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Annulation of Seven-Membered Rings to [2.2]Paracyclophane[‡]

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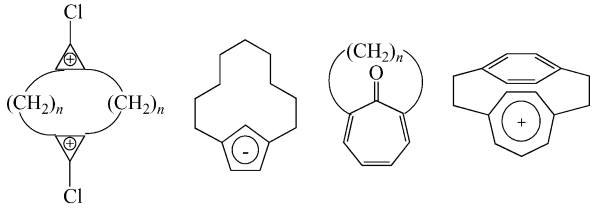
Tropylidenes **16** and **17** were prepared from [2.2]paracyclophane (**10**). On treatment with the corresponding trityl salts they were converted into tropyliophanes **26a** (tetrafluoroborate) and **26b** (perchlorate). With acetone, **26a** furnished trapping product **27**, which underwent a homo-Diels–Alder addition with tetracyanoethylene to afford adduct **29**. All new compounds were characterized by their spectroscopic and analytical data and for most – including **17** and **26b** – the structures were also determined by X-ray diffraction.

Introduction

In comparison to the huge effort that has been devoted to the preparation and study of aromatic cyclophanes during the last half century,[2] little is known about the synthesis of nonbenzenoid cyclophanes.[3] Furthermore, although various cyclopropenyliophanes (**1**),[4a,4b] cyclopentadienidophanes (**2**),[5] troponophanes (**3**),[6a–6f] tropyliophanes (**4**),[7a–7h] (Scheme 1) and phanes containing a nonbenzenoid 10 π-system have been described,[3] little is known about the *chemical behavior* of these compounds.

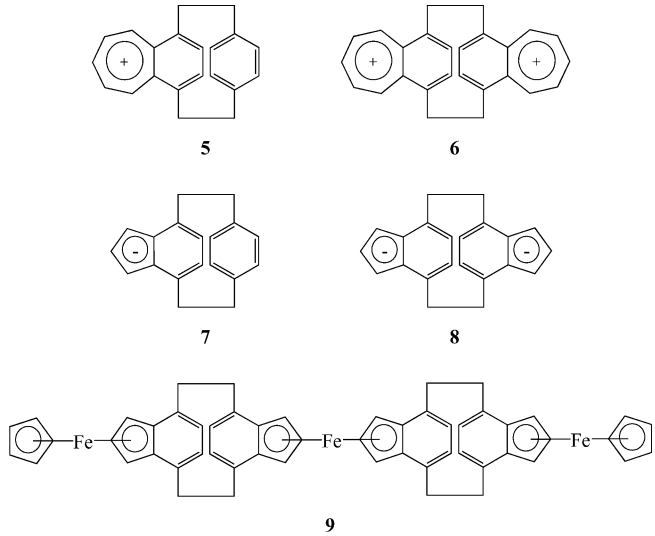


1 (*n* = 3, 5) **2** **3** (*n* = 4, 6, 9) **4**

Scheme 1. A selection of nonbenzenoid cyclophanes.

The main reason for this lack of knowledge is that the syntheses of these unusual compounds are often far from straightforward. In many cases, the amount of material available at the end of a synthetic sequence was just sufficient to obtain the spectroscopic data – the question of the chemical properties, however, had to be left open in the hope that at "some later time" enough material would accumulate to address reactivity questions.

We decided to begin closing this gap by preparing annulated tropyliophane **5** and hoped at the same time that the knowledge gained during its synthesis could be applied to the preparation of bis(tropylium salt) **6**. We were encouraged in these efforts by our previous preparation of the anionic sister molecules of **5** and **6**, viz. **7** and **8**,[8] the electronic properties of which were investigated by NMR spectroscopy and which also served as starting materials for novel metallocenophanes such as **9** (Scheme 2).[9]



5 **6** **7** **8** **9**

Scheme 2. Charged [2.2]phanes with 10 π-electron decks.

[‡] Cyclophanes, LXI. Part LX: Ref.[1]

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An interesting hybrid of the two ion types would be a cyclophane in which one deck is positively charged (benzotropylium cation) and the other negatively (indenyl anion).[10]

Results and Discussion

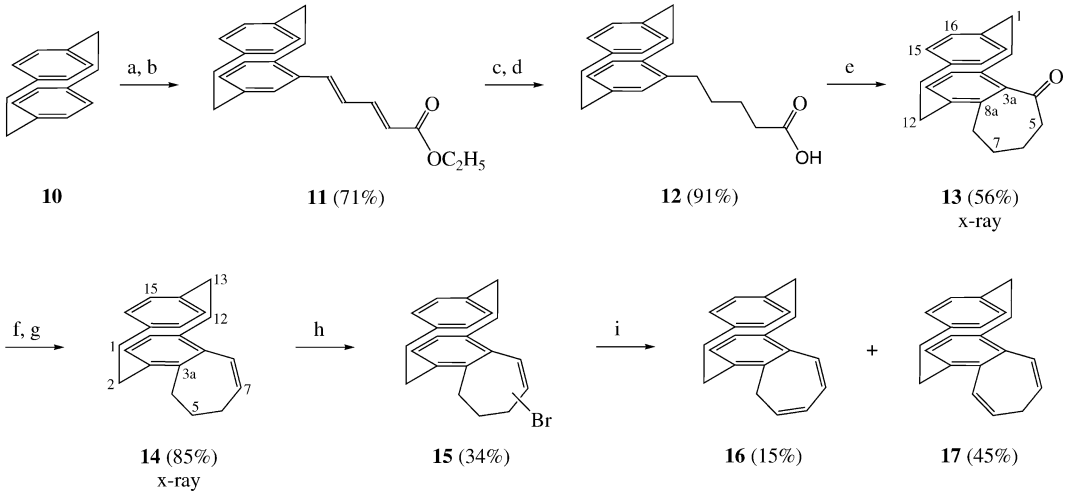
The Preparation of Benzotropylidenophanes 16 and 17

Starting from the commercial substrate [2.2]paracyclophane (**10**) the two isomeric cycloheptatriene derivatives **16** and **17** were prepared as summarized in Scheme 3.

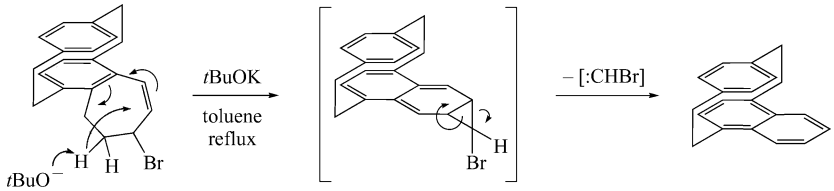
Formylation of **10** under Rieche conditions ($TiCl_4$/Cl_2CHOCH_3) first provided 4-formyl[2.2]-paracyclophane,[11] which was subsequently chain elongated by a Wittig–Horner reaction with triethyl 4-phosphonocrotonate to afford dienoate **11**. The structure of the compound follows from its spectroscopic data (see Experimental Section), in particular its all-*trans* configuration from the two coupling constants $^3J_{17,18}$ = 15.4 Hz and $^3J_{19,20}$ = 15.3 Hz, respectively, for the two double bonds. Catalytic hydrogenation over Pd in ethyl acetate gave the saturated ester (98%), which was saponified to acid **12** with aqueous sodium hydroxide solution in 93% yield. This compound was prepared previously by Nugent and Vigo by a different route and in poorer overall yield.[12] Surprisingly, in our hands the subsequent Friedel–Crafts cyclization in the presence of polyphosphoric acid did not provide the 75% reported in the literature.[12] At best, we could obtain 15% under these conditions, and in the product mixture at least four components were detected in which the ethano bridges of **13** had been ruptured by *ipso* substitution. In the end, a 10% solution of phosphorus pentoxide in methanesulfonic acid[13] gave the best results and furnished ketone **13** in 56% yield. Although the structure of this compound follows unambiguously from the spectroscopic and analytical data, it was also confirmed by X-ray structural analysis (see below). The alcohol obtained from **13** after lithium aluminum hydride reduction in THF (mixture of diastereomers) was not isolated but directly subjected to acid-catalyzed dehydration. Olefin **14** was obtained in a gratifying 85% yield and its structure determined by spectroscopic measurements and X-ray analysis (see below). The allylic bromination of **14** to **15** (mixture of isomers) turned out to be the bottleneck of the synthesis, which resulted in a severe loss of intermediate material. The mixture of bromides **15**, obtained in only 34% yield, was not purified further. The attack of the halogen atom at both the allylic and the benzylic position of **14** was made obvious in the ensuing elimination step (potassium *tert*-butoxide in DMSO at room temperature) that furnished a mixture of the two benzotropylidenes **17** and **16** in 3:1 ratio (total yield 60%). Both hydrocarbons were characterized by the usual spectroscopic methods (see Experimental Section) and **17** also by X-ray diffraction (see below).

A surprising observation was made when the solvent in the above elimination reaction was replaced by toluene, and the reaction temperature increased to reflux (111 °C). Rather than providing dienes **16** and **17**, [2]paracyclo-[2](1,4)-naphthalenophane (**20**) was now isolated in 22% as the sole product. For its formation we propose the pathway presented in Scheme 4.

