J. Am. Chem. Soc. **1986**, *108*, 3453–3460 3453

Consequences of Fixing Three Parallel Coplanar Double Bonds in Close Proximity with Different Geometries. Synthesis and Spectral Parameters of *syn*- and *anti*-Sesquinorbornatriene

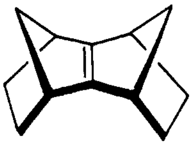
Leo A. Paquette,*[1] Hermann Künzer,[1,2] Kenneth E. Green,[1] Ottorino De Lucchi,*[3] Giulia Licini,[3] Lucia Pasquato,[3] and Giovanni Valle[4]

Contribution from the Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210, and Centro Studi Meccanismi di Reazioni Organiche del C.N.R. and Centro Studi Biopolimeri del C.N.R., Dipartimento di Chimica Organic dell'Università, Via Marzolo 1, I-35131 Padova, Italy. Received November 27, 1985

Abstract: *syn*-Sesquinorbornatriene, possibly the extreme example of π-bond pyramidalization, has been synthesized and characterized. Cycloaddition of (*Z*)-1,2-bis(phenylsulfonyl)ethylene with tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene proceeds with at least 95% below-plane stereoselectivity to give the syn [4 + 2] adduct. Mild reductive desulfonylation of this product leads to the above hydrocarbon. Its ^{13}C NMR shifts are particularly instructive when compared to *syn*-sesquinorbornadiene, which was prepared in comparable fashion. Peracid oxidation of the original adduct, followed by comparable treatment with 1–2% sodium amalgam, affords the structurally related diene epoxide. Sequential photocyclization and periodic acid cleavage of this intermediate delivers [4]peristylane-2,4-dione and constitutes an expedient route to this hemispherical compound. By comparison, the Diels–Alder reaction of tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene with (*E*)-1,2-bis(phenylsulfonyl)ethylene is sterically controlled and proceeds with predominant above-plane dienophile capture. Reductive desulfonylation of this adduct affords *anti*-sesquinorbornatriene. Although this hydrocarbon is sensitive to air oxidation, it is somewhat less so than its syn counterpart. Nonetheless, the ^{13}C chemical shift of its internal olefinic carbon (173.23 ppm) appears slightly to lower field than that of the syn isomer (172.14 ppm). The possible contributory causes to the extreme deshielding of these signals are discussed in light of comparison with lesser unsaturated congeners and orbital interaction patterns. Finally, heating tricyclo[5.2.1.0^{2,6}]-deca-2,5,8-triene with the (*E*)-disulfone in toluene leads efficiently to an angular above-plane adduct. Removal of the sulfonyl groups in this instance gives rise to a structural isomer of the above pair of trienes that does not share their high reactivity toward triplet oxygen.

Norbornenes and norbornadienes have been the focus of considerable attention in chemistry for many decades. Vast amounts of experimental data have engendered extensive mechanistic discussion. Notwithstanding, only recently has it been recognized that the π bonds in these molecules experience deformation in an endo direction. Evidence for pyramidalization first came from NMR studies on norbornadiene in liquid crystal solvents[5] and has since been substantiated by X-ray studies on crystalline norbornenes and 7-oxanorbornenes.[6] Theoretical assessments of this interesting phenomenon have kept pace, although explanations as to the root cause are varied.[7]

In 1980, the syn (**1**) and anti (**2**) isomers of sesquinorbornene were first synthesized independently in the Paquette[8] and Bartlett laboratories,[9] respectively. Soon to follow was crystallographic evidence that derivatives of **1** also experience a hingelike bending of their double bonds. However, the distortions (θ = 16–18°) are considerably larger than those predicted from simpler systems.[10] In contrast, the central double bond in compounds of type **2** is generally planar,[6b,10a–c,10e,11] although certain exceptions to this general trend have been noted.[12] Both **1** and **2** have special properties arising from inherent steric shielding of their double bond, as well as from electronic factors.[9,13] Several computational analyses of **1** and **2** have appeared.[14] Photoelectron spectroscopy has shown both hydrocarbons to undergo ionization more easily than expected, with **1** exhibiting considerably higher π_{cc} ionization energy than **2**.[15]



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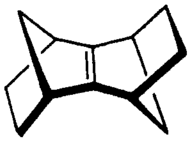

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More recently, introduction of a second double bond as in **3** has been found to enhance the level of downward pyramidal distortion (>20°)[16] and to be accompanied by substantial de-

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[1] The Ohio State University.

