The anomalous reactivity of **2** and **3** toward acid is explained in terms of (i) the relative stabilities of **21–26** and (ii) the affinities in nucleophilic attack of **1–3** to the carbocation intermediates like **21–23**. The molecular structure of the naphthalenophane dimer **10**, which possesses a [6](1,3)naphthalenophane subunit, was determined by single-crystal X-ray analysis, and the geometries were compared with those of the [5]metacyclophane **30** and the oxa[6]metacyclophane **31** as well as those calculated by the MNDO and PM3 methods. Oxidation of **2** and **3** with *m*-chloroperbenzoic acid readily took place to give the bridged dienones **34** and **35**, their overoxidation products **36** and **38**, and the hydroxy esters **37** and **39**, respectively, while cyclophane **1** gave only the dimer of the bridged dienone **33**. The inefficiency toward bridge migration in the epoxides **40** and **41**, the precursors of **34**, **35**, **37**, and **39**, is ascribed to the difference in the relative stabilities of the cation intermediates involved in the isomerization and/or addition processes. The dienones **34** and **35** showed no hint of enolization to their bridged phenol isomers. Treatment of **1** with tetracyanoethylene (TCNE) gave the Diels–Alder adduct **42** as the sole product. On the other hand, naphthalenophane **2** gave the [2 + 2] adduct **43** with TCNE. In the case of anthracenophane **3**, the [2 + 2] adduct **44** was obtained as the sole product in CH_2Cl_2, while in benzene the [4 + 2] adduct **45** was also obtained as a minor product. X-ray crystallographic analysis of **45** was undertaken in order to provide structural information for the [6]paracyclophane system free of perturbation by the carbonyl substituent(s). With dicyanoacetylene (DCNA), **1** gave the [4 + 2] adduct **47**, while the adduct **48**, a [4 + 2] adduct between [6]metacyclophane (**27**) and DCNA, was obtained as a minor product when the reaction was done in CH_2Cl_2. In contrast, naphthalenophane **2** and anthracenophane **3** afforded the [2 + 2] adducts **49** and **51** as sole products in CH_2Cl_2. The cyclopropane-containing products **50** and **52** were also obtained in benzene along with the [2 + 2] adducts. The [2 + 2] cycloadducts **43**, **44**, **49**, and **51** are probably derived through zwitterion intermediates like **46**. The formation of the cyclopropane-containing products **50** and **52** is explained in terms of an ene-like reaction or through diradical intermediates like **53**. Naphthalenophane **2** reacted with dimethyl acetylenedicarboxylate (DMAD) in CH_2Cl_2 to give the lactone **54**, while **1** did not react with DMAD. Reaction of **3** with DMAD yielded the lactone **55** and the 2:1 adduct **56** in CH_2Cl_2. In benzene, the cyclopropane-containing product **57** was also obtained along with **55** and **56**. The formation of the lactones **54** and **55** and the 2:1 adduct **56** is explained in terms of a mechanism involving zwitterion intermediates like **58**. The anomalous reactivity of **2** and **3** toward dienophiles is ascribed to the high double bond character of the 1,2-position of the aromatic rings and to the low ionization potentials.

The chemistry of highly strained cyclophanes possessing a short bridge has been intensively investigated during the past several years.[1-5] As for the [*n*]paracyclophane series, [6]paracyclophane (**1**) is the smallest representative that is stable at room temperature.[1] The distortion of the aromatic ring as well as the hexamethylene bridge of this system has been clarified by the X-ray crystallographic analyses of some crystalline derivatives.[1c,2] We and others have investigated the unusual chemical properties associated with the strain imposed on the benzene ring and the bridge as well.[1c,2a] Much less has been clarified for the lower homologues, [5]- and [4]paracyclophanes, because of their lability at temperatures above 0 °C. While the former was characterized by ^1H NMR spectra at low temperature,[3] the latter was only detected at 77 K by electronic spectra or intercepted as the adduct of an alcohol.[4] With regard to the meta series, Bickelhaupt and

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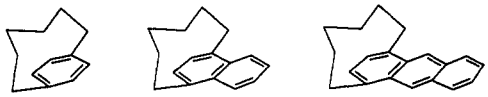
co-workers prepared [5]metacyclophane and its derivatives,[5] which are the smallest ones in this series that are stable at room temperature. They also reported the molecular structure of a dichloro derivative[5b] and some notable reactivity of this system.[5d,e] It has thus been well documented that the reactivity of short-bridged cyclophanes is remarkably different from that of the unstrained planar molecule, i.e., benzene. For example, strained cyclophanes undergo facile thermal[1c,5a] and photochemical[1c,2a,5e] isomerization either by cleavage of the bridge or valence bond isomerization of the benzene ring. Strained cyclophanes are also reactive toward electrophiles because the HOMO levels of these molecules are higher than those of the unstrained planar counterpart. Namely, cyclophanes undergo acid-catalyzed rearrangement to more stable isomers[1c,5e] Diels–Alder ([4 + 2]) cycloaddition with strong dienophiles,[1c,2a,5e,6] 1,2- and/or 1,4-addition of bromine to the benzene ring,[1c,2a] epoxidation of the benzene ring with peracid,[1c] carbene addition to the benzene ring,[7] and so on. Moreover, some unusual reactions of [5]metacyclophane derivatives toward nucleophiles are reported,[5d] which can be ascribed to the relatively low LUMO levels of this system. In the thermodynamic sense, a large amount of strain released during the initial stages of the reaction apparently plays a key role in most of the above reactions.

Recently, we prepared the hexamethylene-bridged naphthalene and anthracene compounds, [6](1,4)naphthalenophane (**2**) and [6](1,4)anthracenophane (**3**), the smallest-bridged cyclophanes with an acene core, and we reported on the spectroscopic and structural studies.[8] Since naphthalene and anthracene are more

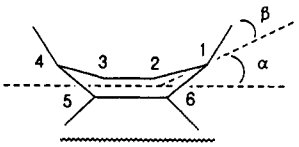


1 2 3

reactive than benzene because of their lower ionization potentials and partial bond fixation,[9] it is expected that the bridged acenophanes **2** and **3** will be more reactive than the benzenophane **1**. Indeed, during the course of our investigations on the reactivity of **2** and **3**, we have found many unusual reactions for them, which have been unknown not only in the chemistry of acenes but also in cyclophane chemistry.[10] In this paper, we report the unusual reactivity of **2** and **3** in reactions with electrophiles: (i) acid-catalyzed telomerization, (ii) peracid oxidation, and (iii) addition with dienophiles.

Calculated Geometries and Energies of [6](1,4)-Bridged Cyclophanes 1–3. Before disclosing the reactivity of cyclophanes **1–3**, it is appropriate to discuss their geometries and energies. Although the molecular structures of **3** and some derivatives of **1** were reported, the structures of the parent systems of **1** and **2** were unknown. In order to compare the geometries and strain energies, semi-empirical molecular orbital calculations were undertaken using the MNDO and MNDO/PM3 methods.[11] The MNDO calculations of **1** have already been reported.[12] The heats of formation, ionization potentials, strain energies, which were estimated using Benson's standard group increments,[13] and deformation angles of the aromatic ring (α and β, see Table I for the definition) are listed in Table I. Some experimental values are also shown for comparison.

Table I. Calculated Heats of Formation, Ionization Potentials, Strain Energies, and Deformation Angles of [6](1,4)-Bridged Cyclophanes **1–3**

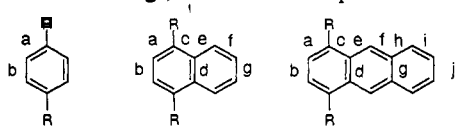


compd		$\Delta H_f°$, kcal/mol	SE,[a] kcal/mol	IP, eV	deformation angle[b] α, deg	β, deg
1[c]	PM3	30.9	36.2	8.77	23.2	16.8
	MNDO[12]	39.1	44.7	8.68	25.3	16.4
	exptl			8.00[12]	19.5[2a]	19.9[2a]
					19.4[2b]	20.0[2b]
2	PM3	48.5	37.5	8.36	25.2	15.8
	MNDO	56.5	44.5	8.30	28.6	13.8
	exptl			7.33[8]		
3	PM3	68.3	41.2	8.07	25.7	15.5
	MNDO	75.5	48.3	8.01	29.8	12.7
	exptl			6.95[8]	21.0	19.5

[a] Strain energies were estimated using Benson's standard group increments (ref 13). [b] The deformation angles for **2** and **3** are the averages of those of two angles, since the structures of **2** and **3** are not symmetrical. [c] C_2 symmetry imposed structure.

It should be noted that PM3 gives geometries which are in better agreement with the observed structures than MNDO. It has already been pointed out that the MNDO method tends to predict aromatic bond lengths longer than those observed and to overestimate nonbonded interactions.[14] The calculations predict that the strain energies of **1–3** increase in the order of **1 < 2 < 3**. The bending angle of the para carbons (α) increases in the order of **1 < 2 < 3**, while that of the benzyl carbons (β) decreases in the order of **1 > 2 > 3**. This is in accord with the observed bending angles determined by X-ray crystallographic analyses of the derivatives of **1** and **3**. These observations imply that it becomes easier to bend the aromatic ring with an increasing number of aromatic rings; in other words, the aromatic ring becomes more flexible in this order.

In Table II are listed the aromatic bond distances and the π bond orders of **1–3**, which are derived by PM3 calculations. Also shown are those of the corresponding 1,4-dimethyl aromatics **4–6** with planar aromatic rings, as reference compounds. Comparison



of the calculated bond lengths of **3** with those observed by X-ray

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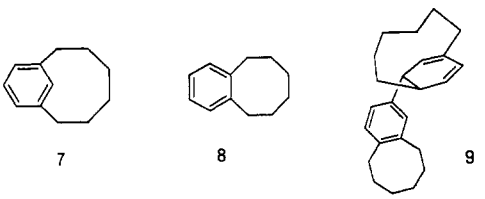
Table II. Bond Lengths and π Bond Orders of the Aromatic Rings of [6](1,4)-Bridged Cyclophanes **1–3** and 1,4-Dimethyl Aromatics **4–6** Calculated by MNDO/PM3

compd	bond a	b	c	d	e	f	g	h	i	j
					Bond Length,[a] Å					
1	1.402	1.388								
4	1.395	1.388								
2	1.376	1.417	1.437	1.410	1.412	1.375	1.408			
5	1.373	1.410	1.430	1.415	1.422	1.368	1.411			
3	1.369	1.426	1.448	1.426	1.387	1.406	1.416	1.428	1.362	1.422
exptl[8]	1.371	1.432	1.443	1.445	1.398	1.405	1.432	1.422	1.377	1.389
6	1.365	1.420	1.442	1.426	1.398	1.396	1.419	1.433	1.360	1.425
					π Bond Order[a]					
1	0.423	0.498								
4	0.442	0.467								
2	0.636	0.295	0.198	0.399	0.311	0.586	0.331			
5	0.618	0.293	0.245	0.385	0.267	0.631	0.293			
3	0.702	0.237	0.144	0.286	0.492	0.351	0.334	0.217	0.686	0.244
6	0.691	0.230	0.183	0.302	0.421	0.409	0.305	0.195	0.713	0.222

[a] The values for bonds a, c, e, f, h, and i are the averages of values for two bonds.

crystallographic analysis indicates the PM3 method nicely predicts the structure of this deformed aromatic molecule. As shown in Table II, there is an apparent trend in the difference between the bond lengths and the π bond orders of **1–3** and those of the respective reference compounds **4–6**, although the absolute difference is relatively small. Moreover, the calculated structures of cyclophanes **1–3** should be discussed with appropriate caution, taking into account the reliability and the accuracy of the calculations. It is pointed out by Bickelhaupt that bent benzene rings in small [*n*]cyclophanes are full-fledged aromatics based on the ring current criterion determined by NMR methods and the fact that their unusual reactivity is mainly due to their high strain energy that is relieved in the initial stage of the reactions.[15] Despite these arguments and the limitation in the calculations, we are inclined to point out the following view: (i) The length of the bridgehead bond a of **1** is longer than that of **4**, while the length of bond b is the same. Similarly, the π bond order of bond a of **1** is smaller, but that of bond b is larger, than that of **4**. This trend is in agreement with that observed in the ab initio calculations for the bent benzene structures.[16] This indicates that bridgehead bond a becomes weaker while bond b becomes stronger by bridging the para positions of benzene with a hexamethylene chain and is understood to be a consequence of poor overlap of the π orbitals in bridgehead bond a. (ii) In contrast, in the case of **2** and **3**, the π bond orders of bond a of **2** and **3** are larger, but those of bond c are remarkably smaller, than those of **5** and **6**, respectively. The π bond orders of bond b of **2** and **3** remain similar to those of **5** and **6**. As for the bond lengths, all of the bonds a–c of **2** and **3** are longer than those of **5** and **6**, respectively, but the difference is somewhat small for bond a. These results indicate that the bridgehead bonds of **2** and **3** possess greater double bond character than planar molecules despite unfavorable overlap of the π orbitals due to bending of the aromatic ring. (iii) Moreover, inspection of the π bond orders and bond lengths in the unbridged rings of **2** and **3** reveals that the bond length alternation characteristic to planar naphthalene and anthracene decreases in the bent acenes **2** and **3**, respectively. Namely, the π bond orders of bond f of **2** and bonds f and i of **3** are smaller than those of the planar references **5** and **6**, while those of bonds e and g of **2** and bonds e, h, and j of **3** are larger than those of **5** and **6**, respectively. The difference in the bond lengths is in accord with this trend. As a result, it becomes apparent that the bridged rings of **2** and **3** are disconnected as a 4π system, i.e., the bridgehead diene systems from the unbridged rings which have more 6π and 10π character than **5** and **6**, respectively. In conclusion, the calculations predict that the bonding of the π systems of **2** and **3** is remarkably different from that of **1**; the π bond orders of the bridgehead bonds of **2** and **3** are larger than those of planar molecules despite unfavorable overlap of the π orbitals.