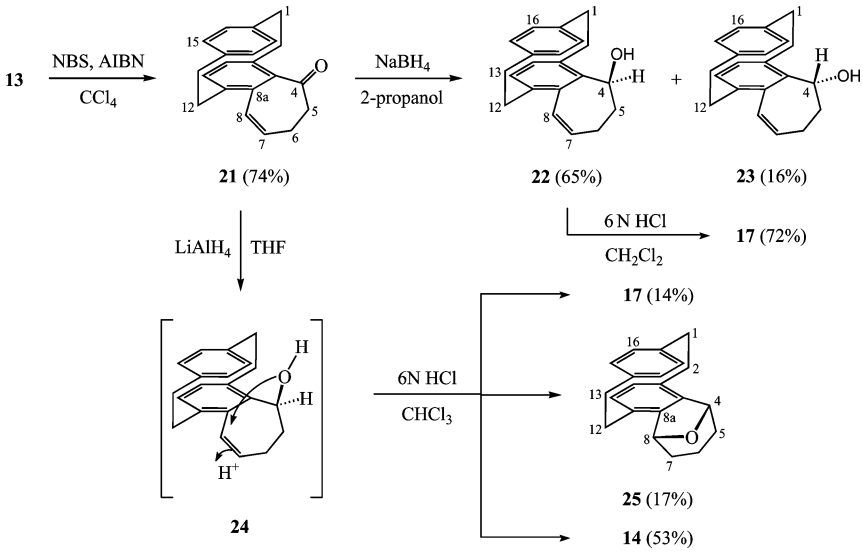
Starting from allyl bromide **18**, dehydrobromination could lead to norcaradiene intermediate **19**, which provides the isolated hydrocarbon by loss of bromocarbene. To the best of our knowledge, such a base-induced process has not been described in the chemical literature, although thermal and photochemical carbene eliminations of cycloheptatriene and benzocyclopheptatriene derivatives have been reported.[14a–14c] Photochemical carbene removal from benzo- and dibenzonorcaradienes has also been observed.[15] The essential role of bromine in the above ring-contraction process was demonstrated in a control experiment, in which



Scheme 3. Annulation of a seven-membered ring to [2.2]paracyclophane (**10**).



Scheme 4. Fragmentation of **18** to naphthalenophane **20**.



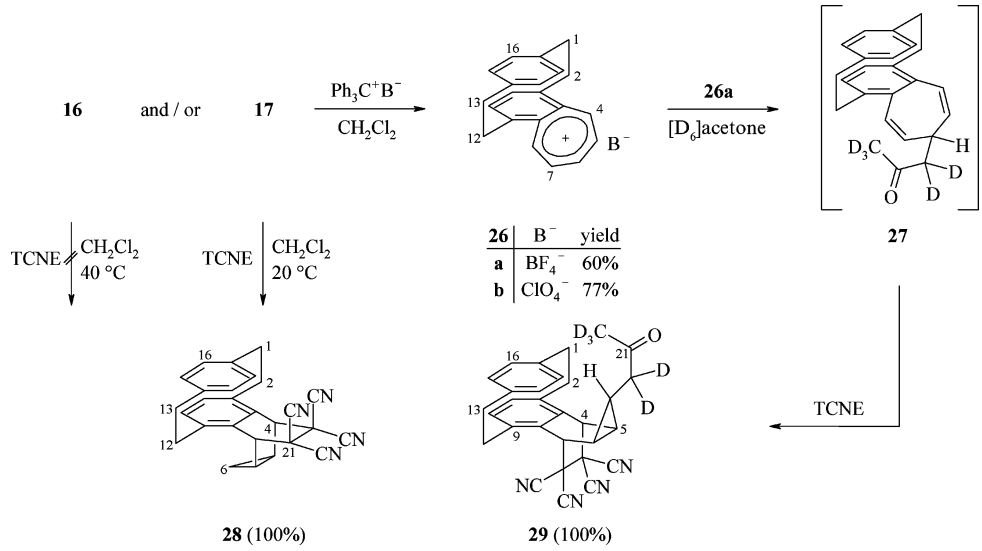
Scheme 5. Some reactions of annulated [2.2]paracyclophanes.

dienes **16** and **17** were subjected to the same conditions as **18**: both hydrocarbons were isolated unchanged after the intended elimination process.

An alternative, higher yielding route to symmetrical benzocycloheptatriene **17** started directly from ketone **13** and is presented in Scheme 5.[16] Heating ketone **13** in the presence of NBS and AIBN in carbon tetrachloride resulted in the direct formation of enone **21**, which was isolated in 74% yield after column chromatography. Reduction of **21** with sodium borohydride in isopropyl alcohol furnished a mixture of alcohols **22** and **23** in 4:1 ratio (combined yield 81%), which was separable by column chromatography on silica gel. The structure assignment follows from the spectroscopic data (Experimental Section) and in particular from the X-ray structural analysis of major product **22**. As shown below, the hydroxy functionality of this isomer points to the "interior" of the cyclophane moiety, which indicates that the hydride transfer takes place preferentially from the sterically less-shielded "outside" of the starting ketone. Still, the reducing agent is able to pass the bridging *p*-xylylene unit of **21**, which thus leads to *exo* alcohol **23** also. Treatment of a solution of **22** in dichloromethane with hydrochloric acid at room temperature provided symmetrical tropylidenophane **17** in essentially quantitative yield. This route makes the compound available in amounts of several hundred mg and, furthermore, provided single crystals suitable for X-ray analysis (see below). The reduction of **21** with lithium aluminum hydride in THF took a different course and led – after workup in the presence of 6 N HCl in chloroform – to a product mixture consisting of unsaturated hydrocarbons **14** (main product) and **17** as well as bridged ether **25**. We assume that initially produced *endo* alcohol **22** (outside hydride attack, see above) has at least three different options to react. Like other unsaturated alcohols,[17] the ate complex present before hydrolysis and/or acid treatment can undergo reduction of its sterically nearby double bond to provide the corresponding saturated alcohol. This, upon acidic workup, furnishes olefin **14** as in the reduction/elimination of **13** (see Scheme 3). Dehydration of **22** leads to benzotropylidene **17**. Finally, regioselective protonation of the double bond of **22** creates a benzylic cation that can be trapped by the opposing hydroxy functionality (see structure **24**), which thus generates *endo* ether **25**. The stereochemistry of the latter was again proved by X-ray structural analysis (see below).

Preparation of Tropyliophane 26

Having sufficient amounts of **16** and/or **17** in hand, the stage was set for the generation of tropylium ion **5**. In fact, reaction of either **16** or **17** with trityl fluoroborate or perchlorate, respectively, in dichloromethane at room temperature gave salts **26a** and **26b** in acceptable yields (Scheme 6).



Scheme 6. Preparation of tropyliophanes **26**.

Both salts are beautifully deep-red, crystalline compounds, the structures of which follow from their spectroscopic data.

The NMR spectra of **26a** and **26b** were identical apart from small chemical shift differences (^{1}H: 0.01–0.02 ppm, ^{13}C: 0.2–0.3 ppm). The values given in Table 1 are averages. The protons of the benzotropylium part of **26** are strongly deshielded (δ = 9.67–7.87 ppm; Table 1) due to the positive charge residing in this part of the molecule. These are downfield shifted between 1.1 and 2.0 ppm relative to naphthalenophane **20**. Similarly, there are strong effects of the positive charge upon the shifts of the ^{13}C nuclei ($\Delta\delta$ = 14.3–26.9 ppm). The largest values of these charge effects are virtually identical with the shift differences between the tropylium cation and benzene ($\Delta\delta_H$ = 2.01 ppm, $\Delta\delta_C$ = 27.1 ppm; see Table 1). At 400 MHz, the four-spin bridge proton spectrum of **26** is completely first-order because of the widely spaced chemical shifts. The assignments were achieved by common 2D techniques (HSQC, HMBC) and started with the observation of the NOE between 2-H_{syn} and 4-H. The ^{1}H,^{1}H coupling constants in **26** are rather similar to those in **20**, yet the geminal coupling in the methylene group adjacent to the charged aromatic system is algebraically smaller by 1.0 Hz.

It seemed interesting to compare the ^{1}H chemical shifts of the *endo* protons 18-H and 19-H of the *para*-phenylene rings in **26** and **20**, which are under the influence of the ring current of the opposing annulated aromatic ring: tropylium in **26** versus benzene in **20**. The magnetic field induced aromatic ring current[18] is normally used to explain the deshielding of aromatic relative to olefinic protons and the shielding of protons residing above aromatic systems. Some theoretical calculations indicate that the ring current is somewhat smaller in the tropylium ion than in benzene. According to Jusélius and Sundholm,[19] for example, the difference is of the order of 20%. The simplistic assumption that the shielding difference of the *endo* protons 18-H and 19-H in benzotropyliophane **26** relative to their analogues in naphthalenophane **20** is solely due to the decrease in the

Table 1. Comparison of the NMR spectroscopic data[a] of **26** and **20**.