[2] Postdoctoral fellowship awardee of the Deutsche Forschungsgemeinschaft, 1985–1986.

[3] Centro Studi Meccanismi di Reazioni Organiche.

[4] Centro Studi Biopolimeri. Author responsible for the X-ray analyses.

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[15] (a) Brown, R. S.; Buschek, J. M.; Kopecky, K. R.; Miller, A. J. *J. Org. Chem.* **1983**, *48*, 3692. (b) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553. (c) Comparative data for sesquibicyclooctene are also available: Nelsen, S. F.; Kapp, D. L. *J. Org. Chem.* **1985**, *50*, 1339.

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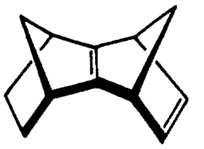
shielding of the central olefinic carbon atoms and a heightened sensitivity to triplet oxygen.[13a] The increased deviation from planarity probably arises chiefly because a pair of sterically demanding endo substituents have been excised, although contributions from through-space interaction cannot be dismissed.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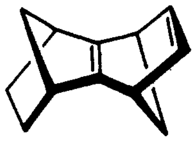
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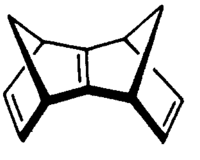
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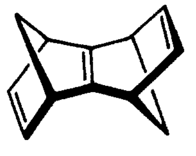
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The readiness with which the sesquinorbornene system responds to changes in the environment of the double bond has prompted synthesis of the maximally unsaturated members of this series, viz., **5** and **6**. Both trienes contain three parallel and equidistant double bonds, which, by virtue of the different geometries imposed by the two methano bridges, are rigidly held in quite different relative orientations (copolanar in **6**, but not in **5**). In both instances, strain energy has also been maximized. Direct comparison with the somewhat related hydrocarbons butalene[17] and 1,4,5,8-tetrahydronaphthalene[18] is not likely warranted. Syn isomer **5** could represent the extreme example of π pyramidalization. The potential effects of the sum of these forces on **6** were not known. At the least, unusual chemical and spectroscopic properties should be in evidence.

When it became clear that parallel investigations in this area had been carried forward independently in Columbus and Padova,[19] the decision was made to publish jointly the details of these studies. A nomenclature issue must first be addressed. The trivial names *syn*- and *anti*-sesquinorbornene were coined for **1** and **2** by Bartlett and co-workers[9,10a] and welcomed in place of their more cumbersome 1,4,5,8-dimethanonaphthalene labels. Strictly speaking, however, direct extension of these newly coined names to **5** and **6** would necessitate that these *trienes* be called *syn*- and *anti*-sesquinorborna*diene*. Obviously, provision must be made for the dienes **3** and **4**. Consequently, we propose to refer to **3** and **4** as the sesquinorbornadienes and to apply to **5** and **6** the term sesquinorbornatriene. In this way, there exists a clear-cut correspondence with the number of double bonds in the molecules involved.

Results

Access to *syn*-Sesquinorbornatriene (5). Synthesis of **5** was achieved by [4 + 2] cycloaddition of the recently reported acetylene equivalent (*Z*)-1,2-bis(phenylsulfonyl)ethylene (**8**)[20] to tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene (**7**).[21] In agreement with the known predilection of **7** for below-plane Diels–Alder capture,[22] disulfone **9**, an air-sensitive compound, was isolated in 82% yield.