Acid-Catalyzed Telomerization. It has been well documented that short-bridged cyclophanes undergo facile acid-catalyzed isomerization to more stable isomers because a large amount of strain is released thereby.[1c,5e,17] One notable exception is the $AlCl_3$/HCl-promoted skeletal rearrangement of [2.2.2](1,3,5)-cyclophane, wherein the formation of intramolecular carbon–carbon bonds between the two aromatic rings leads, at least initially, to a less stable isomer.[18] As for the [*n*]paracyclophanes, we reported earlier that the treatment of **1** (5×10^{-2} M in CH_2Cl_2) with a catalytic amount of trifluoromethanesulfonic acid or trifluoroacetic acid (TFA) yielded the corresponding meta and ortho isomers **7** and **8**.[1c]



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With the cyclophanes of shorter bridge, however, 1,4-addition of a carboxylate anion or other nucleophile to the benzenonium ion intermediates competes with isomerization. Namely, (*Z*)-[6]paracycloph-3-ene and [5]paracyclophane gave the 1,4-adducts together with the meta and ortho isomers, respectively,[6,19] and [4]paracyclophane afforded only 1,4-adducts.[4] The above difference in the reactivity toward acid was explained in terms of the charge distribution and the dihedral angle between the empty p orbital and the migrating bond in the benzenonium ion intermediates, which were estimated by MNDO calculations.[19] These observations led us to study the reactivity of **2** and **3** toward acids.[10b]

Initially, the reaction of **2** and **3** with sulfuric acid was examined. Treatment of a fairly concentrated solution of **2** in CH_2Cl_2 (2.7×10^{-1} M) with a catalytic amount of H_2SO_4 gave, to our surprise, the dimers **10** and **11** as major products (72%), which possess meta- and ortho-bridged naphthalene units, respectively. The relative amount of **11** increased as the reaction time was increased, which indicated that **11** was produced by isomerization of **10**. The structures of **10** and **11** were characterized by spectroscopic and analytical properties. Moreover, the structure of **10** was further confirmed by X-ray crystallographic analysis. The molecular structure is shown in Figure 1. As minor products,

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Table III. Acid-Catalyzed Isomerization/Telomerization of [6](1,4)-Bridged Cyclophanes **1–3** with Trifluoroacetic Acid

compd	concn, M	reactn time[a]	product (ratio, yield) isomer	dimer	trimer
1	1.3×10^{-1}	1 h	**7**, **8** (76:24, 35%)	**9** (45%)	nd
	1.3×10^{-3}	15 h	**7**, **8** (70:30, 93%)	nd	nd
2	1.8×10^{-1}	1 min	nd	**10**, **11** (61:39, 43%)	**12**, **13** (71:29, 30%)
	1.8×10^{-3}	30 min	nd	**10** (86%)	**12** (trace)
3	1.3×10^{-1}	40 s	nd	nd	**14**, **15** (87:13, 86%)
	1.3×10^{-3}	20 min	nd	nd	**14**, **15** (89:11, 60%)

[a] In CH_2Cl_2 at room temperature.

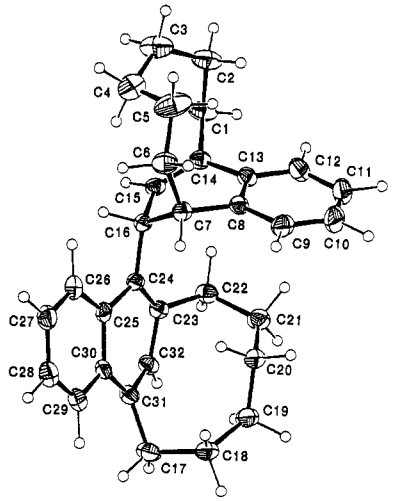


Figure 1. Molecular structure of dimer **10**.

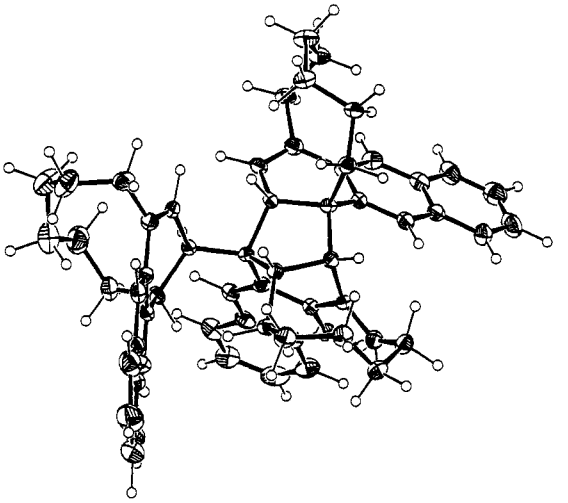
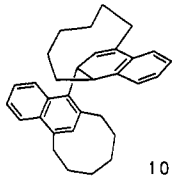


Figure 2. Molecular structure of trimer **14**·$2CH_2Cl_2$. For the sake of clarity, the solvent molecules are not shown.

trimers **12** and **13** (15%) were also isolated. The structures of the trimers **12** and **13** were inferred from the similarities between their ^1H NMR spectra and those of the anthracene trimers **14** and **15** described below. No isomers of **2**, however, were detected.



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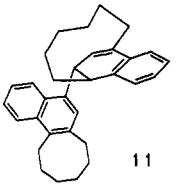

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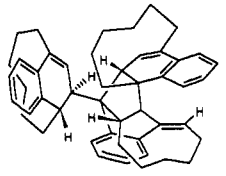

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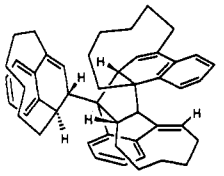

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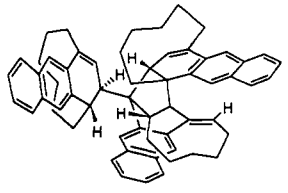
Treatment of **3** under similar conditions (1.5×10^{-1} M) afforded three trimers, **14–16**. No monomeric or dimeric products were detected. The structure of the major trimeric product, **14** (43%), was established by X-ray crystallographic analysis (Figure 2). The structure of a minor product, **15** (8%), is believed to be a stereoisomer of **14**, on the basis of the similarities between the ^1H and ^{13}C NMR spectra of the two compounds (see the Experimental Section). The structure of the third product **16** remains uncertain.



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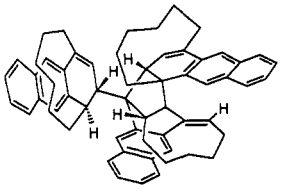


15

The above results prompted us to reexamine the reaction of [6]paracyclophane (**1**) with H_2SO_4 to see whether any dimeric and/or trimeric products were formed. Indeed, when **1** (1.5×10^{-1} M) was treated with H_2SO_4 under similar conditions, the dimer **9** (21%) was obtained as a minor product together with a 1:1 mixture of the isomers **7** and **8** (59%).

In order to examine the effect of substrate concentration, the reaction was undertaken at 10^{-1} and 10^{-3} M using TFA as the acid. The results are summarized in Table III. Cyclophane **1** showed a clear dependence of the product distribution on the concentration. Thus at 10^{-3} M, **1** gave only isomers **7** and **8**, while a considerable amount (45%) of the dimer **9** was formed at 10^{-1} M. Similarly, naphthalenophane **2** gave the dimer **10** almost exclusively under dilute conditions (10^{-3} M), while it gave nearly equal amounts of dimers **10** and **11** and trimers **12** and **13** at 10^{-1} M. No isomers of **2** were detected even when the reaction was run at 10^{-3} M. On the other hand, only trimers **14** and **15** were obtained from anthracenophane **3** even when the reaction was undertaken at 10^{-3} M. No isomers or dimers were detected.

The formation of dimers **9**, **10**, and **11** and trimers **12–15** can be readily explained by positing a series of electrophilic attacks by intermediate cations on the respective substrate, as shown in Scheme I for naphthalenophane **2**. It should be noted that, in the case of **2**, electrophilic attack of ipso-protonated cation **22** on the second substrate molecule to give the dimeric cation **17** predominates over the migration of the hexamethylene bridge. The attack of the dimeric cation **18a**, from which dimer **10** is formed by deprotonation, on the third molecule of the substrate occurs at the ortho position to give the trimeric cation **19**, probably because of the steric hindrance that would arise between two quaternary carbons by the ipso attack. The formation of trimer **12** could also be explained by the reversed order of bond formation: electrophilic attack of cation **18b**, an intuitively less favorable resonance structure of **18a**, to the ipso position to give the trimeric cation **20**. Intramolecular cyclization and deprotonation from either **19** or **20** afford trimer **12**.

In order to explain the anomalous reactivity of **2** and **3** toward acid, MNDO/PM3 calculations[11] are performed for arenium ions **21–23**, which are formed by ipso protonation of **1–3**, respectively.

Scheme I

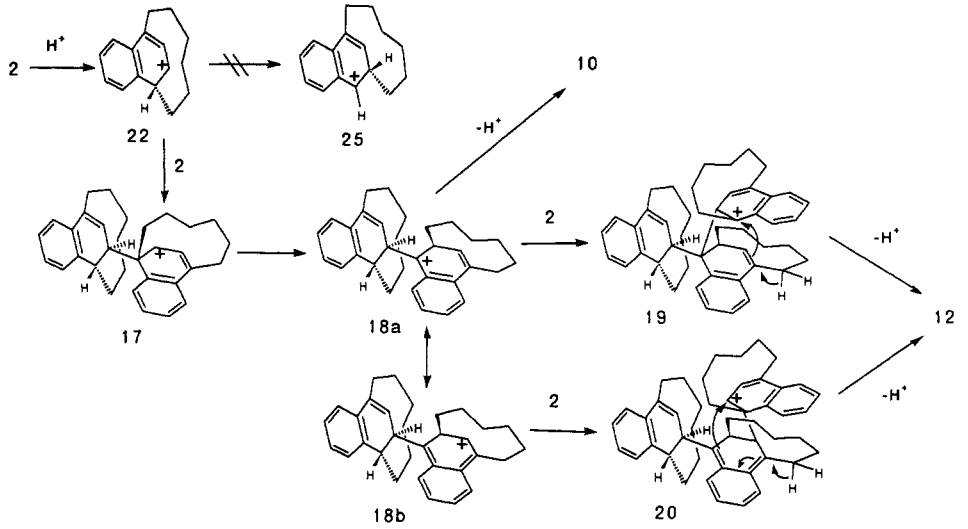


Table IV. Heats of Formation of Arenium Ions **21–26**, Strain Enengies of Arenium Ions **21–23**, and Proton Affinities of Cyclophanes **1–3** and **27–29** Calculated by MNDO/PM3

compd	$\Delta H_f°$, kcal/mol	SE,[a] kcal/mol	cyclophane	proton affinity,[b] kcal/mol
21	196.0	12.1	**1**	202.1
22	202.9	14.0	**2**	212.8
23	217.8	18.4	**3**	217.7
24	197.3		**27**	188.5
25	208.3		**28**	194.9
26	224.5		**29**	196.4

[a] Strain energies were calculated according to the reported procedure using Benson's standard group increments (ref 13), heats of formation of the 1,4-dimethyl aromatics **4–6**, and heats of formation of arenium ions formed by ipso protonation of **4–6** to estimate the electrostatic contribution and the enthalpy of formation of the additional C–H bond (ref 18). [b] Proton affinities of the cyclophanes were calculated using the experimental values: $\Delta H_f°(H^+)$ = 367.2 kcal/mol (see ref 19).

Similarly, PM3 calculations were performed for arenium ions **24–26**, which are produced by a 1,2-shift of the methylene bridge of **21–23**, respectively. The cations **24–26** are also formed by ipso protonation of the corresponding [6](1,3)-bridged benzene ([6]metacyclophane (**27**)), naphthalene **28**, and anthracene **29**. Heats of formation of **21–26** and strain energies of **21–23** are listed in Table IV. Also listed in Table IV are the proton affinities of the corresponding cyclophanes **1–3** and **27–29**. As for the cations **21** and **24**, the MNDO and MINDO/3 calculations have been reported.[19] The strain energies of arenium ions **21–23** increase gradually in the order of **21** < **22** < **23**. This trend is in accord with that observed in the parent hydrocarbons **1–3** (Table I).

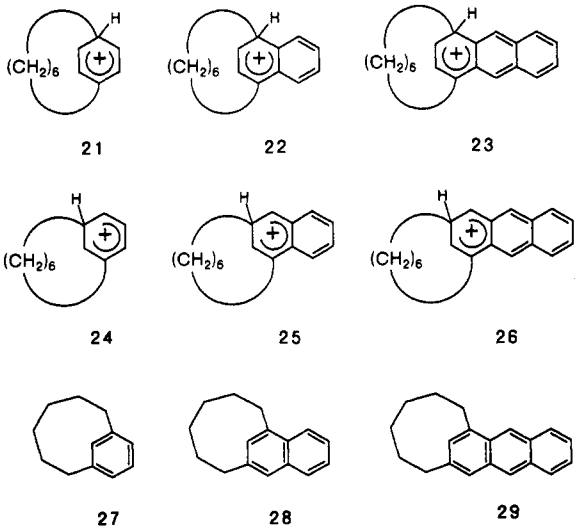
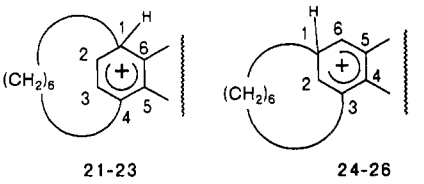


Table V. Net Atomic Charges on Arenium Ions **21–26** Calculated by MNDO/PM3



	atomic charge, z					
compd	C-1	C-2	C-3	C-4	C-5	C-6
21	−0.14	0.11	−0.22	0.30	−0.22	0.11
22	−0.08	0.11	−0.24	0.33	−0.19	0.05
23	−0.06	0.11	−0.24	0.32	−0.20	−0.02
24	−0.14	0.14	−0.17	0.22	−0.20	0.11
25	−0.12	−0.00	−0.12	0.18	−0.18	0.19
26	−0.10	−0.07	−0.09	0.10	−0.19	0.20

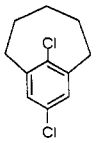
One of the reasons for the unusual reactivity of **2** and **3** is the thermodynamic stabilities of the cation intermediates **21–26**. The results of PM3 calculations show that the heat of formation of the 1,3-bridged benzenonium ion **24** is only slightly larger (1.3 kcal/mol) than that of the 1,4-bridged cation **21**, while the heats of formation of 1,3-bridged arenium ions **25** and **26** are much larger (5.4 and 6.7 kcal/mol, respectively) than those of the corresponding 1,4-bridged cations **22** and **23**. This implies that 1,2-migration of the bridge of **21** is only slightly endothermic, while the migrations of **22** and **23** are considerably endothermic. In order to elucidate the origin of the relative energy difference between 1,4- and 1,3-bridged arenium ions **21–26**, the atomic charge distributions of their bridged rings (C-1–C-6 in Table V) are compared. As shown in Table V, the charge distributions of the 1,4-bridged cations **22** and **23** are different from that of the benzenonium ion **21**; the net charge in one of the ortho positions (C-6) becomes successively negative. In particular, in the case of **23**, there are three consecutive negatively charged carbons (C-5, C-6, C-1) since the charge on C-6 turns slightly negative. Because of electrostatic repulsion between the negative charges, **23** should be more destabilized than **21** and **22** in which the positive and negative charges align alternately.

The difference between the charge distribution of the 1,3-bridged cations **24–26** is more remarkable, especially in the case of **25** and **26** where C-2 turns negative, leading to three consecutive carbons (C-1–C-3) which are negatively charged. As a result, there should be more electrostatic destabilization in **25** and **26** than in **24**. Consequently, it is deduced that the difference in the relative stabilities of arenium ions **21–26** is due to the difference in the charge distribution.