	26	**20**[b,c]	$\Delta\delta$
	Proton chemical shifts [ppm]		
1a[d]	3.40	3.09	0.31
1s	3.23	2.88	0.35
2a	3.73	3.05	0.68
2s	4.29	3.79	0.50
4	9.67	7.68	1.99
5	8.74	7.38	1.36
6	9.05		
10	7.87	6.73	1.14
15	6.77	6.44	0.33
18	5.48	5.58	–0.10
	9.28 ($C_7H_7^+$)	7.27 (C_6H_6)	2.01
	Coupling constants [Hz]		
J(1a,1s)	–13.6	–13.2	
J(1a,2a)	10.4	10.7	
J(1a,2s)	2.7	2.0	
J(1s,2a)	6.1	6.2	
J(1s,2s)	10.2	10.2	
J(2a,2s)	–14.6	–13.6	
	Carbon chemical shifts [ppm]		
1	36.4	34.4	2.0
2	36.7	32.9	3.8
3	150.9[e]	136.6	14.3
3a	150.0[e]	135.3	14.7
4	152.4	125.3	27.1
5	142.1	124.8	17.3
6	156.3		
10	145.0	130.6	14.4
14	141.1	137.9	3.2
15	134.2	132.2	2.0
18	135.2	127.8	7.4
	155.4 ($C_7H_7^+$)	128.5 (C_6H_6)	26.9

[a] Solvents: [D]TFA for **26**, $CDCl_3$ for **20**; internal references: TMS for **26** (^{1}H and ^{13}C) and **27** (^{1}H), $CDCl_3$ (δ = 77.01 ppm) for **27** (^{13}C). [b] A. Akkermann-Kubillus, L. Ernst, H. Hopf, unpublished results, **1987**. [c] To facilitate the comparison with **26**, carbon atoms in **20** are numbered 1–5 and 7–19. [d] a, s: *anti, syn* with respect to the annulated ring. [e] Interchangeable assignments.

ring current would lead one to expect a deshielding of these protons in **26** with respect to **20**. However, the opposite is found, albeit only by a small measure: the protons in question are shielded by 0.10 ppm. We suggest that there is a combination of (at least) three different, partly counteracting, effects: (a) The effect of reduced ring current may be estimated by taking 20% of the difference between the chemical shift of the *endo* protons in **20** (δ = 5.58 ppm) and in [2.2]paracyclophane (δ = 6.48 ppm), that is, –0.18 ppm. (b) Additionally, one would expect a charge-transfer effect of the benzotropylium moiety onto the *para*-phenylene ring. This effect could be taken equal to the difference between the shift of the *exo* protons (15-H, 16-H) in **26** and in **20**, that is, +0.29 ppm. (c) Finally, there should be a geometric effect. As the C–C–C bond angles in an equilateral heptagon are larger (ideally 128.57°) than the 120° angles of a hexagon, the *endo* protons in **26** are closer to the center of the ring current of the tropylium moiety than they are with respect to the center of the annulated benzene ring in **20**, that is, they undergo an effect of relative shielding. The geometric effect would have to be of the order of –0.2 ppm for the total effect to agree with the experimental shift difference between **26** and **20**.

The structure of **26b** was confirmed by X-ray crystallography (see below). Reingold and coworkers have reported that tropylium ions react with enolizable ketones such as acetone to yield α-cycloheptatrienyl ketones.[20] An analogous reaction took place when **26b** was dissolved in acetone: after 30 min at room temperature the sole product isolated was methyl ketone **27**. Repeating this experiment with **26a** in [D_6]acetone in the presence of tetracyanoethylene (TCNE) as a trapping agent resulted in the formation of adduct **29** as the sole product. To learn more about its mechanism of formation, both tropylidenes **16** and **17** were treated with TCNE in dichloromethane at room temperature. Whereas **16** did not react, **17** provided homo-Diels–Alder adduct **28**, the structure of which was determined by spectroscopic (see Experimental Section) and X-ray structural analysis (see below). The cycloaddition of suitable dienophiles to cycloheptatrienes and benzocycloheptatrienes is a well-established phenomenon and has been proposed to take place via a norcaradiene intermediate.[21a–21d] In the present case, evidently only **17** can form this intermediate under the mild conditions used. The important role of the reactivity of the dienophile in the cycloaddition was demonstrated by attempting to add maleic anhydride to either **16** or **17**: both compounds survived the addition experiment even if it was performed in 1,2-dichlorobenzene at 185 °C. In the case of **26a**, a ketone of type **27** is obviously produced first, which is subsequently intercepted by TCNE.

X-ray Structural Analysis of Annulated Compounds 13, 17, 22, 25, 26b, 28, and 29

The seven structures studied here are depicted in Figures 1 (**13**), 2 (**17**), 3 (**22**), 4 (**25**), 5 (**26b**), 6 (**28**), and 7 (**29**). In general, the cyclophane moieties display the usual distortions: the bridge single bonds are elongated, the angles in the bridges are widened, the six-membered rings display flattened boat conformations (whereby the bridge-

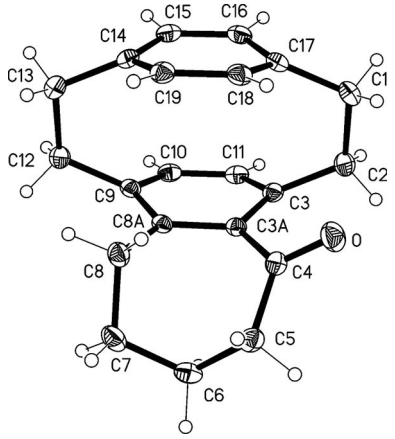


Figure 1. The molecule of compound **13** in the crystal. Ellipsoids represent 30% probability levels.

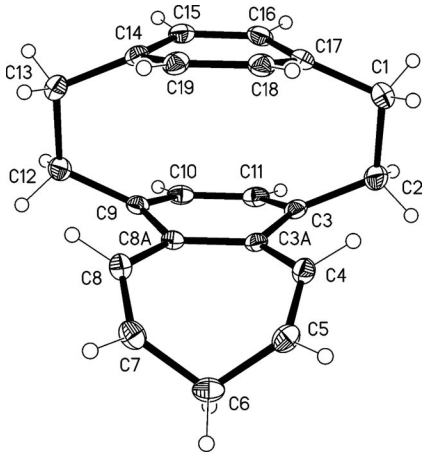


Figure 2. The molecule of compound **17** in the crystal. Ellipsoids represent 30% probability levels.

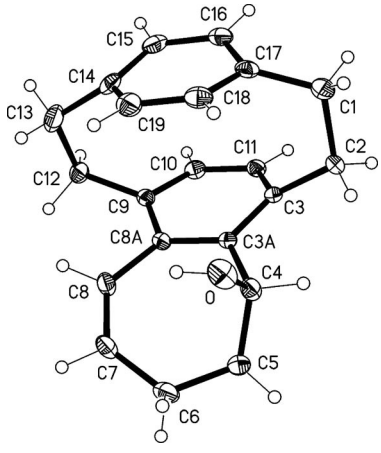


Figure 3. The molecule of compound **22** in the crystal. Ellipsoids represent 30% probability levels.

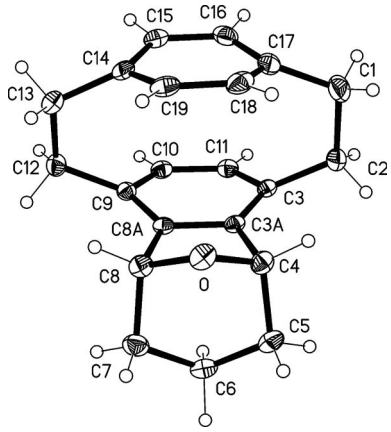


Figure 4. The molecule of compound **25** in the crystal. Ellipsoids represent 30% probability levels.

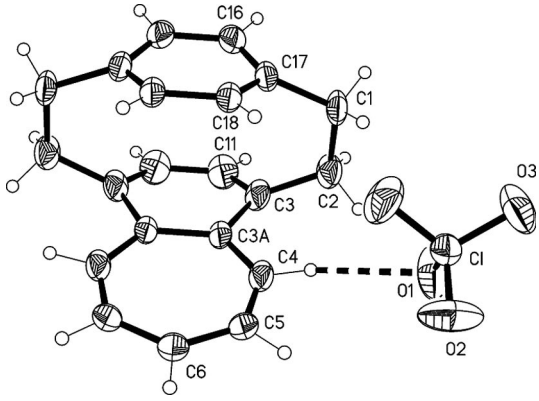


Figure 5. The formula unit of compound **26b** in the crystal. Only the asymmetric unit is numbered. Ellipsoids represent 30% probability levels.

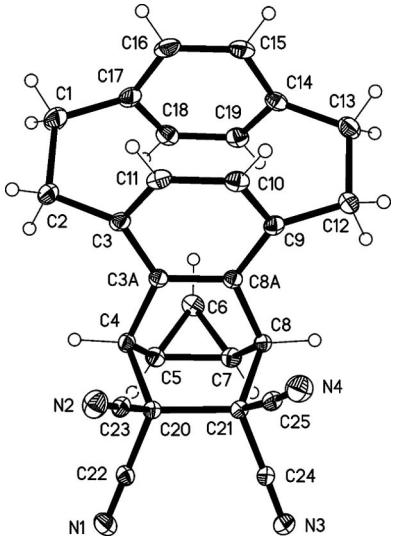


Figure 6. The molecule of compound **28** in the crystal. Ellipsoids represent 30% probability levels.

head atoms lie ca. 0.15–0.20 Å outside the plane of the other four atoms), and the ring angles at the bridgehead atoms are narrowed. Except for Diels–Alder adducts **28** and

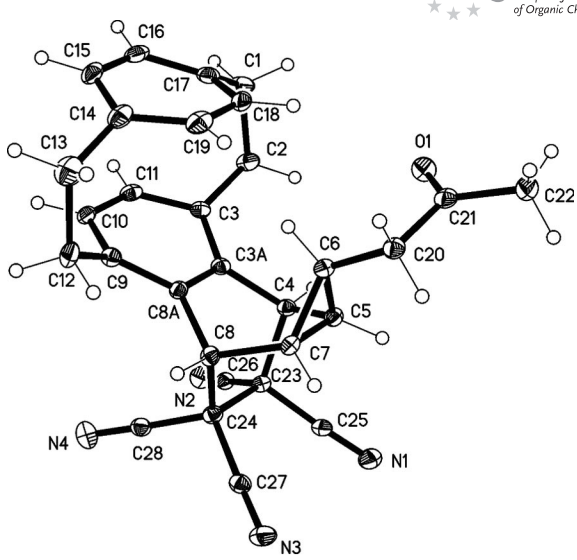


Figure 7. The molecule of compound **29** in the crystal (excluding the solvent molecule). Ellipsoids represent 30% probability levels.