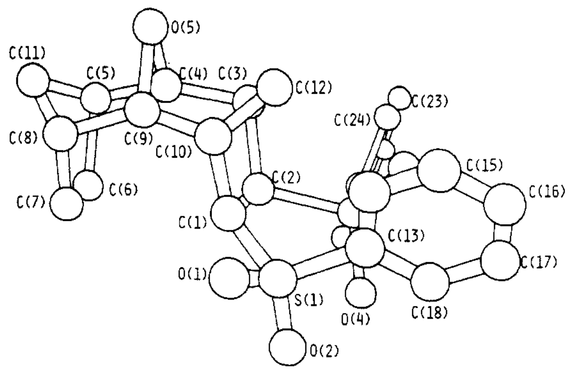
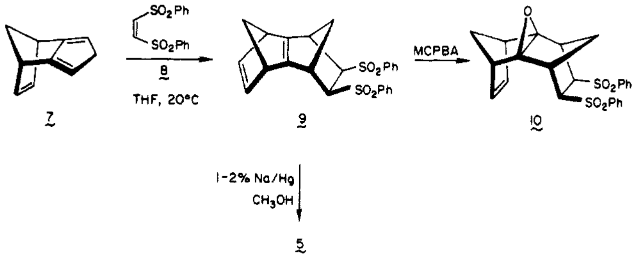


Figure 1. Computer-generated perspective drawing of the final X-ray model of epoxy disulfone **10**. Hydrogens are omitted for clarity.



Characterization of **9** as the syn isomer was realized by peracid oxidation to epoxide **10**.[23] Since this transformation is accompanied by shielding of *both* apical methylene bridge carbons in **10** (44.43 and 43.99 ppm) relative to **9** (48.24 and 46.94 ppm), these centers must simultaneously experience the magnetic anisotropy effects of a proximate oxirane oxygen.[10c,24] Added confirmation was achieved by making recourse to X-ray crystal structure analysis (Figure 1).

With the stereochemistry of **9** solidly established, a search for suitable desulfonylation conditions was sought. Utilization of 6% sodium amalgam in buffered methanol solution,[25] normally a very effective reagent, led to the destruction of this disulfone. However, recourse to a less concentrated amalgam (1–2% Na) proved quite satisfactory. Rigorous exclusion of oxygen during this reductive elimination and in all subsequent handling operations provided **5** (47% isolated) as a highly air-sensitive clear oil. Its 300-MHz ^{1}H NMR spectrum (CDCl$_3$ solution), characterized by four absorptions at δ 6.34, 3.48, 2.18, and 2.02 with relative intensities of 2:2:1:1, shows a reasonable correspondence with norbornadiene.[26] On the other hand, its ^{13}C NMR shifts in CDCl$_3$ [172.14, 140.32, 69.12, 50.02 ppm] have proven particularly informative, as will be discussed subsequently. Significantly, the resonance attributable to the carbon atoms of its central π bond is strongly shifted to lower field relative to that in norbornadiene[27] and exceeds even that in $\Delta^{1,4}$-bicyclo[2.2.0]hexene, long considered to be a record holder for deshielding at an unconjugated olefinic site.[28]

^{13}C NMR Comparison with *syn*-Sesquinorbornadiene (3). In pursuit of an alternative[15b] improved synthesis of **3**, isodicyclopentadiene (**11**) was subjected to Diels–Alder cycloaddition with

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(16) (a) Paquette, L. A.; Green, K. E.; Gleiter, R.; Schäfer, W.; Gallucci, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 8232. (b) Bartlett, P. D.; Combs, G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625.

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(19) Preliminary communications: (a) De Lucchi, O.; Licini, G.; Pasquato, L. *J. Chem. Soc., Chem. Commun.* **1985**, 418. (b) Paquette, L. A.; Künzer, H.; Green, K. E. *J. Am. Chem. Soc.* **1985**, *107*, 4788.

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(23) Air oxidation of **8** also gave **9** but with lower efficiency and higher levels of byproduct contamination.