Another reason for the remarkable reactivity of **2** and **3** is

enhanced reactivity in nucleophilic attack toward carbocation intermediates like **22** and **18a,b** (Scheme I). This reactivity can be estimated from the proton affinities of **1–3** listed in Table IV since the nucleophilic reactivity toward the cation intermediates should be related to the proton affinity. As shown in Table IV, the proton affinities of **2** and **3** are larger than that of **1** by about 6 and 11 kcal/mol, respectively. This is supported experimentally by the observation that **2** and **3** react much faster than **1** under similar conditions (see Table III). The larger proton affinities of **2** and **3** than that of **1** stem from both energetic origins, i.e., lower ionization potentials of **2** and **3** than of **1**, and geometrical origins, i.e., larger double bond character in the bridgehead bonds and larger deformation angles in the aromatic rings of **2** and **3** than in those of **1**.

Molecular Structure of [*n*](1,3)-Bridged Cyclophanes. In contrast to the [*n*]paracyclophane series, significantly fewer structural studies have been done for small [*n*]metacyclophanes. The structures of 8,11-dichloro[5]metacyclophane (**30**)[5b] and the 2-oxa[6]metacyclophane derivative **31**[20] so far have been elucidated by X-ray crystallographic analyses. As for the 1,3-bridged



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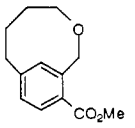


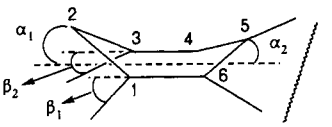
31

cyclophanes with an acene core, [5](1,3)naphthalenophane is hitherto the smallest representative.[21] The higher homologue, [6](1,3)naphthalenophane (**28**), is also known.[22] However, there seems to be no report on the molecular structure of 1,3-bridged naphthaleno- and anthracenophanes, despite the fact that considerable differences in structure and bonding are expected between those of the acenophanes and the corresponding benzene analogues. Since the dimer **10** obtained by the acid-catalyzed dimerization of **2** possessed a [6](1,3)naphthalenophane subunit, we undertook X-ray crystallographic analysis in order to clarify the distortion imposed on this system. We also undertook MNDO and MNDO/PM3 calculations[11] for the 1,3-bridged cyclophanes **27–29** and compared their geometries and energies. The MNDO calculations for **27** have been reported.[14,19] Here we discuss briefly the structures of [6](1,3)-bridged cyclophanes possessing a naphthalene or an anthracene core.

The observed deformation angles (α_1, α_2, and β; see Table VI for definitions) of **10** are listed in Table VI, together with those of **30** and **31** for comparison. Also listed are the heats of formation, strain energies, and bending angles of [6](1,3)-bridged cyclophanes **27–29**. As shown in Table VI, PM3 gave better agreement than MNDO between the calculated geometries of **27** and **28** and those observed for the oxa[6]metacyclophane **31** and the naphthalenophane **10**, respectively, as in the case of the [6](1,4)-bridged cyclophanes **1–3**. The MNDO method predicts considerably larger deformation in α_1 and β. This is attributed to the shortcomings due to overestimation of the nonbonded interactions in the MNDO method.[14]

It can be seen from Table VI that the bending angle α_1 of **10** is comparable to that of the [5]metacyclophane **30** and is substantially larger than that of the benzene analogue **31** having the same number of bridging atoms. However, since the observed deformation angle α_1 of **10** is considerably larger than that calculated by the PM3 method, it seems likely that the large deformation in α_1 of **10** is in part due to the steric effects of the bulky substituent on C4. The other bending angles of **10** are much smaller than those of **30**, probably offsetting the large deformation in α_1. The angles β of **10** are much smaller than those of **31**.

Table VI. Heats of Formation, Strain Energies, and Deformation Angles of [6](1,3)-Bridged Cyclophanes **27–29** Calculated by MNDO/PM3 and Observed Deformation Angles of [*n*](1,3)-Bridged Cyclophanes **10**, **30**, and **31**

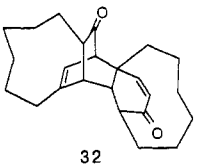


compd		$\Delta H_f°$, kcal/mol	SE,[a] kcal/mol	deformation angle, deg			
				α_1	α_2	β_1[b]	β_2[c]
27	PM3	18.6	23.8	19.5	7.6	20.5	
	MNDO[14a]	26.6	31.9	23.7	7.5	32.9	
28	PM3	36.0	25.0	20.3	8.8	18.6	23.0
	MNDO	43.6	32.6	25.2	8.2	35.2	35.7
29	PM3	56.6	29.4	20.8	9.6	19.2	22.8
	MNDO	63.7	36.5	25.8	8.4	35.1	36.5
10	exptl			25.3[d]	4.6[e]	13.2[f]	18.8[g]
30	exptl[5b]			26.8	12	48	
31	exptl[20]			17.0	6.4	22.9	20.1

[a] Strain energies were estimated using Benson's standard group increments (ref 13). [b] Angle between the base plane (C1–C3–C4–C6) and the C1–benzyl carbon bond. [c] Angle between the base plane (C1–C3–C4–C6) and the C3–benzyl carbon bond. [d] Angle between the plane C23–C24–C30–C31 vs the plane C23–C32–C31 (see Figure 1). [e] Angle between the plane C23–C24–C30–C31 vs the plane C24–C25–C30 (see Figure 1). [f] Angle between the plane C23–C24–C30–C31 vs the bond C17–C31 (see Figure 1). [g] Angle between the plane C23–C24–C30–C31 vs the bond C22–C23 (see Figure 1).

The calculations predict that all of the bending angles gradually increase in the order of **27 < 28 < 29**. Indeed, the overall extent to which the aromatic ring of **10** is deformed into a boat conformation seems to be slightly larger than that of **31**, although the distortion in oxacyclophane **31** would be smaller than that in hydrocarbon **27**, because introduction of an ether linkage in the bridge would release the angle strain imposed on the bridge. The strain energies of **27–29** gradually increase in the order of **27 < 28 < 29** as in the case of the 1,4-bridged cyclophanes **1–3**. Consequently, it becomes apparent from the observed and calculated structures of the 1,3-bridged cyclophanes that the out-of-plane bending in this series increases with an increasing number of aromatic rings, as in the 1,4-bridged cyclophane series.

Peracid Oxidation. It is reported that the aromatic rings of strained cyclophanes suffer from peracid oxidation, though normal aromatic compounds are inert under similar conditions.[17] Previously, we reported that oxidation of [6]paracyclophane (**1**) with *m*-chloroperbenzoic acid (MCPBA) proceeded readily to yield quantitatively the product **32**, a dimer of the meta-bridged dienone **33**.[1c] This reaction should be contrasted with the oxidation of less strained (*E*)-[8]paracycloph-4-ene in which oxidation took place exclusively at the bridge double bond rather than at the aromatic ring.[23] It is reasonable to expect acenophanes **2** and **3** to be more reactive than benzenophane **1** toward oxidation. Moreover, the 1,3-bridged dienones such as **34** and **35** corresponding to **33**, which



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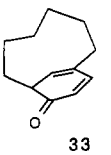

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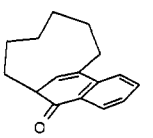

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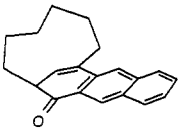

35

(20) Shea, K. J.; Burke, L. D.; Doedens, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5305.
(21) Grice, P.; Reese, C. B. *J. Chem. Soc., Chem. Commun.* **1980**, 424.
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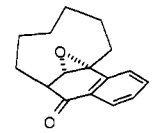
(23) Noble, K.-L.; Hopf, H.; Ernst, L. *Chem. Ber.* **1984**, *117*, 474.

are the keto tautomers of 4-hydroxy[6](1,3)-bridged cyclophanes, would not dimerize due to the benzo and naphtho fusion, respectively. In this connection, we examined the oxidation of **2** and **3** with MCPBA.

When **2** was treated with 1 equiv of MCPBA in CH_2Cl_2 at −78 °C, immediate consumption of **2** was observed. Rapid chromatography gave the unstable 1,3-bridged benzodienone **34** in 27% yield along with the overoxidized epoxide **36** (9%) and the hydroxy ester **37** (26%). Similarly, treatment of **3** with MCPBA (1 equiv) at −78 °C afforded the unstable dienone **35** (27%), epoxide **38** (9%), and hydroxy ester **39** (38%). The 1,3-bridged dienones **34** and **35** are derived from epoxides **40** and **41** (not isolated), respectively, by acid-catalyzed isomerization. The positions of the hydroxyl and the benzoyloxyl groups of **37** and **39**, the products of acid-catalyzed openings of epoxides **40** and **41**, respectively, were not established but only tentatively assigned in the light of the related products obtained by oxidation of [2.2]paracyclophane.[17] It should be noted that the corresponding hydroxy ester was not obtained from **1**, which gave only the dimer of dienone **33**.[1c] The inefficiency toward bridge migration in **40** and **41** is explained in terms of the relative stabilities of the cation intermediates involved in the acid-catalyzed rearrangement and/or addition processes as in the case of the acid-catalyzed rearrangement and/or telomerization of **1**–**3**. The dienones **34** and **35** show no hint of enolization to their bridged phenol isomers because this requires incorporation of an another bridgehead double bond into the systems in which one bridgehead double bond is already present.[24]



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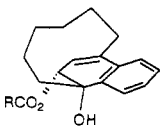
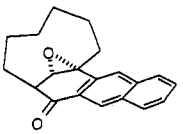


37 R=C_6H_4Cl(*m*)



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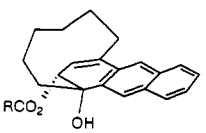
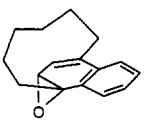


39 R=C_6H_4Cl(*m*)



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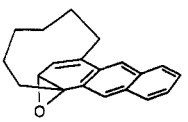
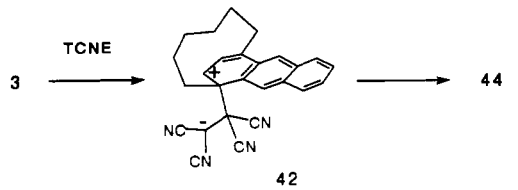


41

Although it has been shown that [6]paracyclophane (**1**) and its derivatives underwent facile addition of bromine in 1,2- and/or 1,4-fashions,[1c,2a] attempted reaction of **2** and **3** with bromine produced a myriad of products which were not investigated.

Addition to Dienophiles. Strained cyclophanes are known to undergo Diels–Alder reaction with strong dienophiles. Thus in the [*n*]paracyclophane series, [8]- and [7]paracyclophanes are reported to give [4 + 2] adducts with hexafluoro-2-butyne, dicyanoacetylene (DCNA), and *N*-phenyltriazolinedione (NPTAD).[25] We found that the [4 + 2] addition of [6]paracyclophane (**1**) with NPTAD and tetracyanoethylene (TCNE) proceeded at room temperature.[1c,6] As for [*n*]metacyclophanes, Diels–Alder reactions of [7]- and [5]metacyclophanes were reported.[5e,25a] It is well documented that acenes are more reactive

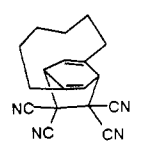
Scheme II



42

than benzene toward [4 + 2] cycloaddition because of the higher HOMO levels as well as the greater degree of partial bond fixation.[9] It is, therefore, not unexpected that the acenophanes with a relatively large bridge undergo [4 + 2] addition with dienophiles. Indeed, [8](1,4)naphthalenophane and [10](1,4)-anthracenophane-4,6-diyne were reported by Wiberg[26] and Misumi,[27] respectively, to react at the unbridged rings to afford [4 + 2] adducts. These observations prompted us to investigate the reactions of **2** and **3**, the smallest-bridged acenophanes, with dienophiles. We undertook reactions of **2** and **3** with TCNE, DCNA, and dimethyl acetylenedicarboxylate (DMAD) as dienophiles and compared the reactivities with that of **1**.[10b] The reactions were performed both in CH_2Cl_2 and in benzene solutions in order to examine the effect of solvent polarity on the reaction. The results are summarized in Table VII.

First, the reaction with TCNE was examined. Although, in all cases, the reaction proceeded at room temperature, the apparent rate of reaction increased in the order of **1** < **2** < **3**. Thus the reactions of **1**, **2**, and **3** were completed in 3.5 h, 1.5 h, and 10 min in CH_2Cl_2 and in 4 days, 2 days, and 30 min in benzene, respectively, under otherwise similar conditions. As reported previously, reaction of **1** with TCNE in CH_2Cl_2 gave the [4 + 2] adduct **42** as the sole product.[6] Similarly, in benzene, **42** was the sole product. On the other hand, naphthalenophane **2** afforded the [2 + 2] adduct **43** exclusively in both solvents (73–74%). In the case of anthracenophane **3**, the [2 + 2] adduct **44** (64%) was obtained as the sole product in CH_2Cl_2, while the [4 + 2] adduct **45** (13%), in which TCNE was added to the 9,10-positions of the anthracene ring, was obtained as a minor product along with **44** (82%) when the reaction was run in benzene. That **43** and **44** were the [2 + 2] cycloadducts with a fused cyclobutane ring at the 1,2-positions of the acene nuclei was elucidated from the NMR spectra. Namely, the ^1H NMR spectra of **43** and **44** involve a vinyl proton doublet (**43**, δ 5.79; **44**, δ 5.91) which couples (J = 7.5 Hz) with a methine proton (doublet, **43**, δ 3.80; **44**, δ 3.86). The ^{13}C NMR spectra of **43** and **44** indicate the presence of three quaternary sp^3 carbons (**43**, δ 56.3, 48.5, 39.6; **44**, δ 56.1, 48.5, 40.0) and one tertiary sp^3 carbon (δ 48.5 both). The formation of the [2 + 2] adducts **43** and **44** represents, to our knowledge, the first example of thermal [2 + 2] cycloaddition of naphthalene and anthracene derivatives. We consider that these are produced through zwitterion intermediates such as **46** shown in Scheme II for the anthracene **3**.



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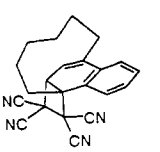
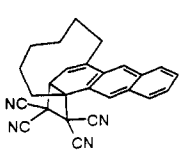
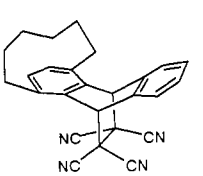


43



44



45

Since the [6]paracyclophane subunit remained unreacted in the [4 + 2] adduct **45**, X-ray crystallographic analysis was un-

(24) While [*n*](1,3)-bridged phenols of $n \geq 7$ have been prepared, those of $n \leq 6$ have been unknown: Prelog, V.; Wiesner, K. *Helv. Chim. Acta* **1947**, *30*, 1465. Prelog, V.; Wiesner, K.; Ingold, W.; Häfliger, O. *Helv. Chim. Acta* **1948**, *31*, 1325. Hirano, S.; Hara, H.; Hiyama, T.; Fujita, S.; Nazaki, H. *Tetrahedron* **1975**, *31*, 2219. Jenneskens, L. W.; van Straten, J. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1984**, *40*, 3117. Jenneskens, L. W.; de Wolf, W. H.; Bickelhaupt, F. *Tetrahedron* **1985**, *41*, 3779.

(25) (a) Noble, K.-L.; Hopf, H.; Jones, M., Jr.; Kammula, S. L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 602. (b) Gassman, P. G.; Bailey, T. F.; Hoye, R. C. *J. Org. Chem.* **1980**, *45*, 2923.