29 (see below) the ring planes remain parallel (interplanar angles <2°). Compound **26b** shows exact mirror symmetry in both cation and anion, whereas compounds **17**, **25**, and **28** display the same symmetry to a good approximation (rms deviations 0.02, 0.09, and 0.09 Å).

In compounds **28** and **29**, the paracyclophane rings are no longer exactly parallel [interplanar angles between non-bridgehead planes are 8.9(1) and 13.3(2)°, respectively]. This may be associated with the formation of very short intramolecular contacts, which can be interpreted as C–H···π interactions from a hydrogen at C6 to the midpoints of the bond C18–C19. Normalizing the C–H bond lengths to 1.08 Å, the H···π distances are 2.44 and 2.31 Å and the C–H···π angles are 176 and 164°, respectively.

The crystal packing of each compound (except that of hydrocarbon **17**) involves weak hydrogen bonds of the form C–H···X (X = O or N). In **13**, the contact H13B···O 2.47 Å connects the molecules to form zigzag chains parallel to

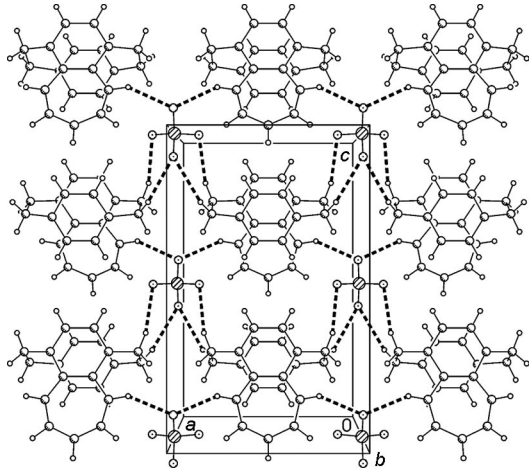


Figure 8. Packing diagram for compound **26b** viewed parallel to the *y* axis. C–H···O interactions are indicated by thick dashed bonds.

the *z* axis. In **22**, the contact H12B···O 2.54 Å connects the molecules to form chains parallel to [011]; surprisingly, the OH hydrogen atom is not involved in secondary interactions. In **25**, the contacts H12A···O 2.52 Å and H13B···O 2.57 Å connect the molecules to form spirals parallel to the *z* axis. In **26b**, the contacts H4···O1 2.28 Å, H1B···O2 2.54 Å, and H2A···O3 2.51 Å connect the ions in layers parallel to the *xz* plane (Figure 8). In **28**, the contacts H7···N1 2.52 Å and H8···N3 2.34 Å connect the molecules to form tapes that are two molecules (or one **b** translation) broad and parallel to the *x* axis (Figure 9). In **29**, the contacts H4···O1 2.41 Å, H2A···N3 2.62 Å, H5···N3 2.55 Å, and H20A···N3 2.46 Å link the molecules in the same manner as that for **28** (Figure 10).

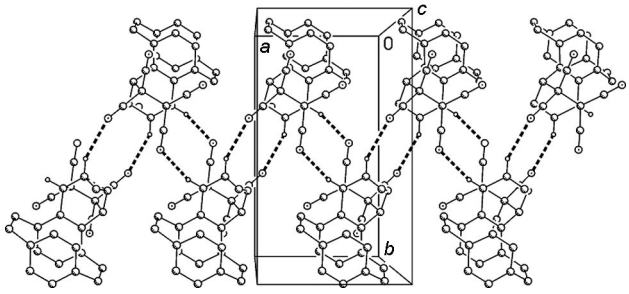


Figure 9. Packing diagram for compound **28** viewed parallel to the *z* axis. C–H···O interactions are indicated by thick dashed bonds. H atoms not involved in short contacts are omitted for clarity.

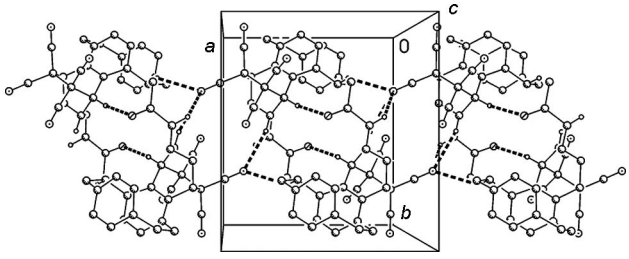


Figure 10. Packing diagram for compound **29** viewed parallel to the *z* axis. C–H···O interactions are indicated by thick dashed bonds. H atoms not involved in short contacts are omitted for clarity.

Conclusions

We prepared tropyliophane system **5**, which is a novel type of cyclophane in which a nonbenzenoid 10 π-electron system forms one of the decks by a short synthetic sequence, from the commercial product [2.2]paracyclophane (**10**). It remains to be seen whether dication **6** can be synthesized by a comparable approach. Because cycloheptatrienes have been used as ligands for novel transition-metal sandwich complexes[22a–22c] **16** and **17** could in principle be employed for the synthesis of novel multilayered metal complexes.

Experimental Section

General Remarks: DSC was performed with commercial DC-plates (Polygram Sil G/UV_{254}) purchased from Macherey, Nagel & Co. (Düren). Column chromatography was performed with Kieselgel 60 (70–230 mesh) purchased from Merck (Darmstadt). Melting points were determined with a Büchi 530 melting-point apparatus or by differential scanning calorimetry (DSA), Rheometric Scientific (Piscataway, USA) and are uncorrected. NMR spectra were recorded with the following instruments: Bruker AC-200 [^{1}H NMR (200.1 MHz), ^{13}C NMR (50.3 MHz)], Bruker WM-400 [^{1}H NMR (400.1 MHz), ^{13}C NMR (100.6 MHz)]. Tetramethylsilane (δ_H = 0.00 ppm) and $CDCl_3$ (δ_C = 77.05 ppm) were used as internal references. IR spectra were recorded with a Nicolet 320 FTIR instrument as KBr pellets. UV/Vis spectra were recorded with a Beckman UV 5230 and HP 8452 A Diode Array. MS were recorded with a Finnigan MAT 8430 (EI, 70 eV) instrument.

Ethyl 5-(4-[2.2]Paracyclophanyl)penta-(2*E*,4*E*)-dienoate (11): To a solution of triethyl 4-phosphonocrotonate[23] (6.35 g, 26 mmol) in anhydrous THF (200 mL) was added *n*-butyllithium (ca. 1.4 M in hexane, 19 mL, ca. 26.6 mmol) under an atmosphere of nitrogen at 0 °C. The solution turned yellow-orange. After stirring for 20 min at room temperature, 4-formyl-[2.2]paracyclophane[11] (6.00 g, 25.4 mmol) was added in portions, and the mixture was stirred for 4 h at room temperature. For workup, ice water was added (200 mL), and the product mixture was extracted carefully with ether. The combined organic phase was washed with water and dried with magnesium sulfate, and the solvent was removed by rotary evaporation. After column chromatography of the remaining oil, 6.33 g (75%) of **11** was isolated as a yellow oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.80–3.18 (m, 7 H) and 3.45–3.50 (m, 1 H, ethano bridges), 4.25 (q, *J* = 7.1 Hz, 2 H, OCH_2), 6.00 (d, *J* = 15.3 Hz, 1 H, 20-H), 6.36–6.62 (m, 7 H, 5-, 7-, 8-, 12-, 13-, 15-, 16-H), 6.67 (dd, *J* = 15.4, 11.2 Hz, 1 H, 18-H), 6.97 (d, *J* = 15.4 Hz, 1 H, 17-H), 7.53 (dd, *J* = 15.3, 11.2 Hz, 1 H, 19-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.3 (CH_3), 33.7, 34.8, 35.1, 35.3 (all CH_2, C-1, -2, -9, -10), 60.3 (OCH_2), 120.6 (CH, C-20), 126.3, 130.1, 130.4, 131.6, 132.9, 133.0, 133.2, 135.1, 138.4 (all CH, C-5, -7, -8, -12, -13, -15, -16, -17, -18), 136.1, 139.0, 139.3, 139.4, 140.1 (all C_q, C-3, -4, -6, -11, -14), 145.1 (CH, C-19), 167.1 (C_q, COO) ppm. IR (KBr): $\tilde{\nu}$ = 3011 (w), 2985 (m), 2915 (s), 2892 (m), 2852 (m), 1703 (vs), 1616 (vs), 1366 (s), 1335 (s), 1295 (m), 1244 (vs), 1177 (s), 1136 (vs), 1035 (s), 1006 (s), 797 (m), 714 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 192 (4.54), 224 (sh, 4.26), 256 (4.09), 330 (4.11) nm. MS (EI, 70 eV): *m*/*z* (%) = 332 (32) [M]$^+$, 259 (9), 228 (22), 227 (100), 199 (66), 182 (34), 181 (54), 155 (28), 154 (21), 153 (20), 141 (14), 128 (13), 104 (822), 103 (5). HRMS: calcd. for $C_{23}H_{24}O_2$ 332.1776; found 332.1776.