(24) Paquette, L. A.; Carr, R. V. C.; Arnold, E.; Clardy, J. *J. Org. Chem.* **1980**, *45*, 4907.

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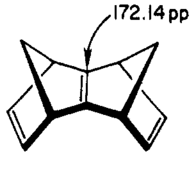
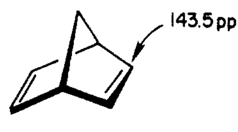
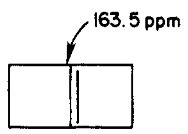
(27) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, 1984; p 125.

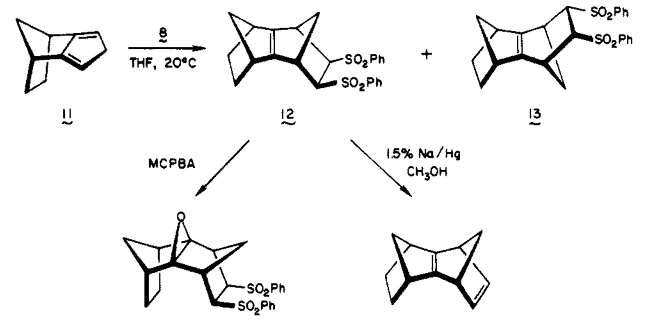
(28) Casanova, J.; Bragin, J.; Cottrell, F. D. *J. Am. Chem. Soc.* **1978**, *100*, 2264.







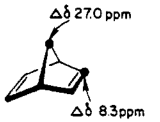
8 in tetrahydrofuran solution at room temperature. After 2 days, there was obtained in 86% combined yield a 1:1.2 mixture of the chromatographically separable disulfones **12** and **13**. The slight preponderance of the above-plane adduct is a likely reflection of the relatively large steric size of the phenylsulfonyl moieties, notwithstanding the sterically driven anti-Alder course of both [4 + 2] cycloadditions. The exo orientation of the $PhSO_2$ groups in **12** and **13** was easily recognized by the absence of strong coupling between the α-sulfonyl and vicinal bridgehead protons. That **12** is the adduct of syn geometry was initially suggested by the appearance of its α-sulfonyl protons at appreciably higher chemical shift (δ 3.22) than the corresponding pair in **13** (δ 4.22). The finding that increased shielding is a characteristic feature of endo protons in *syn*-sesquinorbornenes has been commented upon on several prior occasions.[10e,12b,29]



Additional substantiation was derived by conversion of **12** to epoxide **14**. As anticipated for the syn isomer only, both methano bridge carbons in **12** (50.68 and 46.97 ppm) become substantially shielded in **14** (39.05 and 35.13 ppm).

Treatment of **12** with 1.5% sodium amalgam gave **3**. This diene is a colorless, air-sensitive substance whose symmetry is clearly apparent from its seven-line ^{13}C NMR spectrum. The resonance due to its two central olefinic carbons appears at 157.35 ppm, significantly downfield of the signal observed for the trigonal carbon atoms in *syn*-sesquinorbornene (**1**, 151.6 ppm).[15b] Thus, an enhancement in the level of paramagnetic contributions to the ^{13}C NMR shift manifests itself in nonlinear fashion as progression is made from **1** to **3** and ultimately to **5**. The apical methylene carbons are similarly (**1**, 42.9 ppm; **3**, 47.4 and 70.1 ppm; **5**, 69.1 ppm), though less dramatically, affected.

A pragmatic analysis based upon empirical structural effects appears first warranted. Comparison of norbornene with norbornadiene[27] discloses that introduction of the second double bond results in downfield shifting of the relevant carbon atoms as indicated in **15**. Effects of entirely comparable magnitude are seen upon introduction of a second double bond into **1** (see **16**). However, when the maximum level of unsaturation is attained as in **5**, the extent of downfield drift (Δδ), as summarized in **17**, is quickly discerned as differing appreciably in magnitude.