(26) Wiberg, K. B.; O'Donnell, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 6660.

(27) Misumi, S. *Pure Appl. Chem.* **1987**, *59*, 1627.

Table VII. Reaction of [6](1,4)-Bridged Cyclophanes **1**–**3** with Dienophiles

compd	solvent	product (isolated yield)		
		TCNE	DCNA	DMAD
1	CH_2Cl_2	**42** (80%)	**47** (16%), **48** (6%)	
	C_6H_6	**42** (90%)	**47** (66%)	
2	CH_2Cl_2	**43** (74%)	**49** (26%)[a]	**54** (30%)
	C_6H_6	**43** (73%)	**49** (12%), **50** (8%)[b]	
3	CH_2Cl_2	**44** (64%)	**51** (58%)[c]	**55** (23%), **56** (8%)
	C_6H_6	**44** (82%), **45** (13%)	**51** (35%), **52** (22%)[d]	**55** (2%), **56** (28%), **57** (14%)

[a] Dimers **10** and **11** (36%) and trimer **12** (4%) were also obtained. [b] Dimers **10** and **11** (32%) were also obtained. [c] Trimers **14**–**16** (41%) were also obtained. [d] Trimers **14**–**16** (32%) were also obtained.

Table VIII. Crystal Data and Selected Refinement Parameters for X-ray Crystallographic Analyses of **10**, **14**, **45**, **52**, **54**, and **56**

compd	**10**	**14**	**45**	**52**	**54**	**56**
recryst solvent	pet. ether/ether	CH_2Cl_2	ether/CH_2Cl_2	pet. ether/ether	pet. ether/ether	methanol
formula	$C_{32}H_{36}$	$C_{60}H_{60}\cdot 2CH_2Cl_2$	$C_{26}H_{20}H_4\cdot C_4H_{10}O$	$C_{24}H_{20}N_2$	$C_{21}H_{22}O_4$	$C_{32}H_{32}O_8$
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/a$	$P2_1/c$	$P2_1/a$	$C2/c$
a, Å	12.751 (4)	16.499 (3)	13.253 (5)	9.645 (2)	14.096 (4)	27.755 (5)
b, Å	11.551 (4)	14.299 (4)	11.708 (6)	17.120 (4)	7.835 (3)	13.836 (3)
c, Å	9.592 (2)	11.106 (2)	15.392 (3)	11.433 (4)	16.492 (3)	15.170 (2)
α, deg	109.95 (3)	100.61 (2)				
β, deg	96.82 (3)	88.03 (2)	92.85 (2)	104.22 (2)	104.87 (2)	90.62 (2)
γ, deg	63.67 (2)	77.26 (2)				
V, Å^3	1189.3 (6)	2469.0 (9)	2385 (2)	1830.1 (7)	1760.4 (8)	5615 (2)
Z	2	2	4	4	4	8
d_{calcd}, g cm^{-3}	1.175	1.279	1.286	1.221	1.277	1.289
no. of data collected	3520	7326	5985	5810	4522	4161
no. of unique data	3176	5258	5746	5519	4361	2932
R	0.116	0.108	0.084	0.056	0.052	0.075
R_w	0.189	0.156	0.084	0.062	0.056	0.105

dertaken in order to provide the fourth (but the first example of those without carbonyl substituent(s)[1c,2]) structure analysis of the [6]paracyclophane system. It was hoped that neat information could be provided about the bond lengths and angles of the distorted benzene ring free of perturbation by the carbonyl substituent(s). Unfortunately, however, due to the disordered solvent molecule included in the crystal, the structure analysis was not precise enough to discuss them in detail. The molecular structure and selected bond lengths and angles are shown in Figure 3 (see also Table VIII).

The deformation angle of the para carbon (α) of **45** is somewhat smaller, while that of the benzyl carbon (β) is larger, than those of the experimental values reported for the derivatives of **1** possessing carbonyl substituent(s) (see Table I). Namely, the bending angles α, i.e., the angles between plane C8–C17–C19–C20 and plane C17–C18–C19 and C8–C7–C20, are 18.5° and 17.6°, respectively. The angles β, i.e., the angles between plane C17–C18–C19 and bond C1–C18 and plane C8–C7–C20 and bond C6–C7, are 23.2° and 21.0°, respectively. As shown in Figure 3, the bond lengths of **41** are within a range of 1.37–1.399 Å, similar to those of the carbonyl-substituted derivatives of **1**,[1c,2] indicating little bond length alternation in this system. There does not seem to be as much difference in the aromatic bond lengths (bonds a and b in Table II) as predicted by the MNDO/PM3 calculations. One of the bridge protons, H6, which is located above the bridged aromatic ring (C7–C8–C17–C18–C19–C20), is also above the other aromatic ring (C10–C11–C12–C13–C14–C15). The distance H6···C17 is 2.52 (8) Å, and H6···C15 is 2.79 (8) Å. In the ^{1}H NMR spectrum of **45** taken at −49 °C, the signal of this proton appears at δ −2.44 due to the shielding effect of both benzene rings. The other shielded methylene proton (H7) appears at δ −0.54, a chemical shift similar to that of the parent [6]paracyclophane (**1**) (δ −0.57).[1]

Next, the reaction with DCNA was examined. In benzene, cyclophane **1** gave the [4 + 2] adduct **47** in 66% yield. In CH_2Cl_2, however, adduct **48**, a [4 + 2] adduct between [6]metacyclophane (**27**) and DCNA, was obtained as a minor product (6%) while **47** was still the major product (16%). A similar cycloaddition of [7]- and [5]metacyclophanes has been reported.[5e,25a] Although DCNA was carefully purified by repeated distillations, a trace

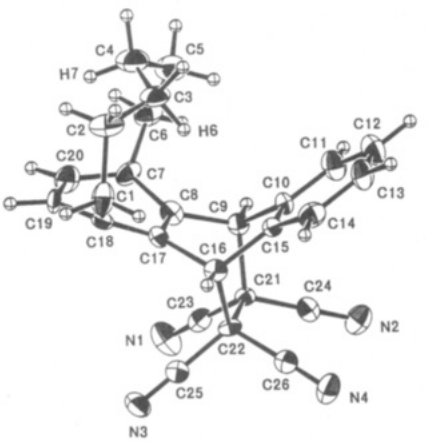


Figure 3. Molecular structure of [4 + 2] adduct **45**·Et_2O. For the sake of clarity, the solvent molecule is not shown. Selected bond lengths (Å) and angles (deg): C7–C8 = 1.387 (9), C7–C20 = 1.37 (1), C8–C17 = 1.399 (9), C17–C18 = 1.394 (9), C18–C19 = 1.39 (1), C19–C20 = 1.37 (1); C8–C7–C20 = 116.5 (8), C7–C8–C9 = 126.1 (7), C7–C8–C17 = 120.0 (7), C8–C17–C18 = 119.9 (7), C16–C17–C18 = 127.1 (7), C17–C18–C19 = 114.8 (8), C18–C19–C20 = 121.5 (9), C7–C20–C19 = 120.3 (9).

of contaminating acid impurities catalyzed the rearrangement of **1** to **27**, which then added to TCNE to give **48**. Similarly, considerable amounts (30–40%) of dimers **10** and **11** and trimers **14**–**16**, produced by acid-catalyzed telomerization of **2** and **3**, respectively, were obtained in the reaction of **2** and **3** with DCNA. In contrast with the reaction of **1** with DCNA, naphthalenophane **2** afforded the [2 + 2] adduct **49** as a single isolable adduct in CH_2Cl_2 (26%). When the reaction was conducted in benzene, the cyclopropane-containing product **50** was obtained as a minor product (8%) together with **49** (12%). Similarly, anthracenophane **3** gave the [2 + 2] adduct **51** (35%) and the cyclopropane-containing product **52** (22%) in benzene, while only **51** was obtained in CH_2Cl_2 (58%). The structures of the [2 + 2] adducts **49** and **51** were elucidated on the basis of their NMR spectra as in the case of the TCNE adducts **43** and **44**. The presence of a cyclo-

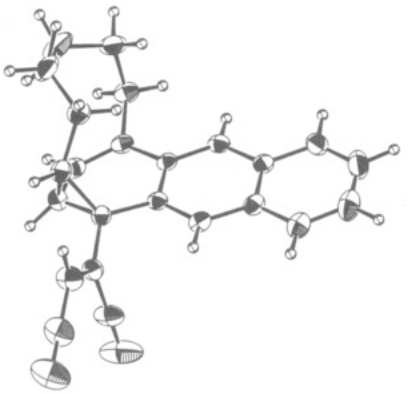
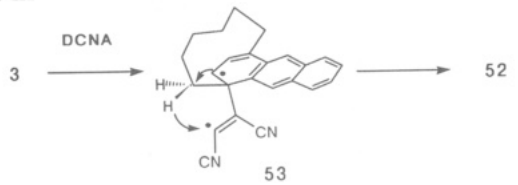
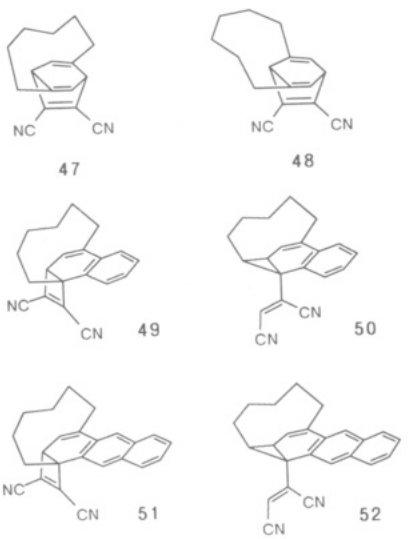


Figure 4. Molecular structure of cyclopropane-containing product **52**.

Scheme III



propane ring in the adducts **50** and **52** was deduced from the ^{13}C NMR spectra, which exhibited two sp^3 doublets (**50**, δ 30.7, 22.0; **52**, δ 29.9, 24.8). The structure of **52** was further confirmed by single-crystal X-ray analysis. The molecular structure is shown in Figure 4.



Like the TCNE adducts **43** and **44**, the [2 + 2] adducts **49** and **51** are probably derived through zwitterion intermediates. Since the cyclopropane-containing products **50** and **52** are obtained only when the reaction is undertaken in a nonpolar solvent (benzene), it is reasonable to assume that they are formed by a concerted ene-like reaction or through diradical intermediates such as **53** shown in Scheme III for anthracenophane **3**. A similar type of reaction has been reported by Gassman for a strained cyclopropane derivative.[28]

In summary, in the reactions with TCNE and DCNA, both **2** and **3** gave [2 + 2] cycloadducts as sole products in a polar solvent (CH_2Cl_2).[29] The reactivity is reminiscent of the well-documented thermal [2 + 2] cycloaddition of electron-rich styrene derivatives to electron-deficient olefins, which proceeds through zwitterionic intermediates.[30] Consequently, it is reasonable to

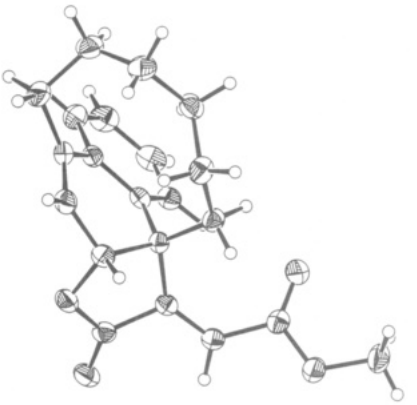
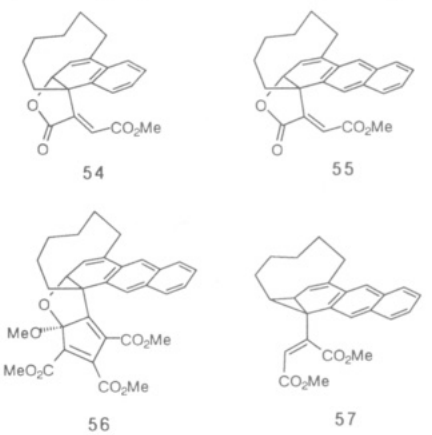


Figure 5. Molecular structure of lactone **54**.

ascribe the unusual reactivity of **2** and **3** to the high double bond character of the 1,2-bonds of the acene cores. Also, the low ionization potentials of **2** and **3** facilitate the charge-transfer process which may take place prior to zwitterion formation.

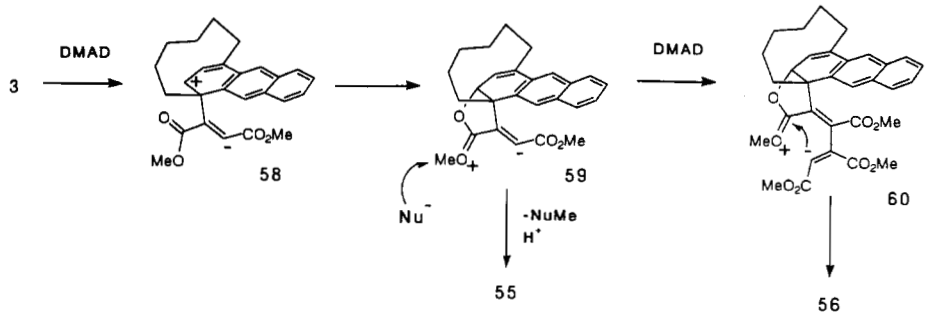
Last, the reaction with DMAD, the least reactive among those examined, was investigated. No reaction occurred when **1** was treated with DMAD (10 equiv) in CH_2Cl_2 (room temperature) or in benzene (80 °C) for several days. In the case of **2**, no distinct product could be isolated when the reaction was run in benzene (80 °C). On the other hand, in CH_2Cl_2 (room temperature), **2** gave the γ-lactone **54** as the sole isolable product (30% yield). It is reported that DMAD undergoes a variety of reactions with heterocyclic compounds, yielding diverse types of products,[31] which has led sometimes to misassignment of the structures.[32] In order to secure the structure of **54**, therefore, single-crystal X-ray analysis was performed. The molecular structure is shown in Figure 5. The reaction of anthracenophane **3** was more complicated. Thus, in CH_2Cl_2 (room temperature), **3** gave the lactone **55** as a major product (23%) while the 2:1 adduct **56** was obtained as a minor product (8%). In benzene (80 °C), the cyclo-



propane-containing product **57** (14%) was obtained along with lactone **55** (2%) and the 2:1 adduct **57** (28%). The structures of **55** and **57** were assigned on the basis of the similarities in their NMR spectra with those of related compounds **54** and **52**, respectively, whose structures were established by X-ray crystallographic analyses. The ^1H NMR spectrum of the 2:1 adduct **56** exhibits a vinyl proton signal (δ 6.29) which couples (J = 6.6 Hz) with a methine proton (doublet, δ 4.93), indicating that the addition of DMAD takes place at the 1,2-positions of the anthracene ring as in lactone **55**. Also observed were three ester methyl (δ 3.94, 3.93, 3.74) and one methoxy methyl (δ 2.51)

(28) Gassman, P. G.; Richmond, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 2090.
(29) The [4 + 2] cycloaddition of a [4]paracyclophane derivative, in which the cyclophane acts as a 2π component, has been reported: Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1989**, *111*, 368.
(30) Huisgen, R. *Acc. Chem. Res.* **1977**, *10*, 117.
(31) (a) Acheson, R. M.; Elmore, N. F. *Adv. Heterocycl. Chem.* **1978**, *23*, 263. (b) Acheson, R. M.; Choi, M. C. K.; Letcher, R. M. *J. Chem. Soc., Perkin Trans. 1* **1981**, 3141. (c) Letcher, R. M.; Choi, M. C. K.; Acheson, R. M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 515 and references cited therein.
(32) For example, see: Acheson, R. M.; Procter, G. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1924. Acheson, R. M.; Wallis, J. D. *J. Chem. Soc., Perkin Trans. 1* **1981**, 415.