5-(4-[2.2]Paracyclophanyl)pentanoic Acid (12): Ester **11** (6.06 g, 18.0 mmol) dissolved in ethyl acetate (300 mL) was hydrogenated over 10% Pd on charcoal (1.8 g) at room temperature under normal pressure. After the hydrogen uptake had ceased, the catalyst was removed by filtration, and the solvent was removed in vacuo. The remaining oil was chromatographed on silica gel (dichloromethane) to furnish 5.94 (98%) of the *saturated ester* as a colorless oil. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.42–1.65 (m, 4 H, 18-, 19-H), 2.22–3.35 (m, 12 H, 1-, 2-, 9-, 10-, 17-, 20-H), 4.10 (q, *J* = 7.2 Hz, 2 H, OCH_2), 6.10 (d, *J* ≈ 1.8 Hz, 1 H, 5-H), 6.35–6.51 (m, 5 H, 7-, 8-, 12-, 13-, 16-H), 6.65 (dd, *J* = 7.8, 1.9 Hz, 1 H, 15-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.2 (CH_3), 24.9 (CH_2, C-19), 29.9 (CH_2, C-17), 33.4, 33.9, 34.18, 34.20 (all CH_2, C-1, -2, -18, -20), 35.0, 35.3 (both CH_2, C-9, -10), 60.1 (OCH_2), 128.7 (CH, C-15), 130.2, 132.0, 133.1, 133.2, 134.5, 134.6 (all CH, C-5, -7, -8, -12, -13, -16), 137.3 (C_q, C-3), 139.31, 139.32, 139.6 (all C_q, C-6, -11, -14), 141.4 (C_q, C-4), 173.6 (C_q, COO) ppm. IR (KBr): $\tilde{\nu}$ = 3028 (w), 2982 (m), 2929 (s), 1733 (vs), 1458 (m), 1442 (m), 1414 (m), 1372 (m), 1300 (m), 1094

(m), 1033 (m), 797 (m), 717 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 194 (4.68), 208 (sh, 4.29), 226 (4.26) nm. MS (EI, 70 eV): *m/z* (%) = 336 (100) $[M]^+$, 291 (40), 232 (29), 231 (60), 229 (26), 187 (17), 159 (21), 158 (34), 143 (51), 142 (42), 141 (33), 129 (18), 118 (19), 105 (20), 104 (40), 91 (13). $C_{23}H_{28}O_2$ (336.52): calcd. C 82.09, H 8.39; found C 81.93, H 8.38.

For saponification, this ester (7.0 g, 20.8 mmol) was heated at reflux in a mixture of ethanol (150 mL) and 15% aqueous sodium hydroxide solution (200 mL) for 15 h. After cooling to room temperature, the solution was neutralized with 2 N hydrochloric acid, and the precipitate thus formed was removed by filtration. The crude acid was dissolved in saturated hydrogen carbonate solution, and the resulting solution filtered. Compound **12** was reprecipitated by the addition of 2 N hydrochloric to pH 2. The precipitate was filtered off and dried under high vacuum to yield 5.96 g (93%) of **12** as colorless needles. M.p. 80–81 °C (ref.[12] 78–80 °C). As the spectroscopic data are incomplete in ref.[12] they are listed here in full. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.47–1.53, 1.56–1.66 (both m, 2 H each, 18-, 19-H), 2.24–2.64 (m, 4 H, 17-, 20-H), 2.73–2.81 (m, 1 H) and 2.88–3.15 (m, 6 H) and 3.28–3.35 (m, 1 H, 1-, 2-, 9-, 10-H), 6.11 (d, $J \approx$ 1.8 Hz, 1 H, 5-H), 6.36–6.42 (m, 3 H) and 6.45 (dd, $J \approx$ 7.8, 1.8 Hz, 1 H) and 6.51 (dd, $J \approx$ 7.8, 1.8 Hz, 1 H, 7-, 8-, 12-, 13-, 16-H), 6.65 (dd, J = 7.8, 1.8 Hz, 1 H, 15-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.5 (CH_2, C-19), 29.8 (CH_2, C-17), 33.5, 33.88, 33.92, 34.2 (all CH_2, C-1, -2, -18, -20), 35.0, 35.3 (both CH_2, C-9, -10), 128.8 (CH, C-15), 130.3, 132.1, 133.1, 133.3, 134.5, 134.7 (all CH, C-5, -7, -8, -12, -13, -16), 137.4 (C_q, C-3), 139.35, 139.39, 139.7 (all C_q, C-6, -11, -14), 141.3 (C_q, C-4), 179.8 (C_q, COOH) ppm. IR (KBr): $\tilde{\nu}$ = 3052 (m), 3002 (m), 2927 (vs), 2854 (s), 1707 (vs), 1699 (vs), 1434 (m), 1413 (m), 1288 (m), 1249 (m), 939 (m), 716 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 194 (4.67), 210 (4.17), 226 (4.23), 228 (4.23), 244 (3.55) nm. MS (EI, 70 eV): *m/z* (%) = 308 (87) $[M]^+$, 204 (37), 203 (81), 145 (100), 144 (40), 129 (23), 118 (27), 114 (20), 105 (31), 104 (52), 91 (17).

2,3-(4,5-[2.2]Paracyclophano)cyclohept-2-en-1-one (13): To freshly distilled methanesulfonic acid (30 mL) was added phosphorus pentoxide (4.5 g) under an atmosphere of nitrogen. After stirring the mixture for 2 h at room temperature, **12** (1.0 g, 3.2 mmol) was added slowly in portions. The mixture quickly turned violet-black, and after stirring for 5 h at room temperature, the cyclization was terminated by the addition of ice water, followed by 15% aqueous sodium hydroxide solution. The hydrolysate was carefully extracted with dichloromethane, and the combined organic phase was dried with magnesium sulfate. The solid obtained after solvent removal by rotary evaporation was purified by silica gel column chromatography (dichloromethane) to yield 0.52 g (56%) of **13** as colorless cubes (ethanol/dichloromethane). M.p. 120 °C (ref.[12] 122–124 °C). As no spectroscopic data are given in ref.[12] we report them here in full. The use of undistilled methanesulfonic acid results in yield reduction of about 15%. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.27–1.38 (m, 1 H) and 1.53–1.65 (m, 2 H) and 1.68–1.78 (m, 1 H, 6-, 7-H), 2.32–3.38 (m, 12 H, 1-, 2-, 5-, 8-, 12-, 13-H), 6.43, 6.59 (both d, J = 7.8 Hz, 1 H each, 10-, 11-H), 6.40, 6.49, 6.54, 6.70 (each m, 1 H each, 15-, 16-, 18-, 19-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.7 (CH_2, C-6), 24.9 (CH_2, C-7), 27.3 (CH_2, C-8), 32.8, 34.0, 34.2, 35.3 (all CH_2, C-1, -2, -12, -13), 42.1 (CH_2, C-5), 128.9, 130.1, 132.1, 132.6, 133.3 (all CH, C-11, -15, -16, -18, -19), 137.2 (CH, C-10), 136.6, 137.3, 137.4, 139.0, 139.1, 139.8 (all C_q, C-3, -3a, -8a, -9, -14, -17), 208.3 (C_q, C-4) ppm. IR (KBr): $\tilde{\nu}$ = 2967 (w), 2929 (vs), 2859 (s), 1668 (vs), 1556 (m), 1440 (m), 1268 (m), 1257 (m), 955 (w), 719 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 192 (4.52), 214 (4.33), 280 (3.48), 326 nm (3.30). MS (EI, 70 eV): *m/z* (%) = 290 (100) $[M]^+$, 275 (13), 186 (49), 185 (74), 183 (25), 171 (63), 143 (16), 128 (22), 115 (21), 104 (30).

1,2-(4,5-[2.2]Paracyclophano)cyclohepta-1,3-diene (14): A solution of **13** (280 mg, 0.96 mmol) in anhydrous THF (10 mL) was added dropwise to lithium aluminum hydride (148 mg, 3.9 mmol) in THF (30 mL) at 0 °C under an atmosphere of nitrogen. After boiling the reaction mixture to reflux (3 h), it was cooled to ice water temperature and hydrolyzed carefully with ice water. Hydrochloric acid (6 N, 10 mL) and chloroform (10 mL) were added, and the reaction mixture was stirred for 2.5 h at room temperature. The phases were separated, and the aqueous phase was extracted with chloroform (2×). The combined organic phase was dried with magnesium sulfate, and the solvent was removed in vacuo. After silica gel chromatography (dichloromethane), 224 mg (85%) of **14** was obtained as colorless cubes (ethanol/dichloromethane). M.p. 158 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.69–1.86 (m, 2 H) and 1.99–2.10 (m, 3 H, 4-, 5-, 6-H), 2.68–3.41 (m, 9 H, 1-, 2-, 4-, 12-, 13-H), 5.99–6.05 (m, 1 H, 7-H), 6.38–6.55 (m, 7 H, 8-, 10-, 11-, 15-, 16-, 18-, 19-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.5, 29.3, 31.9 (all CH_2, C-4, -5, -6), 32.6, 33.7, 33.9, 34.3 (CH_2, C-1, -2, -12, -13), 128.0, 128.4, 128.9, 131.0, 132.5, 132.8, 133.0 (all CH, C-8, -10, -11, -15, -16, -18, -19), 131.2 (C-7), 137.1, 137.5, 137.6, 138.7, 138.9, 141.2 (all C_q, C-3, -3a, -8a, -9, -14, -17) ppm. IR (KBr): $\tilde{\nu}$ = 3423 (m), 2925 (vs), 2845 (vs), 1461 (m), 1435 (s), 1411 (m), 869 (m), 776 (s), 740 (m), 715 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 192 (4.42), 212 (4.43), 240 (sh, 4.11) 282 (3.72) nm. MS (EI, 70 eV): *m/z* (%) = 274 (39) $[M]^+$, 260 (18), 246 (12), 232 (12), 231 (69), 224 (27), 192 (16), 155 (13), 125 (16), 124 (29), 107 (73), 104 (100), 91 (67). $C_{21}H_{22}$ (274.4): calcd. C 91.91, H 8.09; found C 91.97, H 8.25.