Scheme IV



singlets, the latter being considerably shifted upfield.

The salient features of the ^{13}C NMR spectrum of **56** involve a doublet at δ 88.2 (a tertiary sp^3 carbon adjacent to an oxygen atom), a singlet at δ 115.2 (a quaternary sp^3 carbon doubly substituted by oxygen atoms), and a singlet at δ 51.0 (a bridgehead quaternary carbon). However, since the structure of **56** was not fully confirmed solely from the spectroscopic data, X-ray crystallographic analysis was undertaken. The molecular structure is shown in Figure 6.

The formation of methylene γ-lactones has been precedented in the reaction of DMAD with indole derivatives.[31b,c] The proposed mechanism involves the formation of zwitterion intermediates in the initial step of the reaction. Similarly, we suppose that **54** and **55** are formed through zwitterion intermediates like **58** followed by its cyclization to **59**, as shown in Scheme IV for anthracenophane **3**. Thus demethylation with an external nucleophile and protonation of **59** give lactone **55**. The formation of the 2:1 adduct **56**, which to our knowledge is unprecedented, can be explained by addition of a second molecule of DMAD to **59** to give **60**, which then cyclizes to afford **56**. The observation that naphthalenophane **2** reacts only in a polar solvent (CH_2Cl_2) is in accord with the above assumption that the zwitterion intermediates like **58** are formed in the initial stage of the reaction.

In conclusion, the anomalous reactivity observed in the electrophilic reactions of naphthalenophane **2** and anthracenophane **3** is characterized by their enhanced reactivity at the 1,2-positions of the acene cores. This is ascribed to the high double bond characters of this bond, which is predicted by semi-empirical molecular orbital calculations. Particularly noteworthy is the fact that the bonding property of naphthalenophane **2** and anthracenophane **3** is remarkably different from that of the benzene analogue **1**; the double bond character of the bridgehead bonds of **2** and **3** increases despite the fact that overlap of the π orbitals certainly becomes unfavorable because the aromatic ring is bent into a boat shape.

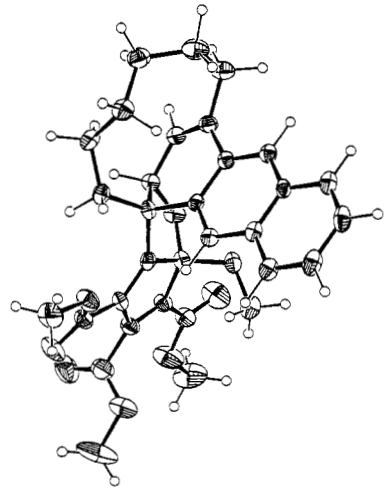


Figure 6. Molecular structure of 2:1 adduct **56**.

Experimental Section

NMR and mass spectra were taken with JEOL JMN-GSX-400 or Bruker AM-600 and JEOL JMS-DX303 spectrometers, respectively, at the Instrumental Analysis Center of the Faculty of Engineering, Osaka University, Osaka, Japan. IR spectra were recorded with a Hitachi 260-10 spectrometer. HPLC was undertaken with a Hitachi 655 chromatograph equipped with a 638-41 UV/VIS detector using a ZORBAX ODS column (15 cm × 4.6 mm), and GLC was carried out with a Hitachi G-3000 gas chromatograph using a OV-1 capillary column (5 m × 0.25 mm).

Acid-Catalyzed Isomerization/Dimerization of [6]Paracyclophane (1) with H_2SO_4. To a solution of 200 mg (1.25 mmol) of **1** in 8 mL of CH_2Cl_2 was added a catalytic amount of H_2SO_4 in CH_2Cl_2, and the mixture was stirred at room temperature for 1.5 h. The reaction was quenched by addition of saturated $NaHCO_3$ solution. The aqueous layer was extracted with CH_2Cl_2, and the combined organic phase was washed with water and dried ($MgSO_4$). The solvent was evaporated and the subsequent chromatography on silica gel (elution with petroleum ether) gave 117 mg (59%) of a mixture of **7** and **8** (1:1 ratio by GLC) followed by 41 mg (21%) of the dimer **9**.

9: colorless oil; ^1H NMR ($CDCl_3$) δ 7.32 (d, J = 7.7 Hz, 1 H), 7.25 (s, 1 H), 7.24 (d, J = 7.7 Hz, 1 H), 6.32 (d, J = 9.3 Hz, 1 H), 6.02 (d, J = 6.8 Hz, 1 H), 5.95 (dd, J = 9.3, 6.8 Hz, 1 H), 3.51 (d, J = 6.8 Hz, 1 H), 2.98 (m, 4 H), 2.7–2.6 (m, 2 H), 2.38 (dt, J = 12.2, 3.9 Hz, 1 H), 2.1–1.5 (m, 17 H), 1.36 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 140.9 (s), 140.8 (s), 138.9 (s), 137.8 (s), 130.0 (d), 128.7 (d), 128.5 (d), 128.4 (d), 125.4 (d), 124.8 (d), 43.6 (br d), 41.1 (d), 36.7 (t), 33.6 (t), 32.34 (t), 32.28 (t, 2C), 31.9 (t), 30.0 (t), 28.4 (br t), 27.5 (br t), 27.0 (t), 26.0 (t), 25.9 (t); IR (neat) 820, 800, 750, 710 cm^{-1}; MS m/z (relative intensity) 320 (M^+, 100), 249 (19), 193 (17), 179 (13), 167 (10), 134 (12); HRMS calcd for $C_{24}H_{32}$ 320.2504, found 320.2514.

Acid-Catalyzed Dimerization/Trimerization of [6](1,4)-Naphthalenophane (2) with H_2SO_4. To a solution of 173 mg (0.823 mmol) of **2** in 3 mL of CH_2Cl_2 was added a catalytic amount of H_2SO_4, and the mixture was stirred at room temperature for 2 min. The reaction was monitored by HPLC and worked up as above. Chromatography on silica gel (elution with petroleum ether/benzene, 100:0–97:3) gave 51 mg (29%) of the dimer **10**, 41 mg of a mixture of **10** and **11**, 33 mg (19%) of the dimer **11** (total of **10** and **11** = 72%), 4 mg (3%) of the trimer **12**, 12 mg of a mixture of **12** and **13**, and 9 mg (5%) of the trimer **13** (total of **12** and **13** = 15%).

10: mp 162–163 °C (recrystallized from petroleum ether/ether); ^1H NMR ($CDCl_3$, 50 °C) δ 8.11 (d, J = 8.4 Hz, 1 H), 8.00 (d, J = 9.2 Hz, 1 H) 7.5–7.3 (br m, 1 H), 7.40 (d, J = 7.7 Hz, 1 H), 7.29 (d, J = 7.3 Hz, 1 H), 7.21 (dd, J = 7.7, 7.3 Hz, 1 H), 7.10 (s, 1 H), 7.04 (dd, J = 7.3, 6.6 Hz, 1 H) 6.82 (d, J = 7.3 Hz, 1 H), 6.22 (d, J = 7.0 Hz, 1 H), 4.40 (d, J = 7.0 Hz, 1 H), 3.3–2.5 (br m, containing br d (J = 13.2 Hz) at 3.08 and m at 3.00, 5 H), 2.41 (m, 1 H), 2.06 (m, 1 H), 1.8 to –0.6 (m, 18 H), at –50 °C, broad multiplets observed at –0.36, –0.66, –1.30, and –2.02; ^{13}C NMR ($CDCl_3$, 50 °C) δ 139.9 (br s), 139.6 (s), 139.2 (s), 137.6 (s), 137.2 (s), 133.4 (br s), 131.9 (br s), 131.7 (s + d), 129.6 (d), 128.5 (d), 127.0 (d), 126.5 (d), 125.3 (d), 124.3 (br d), 124.2 (br d), 123.7 (d), 121.3 (d), 45.2 (br d), 41.2 (br d), 37.6 (t), 33.8 (t), 31.9 (br t), 31.5 (t), 31.2 (t), 29.4 (t), 27.8 (t), 26.9 (t), 26.4 (t), 26.2 (br t), 25.2 (br t, 2C); IR (KBr) 925, 770, 755, 740 cm^{-1}; MS m/z (relative intensity) 420 (M^+, 100), 349 (21), 293 (17), 279 (26), 265 (16), 179 (16), 141 (27). Anal. Calcd for $C_{32}H_{36}$: C, 91.37; H, 8.63. Found: C, 91.65; H, 8.35.

11: mp 175–177 °C (recrystallized from petroleum ether/ether); ^1H NMR ($CDCl_3$) δ 8.15–8.06 (m, 2 H), 7.51–7.45 (m, 2 H), 7.27 (dd, J = 7.3, 1.1 Hz, 1 H), 7.15 (ddd, J = 7.3, 7.3, 1.1 Hz, 1 H), 6.97 (ddd, J = 7.3, 7.3, 1.1 Hz, 1 H), 6.87 (s, 1 H), 6.76 (dd, J = 7.3, 1.1 Hz, 1 H), 6.11 (d, J = 7.0 Hz, 1 H), 4.29 (d, J = 7.0 Hz, 1 H), 3.2–3.1 (m, 3 H), 2.65 (m, 2 H), 2.42 (ddd, J = 13.4, 11.5, 4.0 Hz, 1 H), 2.06 (m, 1 H), 1.8–1.1 (m, 17 H), 0.89 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 139.6 (s), 139.5 (s), 138.1 (s), 136.6 (s), 134.9 (s), 133.4 (s), 132.5 (s), 130.4

(s), 128.7 (d), 127.8 (d), 127.5 (d), 126.8 (d), 126.3 (d), 124.9 (d), 124.8 (d), 124.3 (d), 123.6 (d), 121.7 (d), 45.5 (d), 40.5 (d), 36.8 (t), 34.2 (t), 34.0 (t), 32.3 (t), 30.3 (t), 29.8 (t), 27.5 (br t, 2C), 26.8 (t), 26.0 (t), 25.9 (t, 2C); IR (KBr) 925, 770, 755, 750 cm^{-1}; MS *m/z* (relative intensity) 420 (M^+, 100), 349 (16), 223 (18), 184 (24). Anal. Calcd for $C_{32}H_{36}$: C, 91.37; H, 8.63. Found: C, 91.23; H, 8.60.

12: mp >300 °C; ^1H NMR ($CDCl_3$) δ 7.22 (d, J = 7.3 Hz, 1 H), 7.10 (td, J = 7.3, 1.5 Hz, 1 H), 7.06–7.02 (m, 2 H), 6.94–6.82 (m, 4 H), 6.77 (td, J = 7.3, 1.5 Hz, 1 H), 6.68 (td, J = 7.3, 1.0 Hz, 1 H), 6.59 (d, J = 7.8 Hz, 1 H), 6.49 (dd, J = 7.8, 1.5 Hz, 1 H), 6.17 (d, J = 6.8 Hz, 1 H), 5.79 (d, J = 7.3 Hz, 1 H), 5.60 (dd, J = 8.8, 8.3 Hz, 1 H), 3.51 (d, J = 5.4 Hz, 1 H), 3.26 (d, J = 6.8 Hz, 1 H), 3.09 (br d, J = 13.2 Hz, 1 H), 2.94 (m, 1 H), 2.86 (d, J = 6.8 Hz, 1 H), 2.74 (br d, J = 12.2 Hz, 1 H), 2.37 (br t, J = 11.7 Hz, 1 H), 2.3–2.1 (m, 2 H), 2.1–1.9 (m, 1 H), 1.9–0.5 (m, 28 H), 0.02 (br m, 1 H); because of the limited solubility of **9**, a ^{13}C NMR spectrum was not recorded; IR (KBr) 760, 740 cm^{-1}; MS *m/z* (relative intensity) 630 (M^+, 100), 419 (86), 223 (22), 211 (31), 141 (79); HRMS calcd for $C_{48}H_{54}$ 630.4226, found 630.4211.

13: mp 286–289 °C (recrystallized from CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.28–7.24 (m, 2 H), 7.20–7.16 (m, 2 H), 7.10–7.02 (m, 1 H), 6.95 (td, J = 7.7, 1.5 Hz, 1 H), 6.87 (td, J = 7.7, 1.1 Hz, 1 H), 6.80 (dd, J = 6.6, 1.5 Hz, 1 H), 6.76 (td, J = 7.7, 1.5 Hz, 1 H), 6.66 (dd, J = 7.3, 6.6 Hz, 1 H), 6.57 (d, J = 7.3 Hz, 1 H), 6.44 (d, J = 6.6 Hz, 1 H), 6.06 (d, J = 7.0 Hz, 1 H), 5.66 (d, J = 7.3 Hz, 1 H), 5.61 (dd, J = 9.2, 8.1 Hz, 1 H), 3.48 (m, 1 H), 3.45 (d, J = 5.9 Hz, 1 H), 3.19 (d, J = 7.0 Hz, 1 H), 2.91 (d, J = 7.3 Hz, 1 H), 2.81 (br d, J = 13.2 Hz, 1 H), 2.73 (br d, J = 12.8 Hz, 1 H), 2.3–0.5 (m, 31 H), 0.26–0.14 (m, 1 H), 0.0 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 145.3 (br s), 142.9 (s), 140.5 (s), 139.9 (s), 138.61 (s), 138.59 (s), 137.6 (s), 137.2 (s), 134.4 (s), 128.2 (d, 2C), 128.1 (d), 127.2 (d), 126.8 (d), 126.5 (d), 125.6 (d), 125.3 (d), 125.2 (d), 124.9 (d), 124.3 (d), 122.0 (d), 121.9 (d), 121.4 (d), 120.8 (d), 57.7 (s), 56.5 (d), 54.7 (br d), 47.4 (d), 46.3 (t), 46.2 (s), 39.2 (d), 39.1 (t), 38.2 (d), 35.5 (t), 34.3 (t), 30.4 (t), 29.6 (t, 2C), 29.5 (t), 28.9 (t, 3C), 28.6 (t), 27.1 (br t, 2C), 26.0 (t), 24.4 (t), 23.4 (t); IR (KBr) 835, 765, 745 cm^{-1}; MS *m/z* (relative intensity) 630 (M^+, 100), 419 (82), 223 (22), 211 (41), 141 (78); HRMS calcd for $C_{48}H_{54}$ 630.4226, found 630.4222.