NBS Bromination of 14: To a solution of **14** (158 mg, 0.58 mmol) in anhydrous carbon tetrachloride (30 mL) was added NBS (102 mg, 0.58 mmol) and AIBN (20 mg), and the mixture was heated to reflux for 3 h. After cooling to room temperature, the succinimide was removed by filtration and washed carefully with carbon tetrachloride. The solvent of the combined organic phase was removed in vacuo and the remainder purified by thick-layer chromatography on silica gel (dichloromethane) to yield 70 mg (34%) of **15** as a colorless oil. MS (EI, 70 eV): *m/z* (%) = 354 (16) [M, ^{81}Br]$^+$, 352 (16) [M, ^{79}Br]$^+$, 274 (42), 250 (21), 248 (23), 170 (100), 169 (36), 155 (45), 154 (21), 153 (22), 142 (18), 141 (18), 128 (15), 115 (13), 104 (25).

1,2-(4,5-[2.2]Paracyclophano)cyclohepta-1,3,5-triene (16) and 3,4-(4,5-[2.2]Paracyclophano)cyclohepta-1,3,5-triene (17): To a solution of **15** (433 mg, 1.2 mmol) in anhydrous DMSO (15 mL) was added potassium *tert*-butoxide (202 mg, 1.8 mmol). The reaction mixture quickly turned black, and it was stirred for 1 d at room temperature. For workup, water was added (15 mL), and the product mixture was extracted thoroughly with ether. The residue obtained after solvent removal was purified by thick-layer chromatography on silica gel (dichloromethane/petroleum ether, 40:60) to afford 200 mg (60%) of a mixture of **16** and **17** in a 1:3 ratio (^{1}H NMR spectroscopic analysis). This mixture can be used for the preparation of the tropylium cations (see below). The selective preparation of **17** is described below, and pure **16** was obtained as follows:

To a solution of **14** (768 mg, 2.80 mmol) in anhydrous carbon tetrachloride (80 mL) was added NBS (520 mg, 2.92 mmol) and AIBN (15 mg). The mixture was heated under reflux for 6 h and worked up as described above for the bromination of **14**. Aside from 157 mg (20%) of recovered starting material **14**, 293 mg (38%) of **16** was isolated as colorless needles. M.p. 130 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.28–2.33 (m, 1 H, 4-H), 2.80–3.19 (m,

7-H) and 3.34–3.55 (m, 2 H, 1-, 2-, 4-, 12-, 13-H), 5.63–5.69 and 6.02–5.97 (both m, 1 H each, 5-, 6-H), 6.32–6.60 (m, 7 H, 7-, 10-, 11-, 15-, 16-, 18-, 19-H), 7.06 (d, J = 11.6 Hz, 1 H, 8-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.7 (CH_2, C-4), 33.1, 33.4, 34.2, 34.6 (all CH_2, C-1, -2, -12-, -13), 125.7, 126.9, 128.0, 128.7, 130.1, 130.9, 131.2, 132.5, 132.8, 134.8 (all CH, C-5, -6, -7, -8, -10, -11, -15, -16, -18, -19), 135.5, 136.4, 136.9, 138.4, 138.8 (2 C) (all C_q, C-3, -3a, -8a, -9, -14, -17) ppm. IR (KBr): $\tilde{\nu}$ = 3028 (m), 2968 (m), 2941 (s), 2921 (s), 1585 (w), 1498 (m), 1461 (m), 1437 (m), 1410 (m), 934 (m), 871 (m), 798 (vs), 786 (vs), 771 (s), 718 (vs) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 194 (4.58), 202 (sh, 4.52), 224 (sh, 4.19), 254 (3.83), 298 nm (3.76). MS (EI, 70 eV): m/z (%) = 272 (34) $[M]^+$, 170 (32), 168 (100), 167 (44), 165 (19), 155 (19), 153 (48), 152 (30). $C_{21}H_{20}$ (272.4): calcd. C 92.59, H 7.41; found C 92.62, H 7.40.

[2]Paracyclo[2](1,4)naphthalinophane (20): A solution of **15** (see also structure **18**, 127 mg, 0.36 mmol) and potassium *tert*-butoxide (561 mg, 5 mmol) in anhydrous toluene (10 mL) was heated to 80 °C for 5 h. After cooling to room temperature, water (20 mL) was added, and the reaction mixture was carefully extracted with diethyl ether. The combined organic phase was washed with water and dried (magnesium sulfate), and the solvent was removed by rotary evaporation. Purification by thick-layer chromatography (silica gel, trichloromethane) furnished 20 mg (22%) of **20**, which was identical in all analytic and spectroscopic data with those in the literature.[24] When the experiment was repeated with a mixture of **16** and **17**, hydrocarbon **20** could be detected, in traces at best, by NMR spectroscopic analysis.

2,3-(4,5-[2.2]Paracyclophano)cyclohepta-2,4-dien-1-one (21): To a solution of **13** (2.00 g, 6.9 mmol) in anhydrous carbon tetrachloride (150 mL) was added NBS (1.35 g, 7.6 mmol) and AIBN (20 mg) under an atmosphere of nitrogen. The yellow solution was heated to reflux for 4 h, and after cooling to room temperature, the precipitated succinimide was removed by filtration and washed with carbon tetrachloride. The solvent of the combined organic phase was removed by rotary evaporation, and the remaining solid residue was purified by silica gel chromatography (dichloromethane/pentane, 1:4) to afford 1.47 g (74%) of **21** as colorless needles. M.p. 165 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.19–2.46 (m, 2 H, 6-H), 2.65–3.45 (m, 10 H, 1-, 2-, 5-, 12-, 13-H), 6.06 (dt, J = 11.4, 5.8 Hz, 1 H, 7-H), 6.41–6.72 (m, 7 H, 8-, 10-, 11-, 15-, 16-, 18-, 19-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.9 (CH_2, C-6), 32.8, 33.9, 34.2, 35.4 (all CH_2, C-1, -2, -12, -13), 46.5 (CH_2, C-5), 127.5, 130.0, 130.5, 130.8, 131.9, 133.0, 133.8, 136.6 (all CH, C-7, -8, -10, -11, -15, -16, -18, -19), 133.4, 137.4, 138.2, 138.8, 139.1, 139.8 (all C_q, C-3, -3a, -8a, -9, -14, -17), 204.8 (s, C-4) ppm. IR (KBr): $\tilde{\nu}$ = 3033 (w), 2955 (m), 2935 (s), 2924 (s), 2899 (m), 2855 (m), 1762 (w), 1674 (vs), 1457 (m), 1267 (s), 1255 (s), 1103 (m), 1012 (m), 941 (m), 891 (m), 778 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 192 (4.49), 208 (4.47), 246 (4.03), 262 (sh, 3.93), 294 (sh, 3.35) nm. MS (EI, 70 eV): m/z (%) = 288 (36) $[M]^+$, 185 (26), 184 (56), 183 (100), 171 (18), 169 (34), 155 (25), 141 (28), 128 (20), 115 (20), 104 (22), 69 (16). HRMS: calcd. for $C_{21}H_{20}O$ 288.15142; found 288.151.

2,3-(4,5-[2.2]Paracyclophano-*endo*-1-hydroxycyclohepta-2,4-diene (22) and 2,3-(4,5-[2.2]Paracyclophano-*exo*-1-hydroxycyclohepta-2,4-diene (23): To a solution of **21** (431 mg, 1.5 mmol) in 2-propanol (80 mL) was added sodium borohydride (756 mg, 20.0 mmol), and the mixture was heated under reflux for 6 h. After cooling to 0 °C, water (130 mL) and hydrochloric acid (6 N, 1 mL) were added to decompose excess borohydride. The solution was extracted with ether (3 ×), the combined organic phase was washed with water and dried (magnesium sulfate), and the solvent was removed in vacuo. The oily raw product was purified by silica gel plate chromatography (dichloromethane/pentane, 7:3) to provide 285 mg (65%) of **22** and 70 mg (16%) of **23** as colorless solids. Data for **22**: M.p. 125 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.74–1.83 (m, 1 H), 2.16–2.27 (m, 2 H) and 2.36 (m, 1 H, 5-, 6-H), 2.72 (d, J = 6.9 Hz, 1 H, OH), 2.70–2.78, 2.88–3.03, 3.08–3.21, 3.25–3.44 (all m, 1 H each, 1-, 2-, 12-, 13-H), 4.98–5.03 (m, 1 H, 4-H), 5.94–6.00 (m, 1 H, 7-H), 6.29–6.62 (m, 6 H) and 6.70–6.73 (m, 1 H, 8-, 10-, 11-, 15-, 16-, 18-, 19-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.1 (CH_2, C-6), 32.5, 32.8, 34.3, 35.3, 35.7 (all CH_2, C-1, -2, -5, -12, -13), 68.1 (d, C-4), 126.9, 129.8, 131.7, 132.1, 132.8, 132.9, 133.0, 134.1 (all CH, C-7, -8, -10, -11, -15, -16, -18, -19), 133.5 (C_q, C-3), 138.3, 138.8, 138.9, 139.1, 140.1 (all C_q, C-3a, -8a, -9, -14, -17) ppm. IR (KBr): $\tilde{\nu}$ = 3557 (s), 3020 (w), 2939 (s), 2925 (vs), 2896 (s), 2850 (m), 1439 (m), 1414 (m), 1390 (m), 1176 (m), 1046 (vs), 831 (m), 794 (m), 715 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 192 (4.37), 214 (4.43), 238 (sh, 4.15), 284 (3.80), 290 (sh, 3.72), 310 (sh, 3.13), 324 (sh, 2.86) nm. MS (EI, 70 eV): m/z (%) = 290 (16) $[M]^+$, 185 (12), 168 (34), 167 (24), 155 (14), 153 (16), 129 (12), 88 (12), 86 (64), 84 (95), 51 (34), 49 (100). $C_{21}H_{22}O$ (290.4): calcd. C 86.85, H 7.64; found C 86.92, H 7.75. Data for **23**: M.p. 93 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.04–2.50 (m, 4 H, 5-, 6-H), 2.77–3.16 (m, 7 H) and 3.43–3.55 (m, 2 H, 1-, 2-, 12-, 13-H and OH), 5.01 (br. d, 1 H, 4-H), 6.02 (m, 1 H, 7-H), 6.33–6.56 (m, 7 H, 8-, 10-, 11-, 15-, 16-, 18-, 19-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.3 (CH_2, C-6), 30.1, 33.6, 34.4, 34.85, 34.93 (all CH_2, C-1, -2, -5, -12, -13), 69.3 (d, C-4), 125.6, 129.7, 129.9, 132.7, 132.8, 133.2, 133.4, 134.9 (all CH, C-7, -8, -10, -11, -15, -16, -18, -19), 134.9 (C_q, C-3), 138.7, 138.8, 139.2, 140.1, 141.1 (all C_q, C-3a, -8a, -9, -14, -17) ppm. IR (KBr): $\tilde{\nu}$ = 3386 (s, br.), 3032 (w), 2926 (vs), 2875 (m), 2855 (s), 1718 (m), 1701 (m), 1457 (m), 1411 (m), 1248 (m), 1048 (s), 1028 (m), 794 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 194 (4.49), 214 (sh, 4.31), 226 (sh, 4.22), 248 (sh, 3.82), 286 (3.57), 314 (sh, 2.87) nm. MS (EI, 70 eV): m/z (%) = 290 (20) $[M]^+$, 185 (12), 169 (32), 167 (20), 155 (13), 153 (16), 88 (12), 86 (64), 84 (94), 51 (34), 49 (100).