Acid-Catalyzed Trimerization of [6](1,4)Anthracenophane (3) with H_2SO_4. To a solution of 80 mg (0.31 mmol) of **3** in 2 mL of CH_2Cl_2 was added a catalytic amount of H_2SO_4, and the solution was stirred at room temperature for 30 s. The reaction was monitored by HPLC and worked up as above. The crude product was washed with ether to leave 34 mg (43%) of almost pure trimer **14** as an insoluble solid. The filtrate was concentrated and chromatographed on silica gel (elution with petroleum ether/benzene, 98:2–92:8) to give 6 mg (8%) of the trimer **15** and 7 mg (9%) of an unidentified trimer **16**.

14: mp >300 °C (recrystallized from CH_2Cl_2); ^1H NMR ($CDCl_3$) δ 7.77 (d, J = 8.0 Hz, 1 H), 7.70 (s, 1 H), 7.67 (d, J = 8.4 Hz, 1 H), 7.57 (d, J = 7.7 Hz, 1 H), 7.55 (d, J = 7.7 Hz, 1 H), 7.48 (s, 1 H), 7.37–7.21 (m, containing s at 7.31 and 7.28, 8 H), 7.13 (ddd, J = 8.2, 6.8, 1.1 Hz, 1 H), 7.06 (d, J = 8.0 Hz, 1 H), 6.71 (s, 1 H), 6.49 (s, 1 H), 6.46 (d, J = 7.0 Hz, 1 H), 5.95 (d, J = 7.3 Hz, 1 H), 5.66 (t, J = 8.0 Hz, 1 H), 3.71 (d, J = 5.8 Hz, 1 H), 3.49 (d, J = 7.0 Hz, 1 H), 3.39 (m, 1 H), 3.29 (br d, J = 13.2 Hz, 1 H), 3.04 (d, J = 7.0 Hz, 1 H), 2.74 (br d, J = 12.5 Hz, 1 H), 2.53 (ddd, J = 12.8, 12.8, 4.0 Hz, 1 H), 2.31 (m, 2 H), 2.1–0.9 (m, 26 H), 0.77 (br m, 1 H), 0.55 (br m, 1 H), 0.38 (br m, 1 H), –0.37 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 144.7 (br s), 143.0 (s), 142.5 (s), 140.4 (s), 140.1 (s), 137.7 (s), 136.9 (s), 134.6 (s), 133.4 (s, 2C), 132.6 (s), 132.4 (s), 132.0 (s), 131.9 (s), 131.4 (s), 127.7 (d), 127.43 (d), 127.37 (d, 2C), 127.3 (d), 127.0 (d, 2C), 126.8 (d), 126.4 (d), 125.7 (d), 125.2 (d), 125.0 (d), 124.63 (d), 124.56 (d), 124.5 (d), 124.4 (d), 124.3 (d), 123.2 (br d), 120.5 (d), 120.4 (d), 118.8 (d), 62.2 (s), 56.7 (d), 56.1 (br d), 47.7 (t), 47.4 (d), 47.3 (s), 40.6 (d), 39.5 (t), 39.0 (d), 35.8 (t), 35.4 (t), 30.4 (t), 30.0 (t), 29.7 (t), 29.3 (t), 28.9 (t, 3C), 28.8 (t), 28.2 (br t, 2C), 25.8 (t, 2C), 23.7 (t); IR (KBr) 890, 875, 740 cm^{-1}; MS *m/z* (relative intensity) 780 (M^+, 91), 519 (100), 261 (33), 191 (50). Anal. Calcd for $C_{60}H_{60}\cdot 0.4CH_2Cl_2$: C, 89.00; H, 7.52; Cl, 3.48. Found: C, 89.02; H, 7.46; Cl, 3.30.

15: mp >300 °C; ^1H NMR ($CDCl_3$) δ 7.81 (d, J = 7.3 Hz, 1 H), 7.75 (m, containing s at 7.76, 2 H), 7.74 (d, J = 5.9 Hz, 1 H), 7.65 (s, 1 H), 7.52 (d, J = 9.3 Hz, 1 H), 7.51 (s, 1 H), 7.5–7.4 (m, 2 H), 7.3–7.2 (m, 5 H), 7.11 (ddd, J = 8.3, 6.8, 1.0 Hz, 1 H), 6.99 (d, J = 7.8 Hz, 1 H), 6.61 (s, 1 H), 6.38 (s, 1 H), 6.31 (d, J = 6.8 Hz, 1 H), 5.84 (d, J = 6.8 Hz, 1 H), 5.65 (dd, J = 8.8, 8.3 Hz, 1 H), 3.82 (m, 1 H), 3.64 (d, J = 5.9 Hz, 1 H), 3.43 (d, J = 6.3 Hz, 1 H), 3.13 (d, J = 7.3 Hz, 1 H), 2.95 (br d, J = 14.2 Hz, 1 H), 2.70 (br d, J = 13.2 Hz, 1 H), 2.3–0.7 (m, 29 H), 0.62 (br m, 1 H), 0.46 (br m, 1 H), –0.03 (br m, 1 H), –0.14 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 144.6 (br s), 142.8 (s), 141.4 (s), 140.5 (s), 140.3 (s), 138.6 (s), 137.6 (s), 136.0 (s), 133.4 (s), 133.2 (s), 133.1 (s), 132.4 (s), 131.90 (s), 131.88 (s), 131.4 (s), 129.4 (d), 127.8 (d), 127.3 (d, 2C), 127.1 (d), 127.0 (d), 126.9 (d), 126.8 (d), 126.3 (d), 125.8 (d), 125.3 (d), 125.20 (d), 125.15 (d), 124.6 (d), 124.5 (d), 124.4 (d), 124.2 (d), 123.0 (d), 120.5 (d), 119.6 (d), 118.7 (d), 58.7 (s), 56.8 (d), 55.3 (br d), 47.8 (d), 47.6 (t), 46.9 (s), 40.09 (t), 40.05 (d), 38.9 (d), 35.7 (t), 34.4 (t), 30.3 (t), 29.7 (t, 2C), 29.3 (t), 28.8 (t, 3C), 28.3 (t), 27.4 (br t, 2C), 26.1 (t), 24.7 (t), 23.6 (t); IR (KBr) 875, 740 cm^{-1}; MS *m/z* (relative intensity) 780 (M^+, 100), 519 (95), 261 (53), 191 (54); HRMS calcd for $C_{60}H_{60}$ 780.4695, found 780.4685.

Unidentified trimer **16**: mp >300 °C; ^1H NMR δ 8.63 (d, J = 8.8 Hz, 1 H), 7.9–7.1 (m, 17 H), 6.86 (s, 1 H), 6.72 (d, J = 7.0 Hz, 1 H), 5.58 (d, J = 5.9 Hz, 1 H), 4.09 (m, 1 H), 3.38 (s, 1 H), 3.22 (d, J = 13.2 Hz, 1 H), 2.87 (br m, 1 H), 2.83 (d, J = 5.1 Hz, 1 H), 2.60–0.64 (m, 32 H), 0.64–0.20 (br m, 2 H); ^{13}C NMR δ 144.6 (s), 143.4 (s), 141.3 (s), 140.7 (s), 139.8 (s), 139.0 (s), 136.1 (s), 135.6 (s), 134.1 (s), 133.4 (s), 133.3 (s), 131.7 (d), 131.4 (s), 131.2 (s), 130.9 (d), 130.5 (d), 129.4 (d), 128.8 (d), 127.7 (d), 127.4 (d), 127.02 (d), 126.96 (d), 126.9 (d), 126.0 (d), 125.4 (d), 125.3 (d), 124.9 (d), 124.5 (d), 124.3 (d), 124.0 (d), 122.8 (d), 121.6 (d), 120.1 (d), 116.5 (d), 63.0 (s), 62.1 (s), 58.6 (d), 53.5 (s), 48.9 (br d), 47.6 (d), 44.6 (br d), 44.2 (t), 40.2 (d), 38.5 (t), 35.9 (t), 34.7 (t), 32.9 (t), 30.2 (t), 29.69 (t, 2C), 29.65 (t), 29.5 (t), 29.0 (t), 27.8 (br t), 25.9 (t), 25.4 (br t), 24.6 (t), 24.4 (t), 24.3 (t) (one signal missing); IR (KBr) 1195, 865, 740 cm^{-1}; MS *m/z* (relative intensity) 780 (M^+, 100), 695 (9), 519 (19); HRMS calcd for $C_{60}H_{60}$ 780.4695, found 780.4730.

Isomerization/Telomerization of 1–3 with Trifluoroacetic Acid (TFA). Reactions of **1–3** (0.2–0.4 mmol) with TFA (0.1–0.2 equiv) in CH_2Cl_2 were carried out at substrate concentrations of (1.3×10^{-3})–(1.8×10^{-1}) M. The reaction was worked up as above, and the products were separated by column chromatography. The results are summarized in Table III.

Oxidation of [6](1,4)Naphthalenophane (2) with MCPBA. To a solution of **2** (70 mg, 0.33 mmol) in 3 mL of CH_2Cl_2 was added 64 mg (0.33 mmol) of MCPBA (90%) in one portion at –78 °C. The progress of the reaction was monitored by GLC. The mixture was stirred at –78 °C for 1.5 h, warmed up to room temperature, and then treated with saturated Na_2SO_3 solution. The organic layer was diluted with ether, washed with $NaHCO_3$ solution, and dried ($MgSO_4$). Evaporation of the solvent followed by flash chromatography (elution with petroleum ether/ether, 9:1–8:2) afforded 20 mg (27%) of the enone **34**, 12 mg (9%) of the hydroxy ester **37**, and 21 mg (26%) of the epoxide **36**.

34: pale yellow oil; ^1H NMR ($CDCl_3$) δ 8.07 (dd, J = 7.7, 1.5 Hz, 1 H), 7.60 (dt, J = 1.5, 7.7 Hz, 1 H), 7.46 (d, J = 7.7 Hz, 1 H), 7.33 (dt, J = 1.1, 7.7 Hz, 1 H), 6.14 (d, J = 4.4 Hz, 1 H), 3.37 (dd, J = 8.8, 4.4 Hz, 1 H), 3.05 (dt, J = 13.2, 3.3 Hz, 1 H), 2.27–2.20 (m, 1 H), 2.11 (dt, J = 3.7, 12.8 Hz, 1 H), 1.96–1.88 (m, 1 H), 1.78–1.66 (m, 2 H), 1.41–1.08 (m, 5 H), 0.89–0.76 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 202.2 (s), 140.3 (s), 134.6 (d), 133.0 (s), 131.9 (d), 131.2 (s), 127.09 (d), 127.05 (d), 123.6 (d), 49.4 (d), 34.7 (t), 32.6 (t), 31.6 (t), 26.5 (t), 24.5 (t), 20.3 (t); IR (neat) 1680, 1290, 780 cm^{-1}; MS *m/z* (relative intensity) 226 (M^+, 100), 183 (21), 171 (26), 158 (90), 144 (31), 128 (32); HRMS calcd for $C_{16}H_{18}O$ 226.1358, found 226.1369.

36: mp 118–119 °C (recrystallized from ether); ^1H NMR ($CDCl_3$) δ 8.05 (dd, J = 7.7, 1.5 Hz, 1 H), 7.68 (d, J = 7.0 Hz, 1 H), 7.58 (dt, J = 1.5, 7.3 Hz, 1 H), 7.42 (dt, J = 1.5, 7.7 Hz, 1 H), 3.84 (d, J = 2.2 Hz, 1 H), 3.33 (br t, J = 4.0 Hz, 1 H), 3.10–3.03 (m, 1 H), 2.29–2.20 (m, 1 H), 2.05–1.96 (m, 1 H), 1.85–1.71 (m, 2 H), 1.53–1.00 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 197.8 (s), 141.5 (s), 133.5 (d), 133.1 (s), 128.4 (d), 128.3 (d), 126.9 (d), 61.8 (d), 56.3 (s), 44.9 (d), 32.6 (t), 30.5 (t), 29.8 (t), 24.5 (t), 23.2 (t), 19.5 (t); IR (KBr) 1670, 1590, 1290, 980, 910, 775 cm^{-1}; MS *m/z* (relative intensity) 242 (M^+, 56), 213 (39), 185 (41), 172 (61), 157 (74), 147 (100), 131 (42), 115 (46). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.19; H, 7.50.

37: mp 117–119 °C (recrystallized from hexane); ^1H NMR ($CDCl_3$) δ 7.74 (t, J = 1.8 Hz, 1 H), 7.68 (dd, J = 7.8, 1.5 Hz, 1 H), 7.64 (dt, J = 8.1, 1.5 Hz, 1 H), 7.44 (ddd, J = 1.1, 2.2, 8.1 Hz, 1 H), 7.37 (dt, J = 1.5, 7.7 Hz, 1 H), 7.32 (dt, J = 1.5, 7.7 Hz, 1 H), 7.26 (d, J = 8.4 Hz, 1 H), 7.24 (d, J = 6.7 Hz, 1 H), 6.26 (d, J = 6.6 Hz, 1 H), 5.17 (d, J = 6.6 Hz, 1 H), 2.94 (br d, J = 13.6 Hz, 1 H), 2.40 (br s, 1 H), 2.28 (dt, J = 3.7, 13.2 Hz, 1 H), 1.91 (ddd, J = 2.2, 7.7, 14.3 Hz, 1 H), 1.79–1.18 (m, 8 H), 0.84 (br m, 1 H); IR (KBr) 3450 (br), 1710, 1335, 1290, 1250, 1125, 1070, 965, 920, 745 cm^{-1}; MS *m/z* (relative intensity) 382 (M^+, 7), 364 (17), 243 (10), 226 (95), 158 (95), 156 (100), 139 (76); HRMS calcd for $C_{23}H_{23}O_3Cl$ 382.1335, found 283.1334.

Oxidation of [6](1,4)Anthracenophane (3) with MCPBA. Oxidation of 70 mg (0.27 mmol) of **3** with 52 mg (0.27 mmol) of MCPBA (90%) was carried out as described above to give, after flash chromatography, 20 mg (27%) of the enone **35**, 44 mg (38%) of the hydroxy ester **39**, and 7 mg (9%) of the epoxide **38**.

35: mp 115–116 °C (recrystallized from petroleum ether); ^1H NMR ($CDCl_3$) δ 8.61 (s, 1 H), 7.94 (d, J = 8.1 Hz, 1 H), 7.86 (d, J = 8.4 Hz, 1 H), 7.82 (s, 1 H), 7.56 (ddd, J = 8.1, 6.6, 1.1 Hz, 1 H), 7.47 (ddd, J

= 8.1, 6.9, 1.1 Hz, 1 H), 6.14 (d, J = 4.4 Hz, 1 H), 3.42 (dd, J = 8.4, 4.4 Hz, 1 H), 3.20 (dt, J = 12.8, 3.3 Hz, 1 H), 2.28–2.22 (m, 1 H), 2.17 (dt, J = 4.0, 12.8 Hz, 1 H), 2.02–1.95 (m, 1 H), 1.81–1.67 (m, 2 H), 1.46–1.12 (m, 5 H), 0.91–0.82 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 201.8 (s), 136.5 (s), 135.6 (s), 133.6 (s), 131.7 (s), 130.10 (d), 130.07 (d), 129.5 (s), 128.79 (d), 128.76 (d), 128.0 (d), 126.4 (d), 122.2 (d), 48.9 (d), 34.6 (t), 33.0 (t), 31.7 (t), 26.8 (t), 24.6 (t), 20.5 (t); IR (KBr) 1670, 1615, 1180, 905, 750 cm^{-1}; MS m/z (relative intensity) 276 (M^+, 100), 248 (14), 233 (13), 221 (22), 208 (59), 194 (23), 178 (30); HRMS calcd for $C_{20}H_{20}O$ 276.1515, found 276.1514.

38: mp 172–173 °C (recrystallized from ether/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 8.62 (s, 1 H), 8.09 (s, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 7.89 (d, J = 8.4 Hz, 1 H), 7.62 (dt, J = 1.1, 7.0 Hz, 1 H), 7.54 (dt, J = 1.1, 7.0 Hz, 1 H), 3.91 (d, J = 2.2 Hz, 1 H), 3.41 (br m, 1 H), 3.26–3.20 (m, 1 H), 2.33–2.24 (m, 1 H), 2.13–2.05 (m, 1 H), 1.89–1.75 (m, 2 H), 1.58–1.04 (m, 7 H); ^{13}C NMR ($CDCl_3$) δ 198.3 (s), 136.0 (s), 135.4 (s), 132.1 (s), 130.2 (s + d), 129.9 (d), 129.0 (d), 127.7 (d), 127.3 (d), 126.8 (d), 62.3 (d), 57.0 (s), 45.1 (d), 33.0 (t), 30.8 (t), 29.7 (t), 24.4 (t), 23.6 (t), 19.8 (t); IR (KBr) 1670, 1615, 1175, 970, 940, 880, 735 cm^{-1}; MS m/z (relative intensity) 292 (M^+, 100), 276 (28), 263 (36), 223 (37), 207 (29), 196 (27), 178 (23), 165 (29). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.15; H, 6.89. Found: C, 81.96; H, 6.88.

39: mp 147–148 °C (recrystallized from ether/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 8.15 (s, 1 H), 7.90–7.83 (m, 2 H), 7.75 (t, J = 1.5 Hz, 1 H), 7.69 (s, 1 H), 7.58 (dt, J = 8.0, 1.5 Hz, 1 H), 7.53–7.47 (m, 2 H), 7.40 (ddd, J = 8.1, 2.2, 1.1 Hz, 1 H), 7.18 (t, J = 7.7 Hz, 1 H), 6.39 (d, J = 6.6 Hz, 1 H), 5.28 (d, J = 6.6 Hz, 1 H), 3.11 (dt, J = 13.2, 3.6 Hz, 1 H), 2.57 (br s, 1 H), 2.43–2.34 (m, 1 H), 2.06–1.98 (m, 1 H), 1.90–1.18 (m, 8 H), 0.85 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 165.0 (s), 143.5 (s), 139.3 (s), 134.4 (s), 133.5 (s), 133.0 (d), 132.9 (s), 132.8 (s), 131.7 (s), 129.6 (d), 129.5 (d), 128.1 (d), 127.9 (d), 127.6 (d), 126.3 (d), 126.2 (d), 123.9 (d), 122.3 (d), 122.1 (d), 75.4 (s), 74.6 (d), 42.1 (t), 33.8 (t), 28.8 (t), 26.2 (br t), 25.4 (br t, 2C); IR (KBr) 3450 (br), 1720, 1330, 1295, 1245, 1120, 1070, 960, 895, 745 cm^{-1}; MS m/z (relative intensity) 432 (M^+, 1), 293 (1), 276 (100), 208 (59). Anal. Calcd for $C_{27}H_{25}O_3Cl$: C, 74.91; H, 5.82; Cl, 8.19. Found: C, 74.76; H, 5.78; Cl, 8.48.

General Procedure for Reaction of 1–3 with TCNE. To a solution of TCNE in benzene was added a solution of a cyclophane in benzene at room temperature. As for the reactions in CH_2Cl_2, TCNE was added to a solution of a cyclophane. The progress of the reaction was monitored by HPLC. After completion of the reaction, the solvent was evaporated, and the residue was washed with ether to give the products. Flash chromatography (elution with petroleum ether/ether, 9:1–8:2) of the ether washing gave an additional amount of the product(s).

Reaction of [6]Paracyclophane (1) with TCNE in Benzene. Reaction of **1** (42 mg, 0.26 mmol) with 64 mg (0.53 mmol) of TCNE in 5 mL of benzene for 4 days gave 65 mg (90%) of the [4 + 2] adduct **42**.[6]

Reaction of [6](1,4)Naphthalenophane (2) with TCNE. Reaction of 82 mg (0.39 mmol) of **2** with 79 mg (0.59 mmol) of TCNE in 12 mL of CH_2Cl_2 for 1.5 h gave 98 mg (74%) of the [2 + 2] adduct **43** as a white solid. Reaction of 69 mg (0.33 mmol) of **2** with 84 mg (0.66 mmol) of TCNE in 5 mL of benzene for 2 days afforded 81 mg (73%) of **43**.

43: mp 205–209 °C dec (recrystallized from CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 50 °C) δ 7.5–7.4 (m, 4 H), 5.79 (d, J = 7.5 Hz, 1 H), 3.80 (d, J = 7.5 Hz, 1 H), 3.10 (dt, J = 13.1, 3.9 Hz, 1 H), 2.34 (dt, J = 4.3, 12.5 Hz, 1 H), 2.24 (dd, J = 13.6, 7.9 Hz, 1 H), 1.84 (t, J = 12.5 Hz, 1 H), 1.7–1.3 (m, 6 H), 1.01 (br m, 1 H), 0.54 (br m, 1 H); ^{13}C NMR ($CDCl_3$, 50 °C) δ 148.8 (s), 136.0 (s), 131.5 (s), 130.2 (d), 129.5 (d), 128.7 (d), 124.8 (d), 113.6 (d), 110.6 (s), 110.3 (s), 109.7 (s), 108.8 (s), 56.3 (s), 48.5 (s), 48.3 (br d), 40.3 (t), 39.6 (s), 35.0 (t), 29.1 (t), 27.2 (br t), 26.0 (br t), 24.5 (t); IR (KBr) 2250, 1640, 780, 770, 750 cm^{-1}; MS m/z (relative intensity) 338 (M^+, 7), 268 (33), 210 (100), 167 (50), 154 (74); HRMS calcd for $C_{22}H_{18}N_4$ 338.1531, found 338.1538.

Reaction of [6](1,4)Anthracenophane (3) with TCNE. Reaction of 87 mg (0.34 mmol) of **3** with 134 mg (1.01 mmol) of TCNE in 17 mL of CH_2Cl_2 for 1 h yielded 83 mg (64%) of the [2 + 2] adduct **44** as a white solid. Reaction of 95 mg (0.37 mmol) of **3** with 74 mg (0.58 mmol) of TCNE in 5 mL of benzene for 30 min gave 103 mg (82%) of **44** and 18 mg (13%) of the [4 + 2] adduct **45**.

44: mp 190–195 °C dec (recrystallized from CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 50 °C) δ 8.03 (s, 1 H), 7.9–7.8 (m, 2 H), 7.86 (s, 1 H), 7.6–7.5 (m, 2 H), 5.91 (d, J = 7.5 Hz, 1 H), 3.86 (d, J = 7.5 Hz, 1 H), 3.27 (dt, J = 13.2, 3.7 Hz, 1 H), 2.44 (dt, J = 4.4, 12.0 Hz, 1 H), 2.4–2.3 (m, 1 H), 1.98 (ddd, J = 13.2, 11.0, 2.2 Hz, 1 H), 1.8–0.9 (m, 6 H), 0.9–0.8 (m, 1 H), 0.47 (br m, 1 H); ^{13}C NMR ($CDCl_3$, 50 °C) δ 148.9 (s), 133.5 (s), 133.0 (s), 132.2 (s), 129.7 (br s), 129.6 (d), 128.4 (d), 128.1 (d), 128.0 (d), 127.7 (d), 124.2 (d), 114.5 (d), 110.6 (s), 110.4 (s), 109.8 (s), 108.8 (s), 56.1 (s), 48.5 (s), 48.4 (br d), 41.5 (t), 40.0 (s), 35.3 (t), 29.2 (t), 27.4 (br t), 26.5 (br t), 24.4 (t); IR (KBr) 2250, 1640, 890, 760 cm^{-1}; MS m/z (relative intensity) 388 (M^+, 23), 297 (100), 296 (93), 260 (78); HRMS calcd for $C_{26}H_{20}N_4$ 388.1688, found 388.1690.

45: mp 144–146 °C dec (recrystallized from ether/CH_2Cl_2); ^{1}H NMR ($CDCl_3$, −49 °C) δ 7.71 (dd, J = 7.6, 1.8 Hz, 1 H), 7.65 (dd, J = 7.2, 2.2 Hz, 1 H), 7.54–7.47 (m, 2 H), 7.43 (d, J = 8.4 Hz, 1 H), 7.30 (d, J = 8.1 Hz, 1 H), 5.45 (s, 1 H), 5.34 (s, 1 H), 3.20 (dd, J = 12.8, 5.9 Hz, 1 H), 2.97 (dd, J = 12.8, 5.9 Hz, 1 H), 2.30 (dd, J = 12.1, 5.9 Hz, 1 H), 2.25 (dd, J = 12.1, 5.9 Hz, 1 H), 1.60–1.39 (m, 2 H), 0.99–0.85 (m, 1 H), 0.54 (ddd, J = 12.3, 6.6, 6.4 Hz, 1 H), 0.34 (br m, 1 H), −0.11 (ddd, J = 12.8, 6.6, 6.2 Hz, 1 H), −0.52 (ddd, J = 15.7, 8.0, 7.7 Hz, 1 H), −2.43 (ddd, J = 13.3, 7.0, 6.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$, −50 °C) δ 142.0 (s), 141.1 (s), 137.6 (s), 134.9 (s), 134.6 (s), 134.5 (d), 132.7 (s), 130.5 (d), 129.7 (d), 129.5 (d), 126.8 (d), 126.4 (d), 111.0 (s, 2C), 110.9 (s), 110.8 (s), 49.3 (d), 48.9 (d), 45.9 (s, 2C), 35.3 (t), 33.8 (t), 33.0 (t, 2C), 25.7 (t), 23.4 (t); IR (KBr) 2230, 795, 760, 740, 725, 660 cm^{-1}; MS m/z (relative intensity) 388 (M^+, 24), 297 (70), 260 (100); HRMS calcd for $C_{26}H_{20}N_4$ 388.1688, found 388.1720.

General Procedure for Reaction of 1–3 with DCNA. DCNA was prepared according to the reported procedure[33] and was purified by trap to trap distillation. A mixture of a cyclophane and DCNA was stirred at room temperature in CH_2Cl_2 or benzene. In the case of **1**, the reaction was undertaken in a sealed tube. After most of the substrate has been consumed, the solvent was evaporated. The products were analyzed by HPLC and separated by flash chromatography (elution with petroleum ether/ether, 95:5–9:1).

Reaction of [6]Paracyclophane (1) with DCNA. Reaction of 101 mg (0.63 mmol) of **1** with 150 mg (1.97 mmol) of DCNA in 3.5 mL of CH_2Cl_2 for 17 days yielded 24 mg (16%) of the [4 + 2] adduct **47** and 9 mg (6%) of the adduct **48** as white solids. Reaction of **1** (241 mg, 1.51 mmol) with 174 mg (2.29 mmol) of DCNA in 7 mL of benzene for 48 h gave 32 mg of unreacted **1** and 204 mg (66%) of **47**.

47: mp 152–154 °C (recrystallized from ether/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 6.43 (d, J = 5.9 Hz, 2 H), 4.47 (dd, J = 5.9, 1.8 Hz, 2 H), 2.40 (dt, J = 12.5, 2.8 Hz, 2 H), 1.97–1.80 (m, 6 H), 1.10–0.98 (m, 2 H), 0.34–0.27 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 151.9 (s), 134.7 (s), 130.1 (d), 114.3 (s), 54.8 (d), 34.8 (t), 29.1 (t), 26.6 (t); IR (KBr) 2220, 1080, 980, 855, 810, 730, 655 cm^{-1}; MS m/z (relative intensity) 236 (M^+, 100), 179 (60), 167 (50), 154 (50), 95 (66). Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.83; N, 11.86. Found: C, 81.15; H, 6.80; N, 11.79.

48: mp 150–152 °C (recrystallized from ether); ^{1}H NMR ($CDCl_3$) δ 6.28 (dt, J = 5.5, 1.8 Hz, 2 H), 4.85 (t, J = 1.8 Hz, 1 H), 4.77 (t, J = 5.5 Hz, 1 H), 2.48–2.40 (m, 2 H), 2.30 (ddd, J = 14.6, 12.8, 4.4 Hz, 2 H), 1.97–1.86 (m, 2 H), 1.72–1.63 (m, 2 H), 1.45–1.36 (m, 2 H), 1.13–1.04 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 154.6 (s), 138.0 (s), 135.3 (s), 130.6 (d), 114.5 (s), 114.1 (s), 54.5 (d), 50.3 (d), 31.4 (t), 24.2 (t), 21.1 (t); IR (KBr) 2220, 1650, 1210, 1180, 915, 825, 785, 710 cm^{-1}; MS m/z (relative intensity) 236 (M^+, 100), 180 (66), 166 (75). Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.83; N, 11.86. Found: C, 81.20; H, 6.77; N, 11.80.

Reaction of [6](1,4)Naphthalenophane (2) with DCNA. Reaction of 165 mg (0.79 mmol) of **2** with 61 mg (0.80 mmol) of DCNA in 6 mL of CH_2Cl_2 for 5 h gave 60 mg (36%) of a mixture of dimers **10** and **11** (3:2), 6 mg (4%) of trimer **12**, and 59 mg (26%) of the [2 + 2] adduct **49** as a viscous oil which solidified in a refrigerator. Reaction of 95 mg (0.45 mmol) of **2** with 197 mg (2.6 mmol) of DCNA in 4 mL of benzene for 26 h furnished 30 mg (32%) of a mixture of dimers **10** and **11**, 15 mg (12%) of **49** as a pale yellow solid, and 10 mg (8%) of the cyclopropane-containing product **50** as a yellow solid.