Dehydration of 22 to 17: To a solution of **22** (250 mg, 0.86 mmol) in dichloromethane (20 mL) was added hydrochloric acid (6 N, 10 mL), and the mixture was stirred for 30 h at room temperature. The two phases of the green solution were separated. The aqueous phase was extracted with dichloromethane, and the combined organic phase was dried (magnesium sulfate). After solvent removal by rotary evaporation, the remaining solid was purified by silica gel column chromatography (dichloromethane) to afford 215 mg (92%) of **17** as colorless needles (ethanol/dichloromethane). M.p. 181–183 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.55 (dtt, J = 13.4, 5.6, 1.9 Hz, 1 H, 6-H), 2.59 (dt, J = 13.4, 7.9 Hz, 1 H, 6-H), 2.82–2.90, 2.99–3.09, 3.14–3.21, 3.50–3.57 (all m, 2 H each, 1-, 2-, 12-, 13-H), 5.90 (ddd, J = 10.0, 8.0, 5.6 Hz, 2 H, 5-, 7-H), 6.32–6.33 (m, 2 H, 18-, 19-H), 6.47 (s, 2 H, 10-, 11-H), 6.53–6.56 (m, 4 H, 4-, 8-, 15-, 16-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.8 (CH_2, 1 C, C-6), 33.0, 33.8 (both CH_2, C-1, -2, -12, -13), 126.7 (CH, C-4, -8), 127.8 (CH, C-5, -7), 129.4 (CH, C-18, -19), 131.3 (CH, C-10, -11), 132.9, (CH, C-15, -16), 136.9, 138.2, 138.6 (all C_q, C-3, -3a, -8a, -9, -14, -17) ppm. IR (KBr): $\tilde{\nu}$ = 3032 (vs), 3006 (s), 2925 (vs), 2900 (vs), 2853 (s), 1499 (m), 1441 (s), 1413 (m), 932 (m), 868 (m), 796 (vs), 778 (vs), 719 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 192 (4.47), 208 (sh, 4.42), 216 (4.45), 238 (4.23), 266 (4.05), 286 (sh, 3.64), 320 (sh, 2.95) nm. MS (EI, 70 eV): m/z (%) = 272 (56) $[M]^+$, 169 (16), 168 (100), 167 (80), 165 (24), 153 (55), 152 (38), 115 (10). $C_{21}H_{20}$ (272.4): calcd. C 92.59, H 7.41; found C 92.67, H 7.46.

Reduction of 21 Followed by Dehydration to 14, 17, and 25: To a suspension of lithium aluminum hydride (584 mg, 15.0 mmol) in THF (50 mL) was added a solution of **21** (1.11 g, 3.85 mmol) in anhydrous THF (80 mL) under an atmosphere of nitrogen at room temperature. After heating to reflux for 5.5 h, the reaction mixture was cooled to 0 °C and hydrolyzed with water (20 mL), followed by 6 N hydrochloric acid until acidic. The mixture was extracted carefully with ether, and the combined organic phase was washed with water and dried (magnesium sulfate). After solvent removal, the raw reaction mixture was separated by thick-layer plate chromatography (silica gel; dichloromethane/pentane, 1:4) to provide three fractions: **14** (560 mg, 53%), **17** (150 mg, 14%), and ether **25** (190 mg, 17%) as colorless needles. M.p. 154 °C. ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 0.97–1.10 (m, 1 H, 6-H), 1.96–2.05 (m, 2 H, 5-, 7-H), 2.21–2.38 (m, 3 H, 5-, 6-, 7-H), 2.85–3.10 (m, 8 H, 1-, 2-, 12-, 13-H), 4.90 (d, J = 3.0 Hz, 2 H, 4-, 8-H), 6.35 (s, 2 H, 10-, 11-H), 6.52–6.53 and 6.59–6.60 (m, 2 H each, 15-, 16-, 18-, 19-H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.5 (CH_2, 1 C, C-6), 29.0 (CH_2, C-5, -7), 32.1 (CH_2, C-2, -12), 34.6 (CH_2, C-1, -13), 78.2 (CH, C-4, -8), 131.2, 132.7, 133.8 (all CH, C-10, -11, -15, -16, -18, -19), 130.7, 139.0, 143.6 (all C_q, C-3, -3a, -8a, -9, -14, -17) ppm. IR (KBr): $\tilde{\nu}$ = 3010 (w), 2941 (vs), 2913 (m), 2894 (m), 1433 (w), 1060 (m), 1022 (s), 934 (m), 863 (s), 796 (m), 777 (m), 716 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 196 (4.62), 212 (sh, 4.23),228 (4.26), 254 (sh, 3.38) nm. MS (EI, 70 eV): *m*/*z* (%) = 290 (70) [M]$^+$, 187 (20), 186 (100), 171 (16), 158 (26), 143 (24), 128 (16), 115 (16), 104 (45). $C_{21}H_{20}O$ (290.4): calcd. C 86.85, H 7.64; found C 86.77, H 7.67.

Diels–Alder Addition of TCNE to 17 and 16: To a solution of **17** (40 mg, 0.15 mmol) in $CDCl_3$ (0.7 mL) in an NMR tube at room temperature was added TCNE (19 mg, 0.15 mmol). The progress of the cycloaddition was monitored by ^{1}H NMR spectroscopy, and after 1 week at room temperature the cycloaddition to **28** was complete. The solid isolated after solvent removal (59 mg, 100%) was recrystallized from acetone to afford colorless needles. M.p. 165 °C (decomp.). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.08 (dt, J = 7.8, 5.6 Hz, 1 H, 6-H), 1.22 (m, 1 H, 6-H), 1.86–1.91 (m, 2 H, 5-, 7-H), 3.07–3.20, 3.25–3.32 (both m, 4 H each, 1-, 2-, 12-, 13-H), 4.84 (m, 2 H, 4-, 8-H), 6.56 (s, 2 H, 10-, 11-H), 6.38, 6.96 (both m, 2 H each, 15-, 16-, 18-, 19-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 7.2 (CH_2, C-6), 8.7 (CH, C-5, -7), 31.2, 35.6 (both CH_2, C-1, -2, -12, -13), 44.0 (CH, C-4, -8), 45.7 (C_q, C-20, -21), 112.0, 113.3 (both C_q, C≡N), 128.2 (both C_q, C-3a, -8a), 132.1, 134.1, 136.8 (all CH, C-10, -11, -15, -16, -18, -19), 137.5, 140.3 (both C_q, C-3, -9, -14, -17) ppm. IR (KBr): $\tilde{\nu}$ = 3036 (w), 2994 (m), 2956 (vs), 2931 (vs), 2890 (m), 2854 (m), 2249 (w), 1586 (m), 1503 (m), 1054 (m), 896 (s), 879 (m), 821 (s), 798 (s), 755 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 196 (4.63), 218 (sh, 4.23), 228 (4.21), 244 (sh, 3.93), 270 (3.18) nm. MS (EI, 70 eV): *m*/*z* (%) = 400 (15) [M]$^+$, 273 (18), 272 (68), 168 (100), 167 (70), 165 (36), 128 (30), 153 (60), 15 (48), 128 (30), 104 (55), 84 (25), 76 (22). HRMS: calcd. for $C_{27}H_{20}N_4$ 400.1688; found 400.168.

Under nearly the same conditions (dichloromethane, 40 °C) **16** did not react with TCNE.