49: mp 113–114 °C (recrystallized from ether/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.39–7.36 (m, 1 H), 7.31–7.27 (m, 3 H), 5.67 (d, J = 7.8 Hz, 1 H), 3.84 (br d, J = 6.3 Hz, 1 H), 2.99 (dt, J = 12.7, 3.9 Hz, 1 H), 2.25–1.20 (m, 9 H), 1.05–0.50 (br m, 2 H); ^{13}C NMR ($CDCl_3$) δ 145.2 (s), 139.3 (s), 136.6 (s), 133.6 (s), 128.8 (d), 127.9 (d), 127.1 (d), 124.9 (s), 124.2 (d), 118.2 (d), 111.0 (s), 110.7 (s), 56.0 (s), 51.4 (br d), 35.3 (br t), 35.0 (br t), 29.5 (br t), 27.3 (br t, 2C), 24.1 (br t); IR (KBr) 2220, 1630, 855, 775, 740 cm^{-1}; MS m/z (relative intensity) 286 (M^+, 61), 216 (100), 215 (82); HRMS calcd for $C_{20}H_{18}N_2$ 286.1470, found 286.1461.

50: mp 138–140 °C (recrystallized from ether/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.49 (dd, J = 7.7, 1.5 Hz, 1 H), 7.36 (dt, J = 1.5, 7.7 Hz, 1 H), 7.30 (dt, J = 1.5, 7.7 Hz, 1 H), 7.21 (dd, J = 7.7, 1.5 Hz, 1 H), 6.11 (s, 1 H), 5.99 (d, J = 4.4 Hz, 1 H), 3.05 (ddd, J = 13.6, 5.9, 3.3 Hz, 1 H), 2.31 (dd, J = 8.8, 4.4 Hz, 1 H), 2.22 (ddd, J = 13.5, 10.6, 3.7 Hz, 1 H), 2.14 (dt, J = 7.0, 8.8 Hz, 1 H), 1.68–1.23 (m, 7 H), 0.36–0.25 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 137.9 (s), 134.3 (s), 133.4 (s), 129.6 (s), 128.0 (d), 127.7 (d), 127.4 (d), 123.6 (d), 121.3 (d), 114.7 (s), 113.9 (s), 113.7 (d), 38.1 (s), 32.6 (t), 30.7 (d), 26.7 (t), 26.2 (t), 25.3 (t), 22.0 (d), 18.5 (t); IR (KBr) 2220, 870, 765, 750 cm^{-1}; MS m/z (relative intensity) 286 (M^+, 70), 243 (73), 230 (60), 218 (64), 204 (100); HRMS calcd for $C_{20}H_{18}N_2$ 286.1470, found 286.1489.

(33) Bloomquist, A. T.; Winslow, E. C. *J. Org. Chem.* **1945**, *10*, 149.

Reaction of [6](1,4)Anthracenophane (3) with DCNA. Reaction of 51 mg (0.20 mmol) of **3** with 60 mg (0.79 mmol) of DCNA in 4 mL of CH_2Cl_2 for 1.5 h afforded 21 mg (41%) of a mixture of trimers **14–16** and 38 mg (58%) of the [2 + 2] adduct **51** as a white solid. Reaction of 105 mg (0.40 mmol) of **3** with 119 mg (1.5 mmol) of DCNA in 7 mL of benzene for 17 h gave 34 mg (32%) of a mixture of trimers **14–16**, 48 mg (35%) of **51**, and 30 mg (22%) of the cyclopropane-containing product **52** as a yellow solid.

51: mp 160–162 °C (recrystallized from ether); ^{1}H NMR ($CDCl_3$) δ 7.84 (s, 1 H), 7.82–7.78 (m, 2 H), 7.73 (s, 1 H), 7.51–7.45 (m, 2 H), 5.80 (d, J = 7.7 Hz, 1 H), 3.91 (br d, J = 7.0 Hz, 1 H), 3.17 (dt, J = 12.8, 3.7 Hz, 1 H), 2.3–1.2 (m, 9 H), 1.1–0.8 (m, 1 H), 0.5 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 145.2 (s), 138.0 (br s), 136.5 (br s), 133.2 (s), 132.7 (s), 131.6 (br s), 128.1 (d), 127.6 (d), 126.9 (d), 126.8 (d, 2C), 125.9 (br s), 123.2 (d), 119.2 (d), 111.1 (s), 110.8 (s), 55.8 (s), 51.2 (br d), 36.4 (t), 35.3 (t), 29.7 (br t), 27.4 (br t, 2C), 24.2 (br t); IR (KBr) 2230, 885, 750 cm^{-1}; MS m/z (relative intensity) 386 (M^+, 100), 266 (82); HRMS calcd for $C_{24}H_{20}N_2$ 336.1627, found 336.1616.

52: mp 197–199 °C (recrystallized from ether/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.90 (s, 1 H), 7.86–7.80 (m, 2 H), 7.62 (s, 1 H), 7.50–7.46 (m, 2 H), 6.18 (s, 1 H), 6.06 (d, J = 4.4 Hz, 1 H), 3.21 (ddd, J = 13.2, 5.5, 3.3 Hz, 1 H), 2.33 (dd, J = 9.2, 4.4 Hz, 1 H), 2.28 (ddd, J = 12.9, 9.9, 3.6 Hz, 1 H), 2.17 (dt, J = 7.0, 8.8 Hz, 1 H), 1.77–1.24 (m, 7 H), 0.53–0.42 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 137.9 (s), 133.4 (s), 132.7 (s), 132.4 (s), 132.0 (s), 129.0 (s), 127.9 (d), 127.5 (d), 127.3 (d), 126.5 (d), 126.3 (d), 122.5 (d), 121.8 (d), 114.8 (s), 114.0 (s), 113.6 (d), 37.7 (s), 32.9 (t), 29.9 (d), 26.7 (t), 26.0 (t), 25.4 (t), 24.8 (d), 19.3 (t); IR (KBr) 2210, 880, 745 cm^{-1}; MS m/z (relative intensity) 336 (M^+, 100), 254 (64). Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.69; H, 5.94; N, 8.57.

Reaction of [6](1,4)Naphthalenophane (2) with DMAD. To a solution of 125 mg (0.60 mmol) of **2** in 2 mL of CH_2Cl_2 were added 845 mg (6.0 mmol) of DMAD and 3 mL of CH_2Cl_2. After the mixture was stirred at room temperature for 50 h, another 845 mg of DMAD was added. After another 26 h, DMAD (845 mg) was added again. The solvent and the excess DMAD were distilled off under reduced pressure. The product **54** (59 mg, 30%) was isolated as a white solid by flash chromatography (elution with petroleum ether/ether, 8:2). No isolable products were obtained when the reaction was carried out in benzene (sealed tube) at 80 °C.

54: mp 118–119 °C (recrystallized from ether/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.67–7.63 (m, 1 H), 7.34–7.25 (m, 3 H), 7.00 (s, 1 H), 6.13 (d, J = 6.8 Hz, 1 H), 4.65 (d, J = 6.8 Hz, 1 H), 3.85 (s, 3 H), 3.07 (dt, J = 16.6, 3.4 Hz, 1 H), 2.43 (t, J = 4.4 Hz, 1 H), 2.29 (dt, J = 12.7, 4.4 Hz, 1 H), 1.83–1.67 (m, 4 H), 1.57–1.35 (m, 2 H), 1.30–1.20 (m, 1 H), 0.87 (br m, 1 H), 0.39 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 169.9 (s), 165.5 (s), 147.1 (s), 146.3 (s), 134.7 (s), 134.2 (s), 129.3 (d), 129.0 (d), 128.1 (d), 125.8 (d), 123.3 (d), 117.7 (d), 77.6 (d), 52.6 (s), 52.3 (q), 35.1 (t), 34.4 (t), 29.7 (br t), 29.6 (t), 29.0 (br t), 24.4 (t); IR (KBr) 1755, 1720, 1220, 960, 770 cm^{-1}; MS m/z (relative intensity) 338 (M^+, 100), 278 (57), 237 (60), 207 (60), 165 (69). Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55. Found: C, 74.34; H, 6.56.

Reaction of [6](1,4)Anthracenophane (3) with DMAD. To a solution of **3** (30 mg, 0.12 mmol) in 2 mL of CH_2Cl_2 was added 71 μL (0.6 mmol) of DMAD, and the mixture was stirred at room temperature. After 23 h, another 71 μL of DMAD was added and the mixture was stirred for another 61 h. A workup similar to that described above gave 10 mg (23%) of lactone **55** as a white solid and 5 mg (8%) of the 2:1 adduct **56** as a yellow solid.

A mixture of 111 mg (0.43 mmol) of **3** and 610 mg (4.3 mmol) of DMAD in 7 mL of benzene was heated at 80 °C in a sealed tube for 19 h. The solvent and excess DMAD were distilled off, and the residue was washed with ether to leave 43 mg of **56** as a yellow solid. The ether washing was chromatographed (elution with petroleum ether/ether, 8:2–5:5) to give 24 mg (14%) of the cyclopropane-containing product **57**, 4 mg (2%) of lactone **55**, and 22 mg of **56** (total 65 mg, 28%).

55: mp 147–149 °C (recrystallized from petroleum ether/ether); ^{1}H NMR ^{1}H NMR ($CDCl_3$) δ 8.11 (s, 1 H), 7.81–7.76 (m, 2 H), 7.76 (s, 1 H), 7.48–7.43 (m, 2 H), 7.06 (s, 1 H), 6.24 (d, J = 6.8 Hz, 1 H), 4.70 (d, J = 6.8 Hz, 1 H), 3.90 (s, 3 H), 3.23 (dt, J = 13.3, 3.8 Hz, 1 H), 2.46–2.41 (m, 1 H), 2.38 (dd, J = 12.8, 4.8 Hz, 1 H), 1.9–1.2 (m, 7 H), 0.91 (br m, 1 H), 0.42 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 170.1 (s), 165.7 (s), 147.2 (s), 146.5 (s), 133.4 (s), 132.9 (s), 132.8 (s), 132.0 (s), 129.4 (d), 128.1 (d), 127.7 (d), 126.7 (d), 126.5 (d), 125.4 (d), 122.3 (d), 118.6 (d), 77.7 (d), 52.8 (s), 52.4 (q), 35.9 (t), 34.6 (t), 29.7 (t), 29.6 (t), 28.9 (t), 24.6 (t); IR (KBr) 1760, 1725, 1230, 1210, 970, 890, 750 cm^{-1}; MS m/z (relative intensity) 388 (M^+, 100), 328 (12), 287 (17), 257 (20), 215 (21); HRMS calcd for $C_{25}H_{24}O_4$ 388.1674, found 388.1664.

56: mp 207–208 °C (recrystallized from ether/CH_2Cl_2); ^{1}H NMR ($CDCl_3$) δ 7.86 (s, 1 H), 7.85–7.75 (m, 2 H), 7.83 (s, 1 H), 7.48–7.43 (m, 2 H), 6.29 (d, J = 6.6 Hz, 1 H), 4.93 (d, J = 6.6 Hz, 1 H), 3.94 (s, 3 H), 3.93 (s, 3 H), 3.74 (s, 3 H), 3.3–3.2 (m, 1 H), 2.51 (s, 3 H), 2.3 (m, 2 H), 1.9–1.5 (m, 5 H), 1.3–1.2 (m, 1 H), 1.2–1.1 (m, 1 H), 0.83 (br m, 1 H), 0.25 (br m, 1 H); ^{13}C NMR ($CDCl_3$) δ 168.3 (s), 164.4 (s), 162.6 (s), 161.2 (s), 146.6 (s), 145.0 (s), 135.4 (s), 133.1 (s), 132.8 (s), 132.3 (s), 131.8 (s), 128.5 (d), 127.3 (d), 126.4 (d, 2C), 126.1 (d), 125.8 (s), 123.3 (d), 122.6 (d), 115.2 (s), 88.2 (d), 52.7 (q), 52.5 (q), 52.3 (q), 51.0 (s), 50.2 (q), 37.8 (t), 35.1 (t), 30.0 (br t), 29.8 (t), 28.7 (t), 24.1 (t); IR (KBr) 1730, 1715, 1630, 1585, 1260, 1195, 1150, 1060, 950, 905, 790, 740 cm^{-1}; MS m/z (relative intensity) 544 (M^+, 40), 512 (81), 484 (62), 452 (100). Anal. Calcd for $C_{32}H_{32}O_8$: C, 70.57; H, 5.92. Found: C 70.17; H, 5.91.

57: mp 127–129 °C (recrystallized from petroleum ether/ether); ^{1}H NMR ($CDCl_3$) δ 7.89 (s, 1 H), 7.83 (s, 1 H), 7.81–7.78 (m, 2 H), 7.42–7.38 (m, 2 H), 6.21 (s, 1 H), 6.10 (d, J = 4.5 Hz, 1 H), 3.90 (s, 3 H), 3.83 (s, 3 H), 3.20 (ddd, J = 13.3, 5.3, 3.6 Hz, 1 H), 2.40 (dd, J = 8.6, 4.5 Hz, 1 H), 2.26 (ddd, J = 13.8, 11.3, 4.0 Hz, 1 H), 2.12 (dt, J = 7.0, 8.8 Hz, 1 H), 1.7–1.3 (m, 6 H), 1.0–0.9 (m, 1 H), 0.5–0.4 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 167.9 (s), 165.7 (s), 151.1 (s), 132.8 (s), 132.6 (s), 132.5 (s), 132.4 (s), 131.3 (s), 128.1 (d), 127.8 (d), 127.4 (d), 125.7 (d), 125.6 (d), 124.5 (d), 123.7 (d), 121.4 (d), 52.3 (q), 51.9 (q), 37.9 (s), 33.0 (t), 29.3 (d, J = 167 Hz), 27.3 (t), 26.2 (t), 25.7 (t), 24.1 (d, J = 165 Hz), 19.4 (t); IR (KBr) 1730, 1640, 1260, 1200, 1170, 880, 750 cm^{-1}; MS m/z (relative intensity) 402 (M^+, 75), 342 (100), 311 (61); HRMS calcd for $C_{26}H_{26}O_4$ 402.1831, found 402.1863.

X-ray Crystallographic Studies. Diffraction intensities were measured with a Rigaku four-circle diffractometer using Cu Kα (for compounds **10**, **14**, and **56**) or Mo Kα irradiation (for compounds **45**, **52**, and **54**). The structures were solved by direct methods, MULTAN-78[34] for **14** and **56** or SHELXS-86[35,36] for **10**, and refined by full-matrix least-squares (X-RAY SYSTEM[37]). The structures of **45**, **52**, and **54** were solved and refined using the program package TEXAN.[38] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were refined isotropically. The positions of the hydrogens of the solvent molecule (diethyl ether) in the crystal of **45** were not determined because of the disordered nature of the solvent molecule. Crystal data and selected refinement parameters are summarized in Table VIII. Bond distances, bond angles, fractional atomic coordinates, and anisotropic thermal parameters are given in the supplementary material.

Acknowledgment. We thank the Crystallographic Research Center of the Institute for Protein Research and the Instrumental Analysis Center of the Faculty of Engineering, Osaka University, for the use of the X-ray and NMR and MS facilities, respectively. The authors are grateful to the Ministry of Education, Science, and Culture of Japan for partial support of this work through a Grant-in-Aid for Scientific Research on Priority Areas (No. 02230217).

Supplementary Material Available: Tables of bond distances and angles, fractional atomic coordinates, and anisotropic thermal parameters for non-hydrogen atoms for **10**, **14**, **45**, **52**, **54**, and **56** (40 pages). Ordering information is given on any current masthead page.

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