(4,5-[2.2]Paracyclophano)tropylium Tetrafluoroborate (26a): To a solution of either pure **16** or **17** or a mixture of both hydrocarbons (50 mg, 0.18 mmol) in anhydrous dichloromethane (5 mL) was added tritylium tetrafluoroborate (61 mg, 0.18 mmol) in dichloromethane (5 mL). The reaction mixture turned deep red immediately. Out of the solution, 39 mg (60%) of **26a** crystallized in the form of deep-red needles. M.p. 201 °C. ^{1}H and ^{13}C NMR: see main part. IR (KBr): $\tilde{\nu}$ = 3010 (w), 2930 (w), 1590 (w), 1374 (s), 1174 (s), 1122 (vs), 1085 (vs), 973 (m), 838 (m), 765 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 192 (4.53), 212 (sh, 4.38), 230 (4.31), 284 (4.20), 352 (3.90), 396 (sh, 3.55), 464 (sh, 3.06) nm. UV (dichloromethane): λ_{max} (log ε) = 232 (4.32), 288 (4.24), 358 (3.92), 444 (sh, 3.32), 488 (sh, 3.09) nm. MS (FAB+, NBA): *m*/*z* (%) = 987 (1) [(**5**)$_3$(BF$_4$)$_2$], 629 (5) [(**5**)$_2$BF$_4$], 271 (100) [**5**], 167 (30) [**5** – 104]. MS (FAB–, NBA): *m*/*z* (%) = 1160 (1) [(**5**)$_3$(BF$_4$)$_4$], 802 (3) [(**5**)$_2$(BF$_4$)$_3$], 445 (22) [**5**(BF$_4$)$_2$], 87 (100) [BF$_4$].

(4,5-[2.2]Paracyclophano)tropylium Perchlorate (26b): Tritylium perchlorate was prepared from triphenylmethanol (104 mg, 0.4 mmol) and perchloric acid (16% aqueous solution, 68 mg, 0.4 mmol). After the addition of dichloromethane (8 mL, orange solution) either **16** or **17** or a mixture of these two components (109 mg, 0.4 mmol) in dichloromethane (8 mL) was added, and the color of the reaction mixture turned to deep red. Out of the solution, salt **26b** (114 mg, 77%) crystallized as dark-red prisms. M.p. 185 °C (decomp.). Whether the pure benzotropylidenes or their mixture is employed has no influence on the yield of the process. ^{1}H and ^{13}C NMR: see main part. IR (KBr): $\tilde{\nu}$ = 3028 (w), 2930 (w), 1588 (w), 1567 (w), 1374 (m), 1143 (vs), 1088 (vs), 752 (w), 636 (s), 627 (s) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 192 (4.21), 206 (sh, 4.11), 232 (4.03), 284 (3.95), 352 (3.65), 390 (sh, 3.35), 448 (sh, 2.82) nm. UV (dichloromethane): λ_{max} (log ε) = 234 (4.14), 288 (4.07), 358 (3.76), 464 (sh, 2.98), 480 (sh, 2.88), 490 (2.84) nm. MS (FAB+, NBA): *m*/*z* (%) = 641 (1) [(**5**)$_2$ClO$_4$], 271 (100) [**5**], 167 (40) [**5** – 104]. MS (FAB–, NBA): *m*/*z* (%) = 837 (1) [(**5**)$_2$(ClO$_4$)$_3$], 471 (4) [**5**(ClO$_4$)$_2$], 469 (7) [**5**(ClO$_4$)$_2$], 101 (34) [ClO$_4$], 99 (100) [ClO$_4$].

Addition of [D$_6$]Acetone and TCNE to 26a: In an NMR tube, **26a** (60 mg, 0.17 mmol) and TCNE (22 mg, 0.17 mmol) were dissolved in [D$_6$]acetone (1 mL), and the reaction mixture was left until the solvent had evaporated. The remaining solid (**29**, 82 mg, 100%), was washed with dichloromethane to afford colorless needles. M.p. 185 °C (decomp.). ^{1}H NMR (400.1 MHz, [D$_6$]acetone): δ = 1.73–1.75 (m, 2 H, 5-, 7-H), 1.79–1.83 (m, 1 H, 6-H), 3.08–3.33 (m, 8 H, 1-, 2-, 12-, 13-H), 4.87 (m, 2 H, 4-, 8-H), 6.57 (s, 2 H, 10-, 11-H), 6.59, 6.96 (both m, 2 H each, 15-, 16-, 18-, 19-H) ppm. ^{13}C NMR (100.6 MHz, [D$_6$]acetone): δ = 15.0 (CH, C-5, -7), 15.5 (CH, 1 C, C-6), 31.3 (CH_2, C-2, -12), 35.7 (CH_2, C-1, -13), 43.6 (CH, C-4, -8), 45.5 (C_q, C-23, -24), 111.9, 113.2 (both C_q, C≡N), 128.7 (C_q, C-3a, -8a), 132.7, 133.8, 136.6 (all CH, C-10, -11, -15, -16, -18, -19), 137.4, 140.2 (both C_q, C-3, -9, -14, -17), 206.1 (C_q, C-21) ppm; signals of deuterated carbon atoms C-20 and C-22 not observed. IR (KBr): $\tilde{\nu}$ = 3111 (w), 3030 (w), 2957 (m), 2932 (m), 2249 (w), 1707 (vs), 1262 (m), 1256 (m), 798 (w), 740 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 196 (4.59), 214 (sh, 4.25), 228 (4.17), 250 (sh, 3.81) nm. MS (EI, 70 eV): *m*/*z* (%) = 461 (9) [M]$^+$, 333 (21), 270 (11), 229 (53), 183 (30), 167 (53), 166 (23), 165 (32), 152 (16), 128 (16), 104 (100), 76 (14). HRMS: calcd. for $C_{30}H_{19}D_5N_4O$ 461.22640; found 461.226.

X-ray Structure Determinations: Crystal data and refinement details are presented in Tables 2 and 3. Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (**13**, **26b**: Siemens R3; **17**, **22**, **28**: Siemens P4; **25**, **29**, Stoe STADI-4, with appropriate low-temperature attachments). Measurements were performed with monochromated Mo-K_α radiation. The structures were refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included with rigid methyl groups or a riding model. For **22**, the OH hydrogen was poorly resolved; the group was refined as a rigid group allowed to rotate. In the absence of significant anomalous dispersion, Friedel opposite reflections were merged and the Flack parameter is thus indeterminate. To improve

Table 2. Details of X-ray structure analyses.

Compound	**13**	**17**	**22**	**25**	**26b**
Formula	$C_{21}H_{22}O$	$C_{21}H_{20}$	$C_{21}H_{22}O$	$C_{21}H_{22}O$	$C_{21}H_{19}ClO_4$
M_r	290.39	272.37	290.39	290.39	370.81
Habit	colorless block	colorless block	colorless prism	pale-yellow prism	red prism
Crystal size [mm]	$0.8\times0.7\times0.4$	$0.8\times0.7\times0.6$	$0.8\times0.6\times0.4$	$0.8\times0.4\times0.3$	$0.45\times0.25\times0.2$
Crystal system	monoclinic	monoclinic	orthorhombic	rhombohedral	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$Pna2_1$	$R\bar{3}$	$Cmc2_1$
Cell constants:					
a [Å]	12.102(4)	13.3494(14)	13.876(2)	28.468(4)	9.221(2)
b [Å]	9.570(3)	8.1539(10)	13.654(2)	28.468(4)	12.243(3)
c [Å]	13.270(4)	13.1895(14)	7.9586(10)	9.889(2)	14.872(3)
α [°]	90	90	90	90	90
β [°]	91.98(3)	94.057(8)	90	90	90
γ [°]	90	90	90	120	90
V [Å^3]	1536.0	1432.1	1507.8	6940	1678.9
Z	4	4	4	18	4
D_x [mg m^{-3}]	1.256	1.263	1.279	1.251	1.467
μ [mm^{-1}]	0.08	0.07	0.08	0.08	0.25
$F(000)$	624	584	624	2808	776
T [°C]	–95	–100	–100	–120	–95
$2\theta_{max}$	50	50	55	55	55
No. of reflections					
Measured	3234	4850	2827	3904	1966
Independent	2716	2511	1856	3539	1405
R_{int}	0.017	0.016	0.018	0.031	0.035
Parameters	199	191	201	199	124
wR (F^2, all refl.)	0.127	0.105	0.106	0.143	0.145
R [F, $>4\sigma(F)$]	0.042	0.039	0.041	0.059	0.046
S	1.01	1.05	1.01	1.07	1.00
max. $\Delta\rho$ [e Å^{-3}]	0.31	0.24	0.25	0.24	0.20

Table 3. Details of X-ray structure analyses.

Compound	**28**	**29**·C_3D_6O
Formula	$C_{27}H_{20}N_4$	$C_{33}H_{19}D_{11}N_4O_2$
M_r	400.47	530.61
Habit	colorless tablet	colorless tablet
Crystal size [mm]	$0.8\times0.35\times0.2$	$0.55\times0.25\times0.15$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Cell constants:		
a [Å]	7.8407(8)	10.685(3)
b [Å]	13.972(2)	11.769(3)
c [Å]	17.963(2)	20.951(5)
α [°]	90	90
β [°]	93.228(8)	93.25(3)
γ [°]	90	90
V [Å^3]	1964.8(4)	2630.4
Z	4	4
D_x [mg m^{-3}]	1.354	1.327
μ [mm^{-1}]	0.08	0.08
$F(000)$	840	1088
T [°C]	–100	–120
$2\theta_{max}$	50	50
No. of reflections		
Measured	4135	7730
Independent	3447	4634
R_{int}	0.015	0.058
Parameters	280	355
wR (F^2, all refl.)	0.098	0.149
R [F, $>4\sigma(F)$]	0.039	0.062
S	0.97	1.03
max. $\Delta\rho$ [e Å^{-3}]	0.18	0.30

stability of refinement, restraints (SIMU; DELU) to displacement parameters were employed (applies also to **29**). For **26b**, the Flack parameter refined to –0.1(2). For **29**, which crystallized as a deuterioacetone solvate, one acetone methyl group (at C91) was poorly resolved. Hydrogen atoms at C20 and C22 were assumed to have been replaced by deuterium. CCDC-663211 (for **13**), -663248 (for **17**), -663246 (for **22**), -663247 (for **25**), -663208 (for **26b**), -663212 (for **28**), and -663209 (for **29**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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