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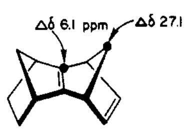

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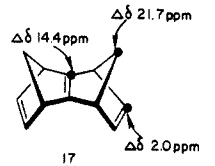

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It is obvious that the degree to which electron transfer occurs from the orbitals of the methano bridge to the antibonding orbitals of the π bonds is nonregular within the *syn*-sesquinorbornene triad. The possibility exists that this phenomenon is linked to increased pyramidal distortion. Alternatively, the distortions from planarity may play a significantly less than dominant role. To distinguish between these models, a similar spectral comparison of *anti*-sesquinorbornene (**2**) with its more highly unsaturated derivatives **4** and **6** was undertaken.

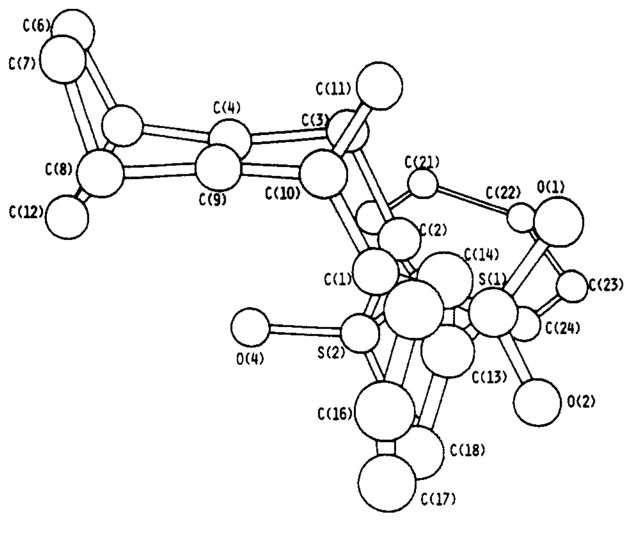


Figure 2. Computer-generated perspective drawing of the final X-ray model of diene disulfone **19**. Hydrogens are omitted for clarity.

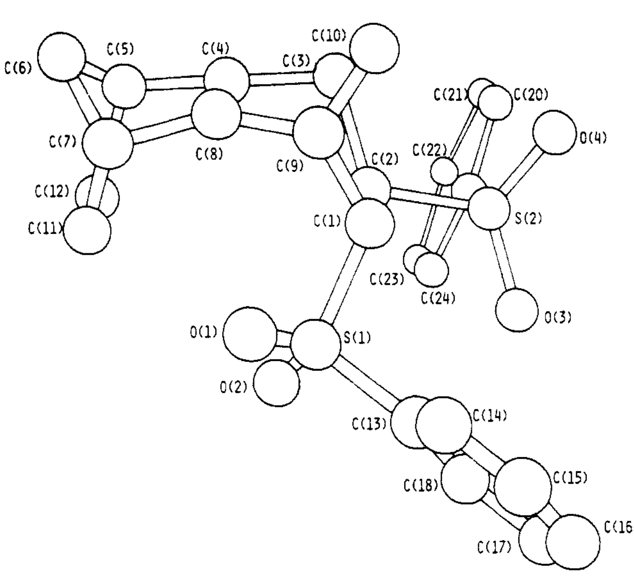
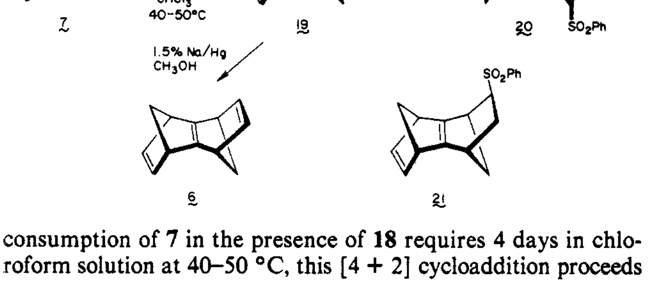


Figure 3. Computer-generated perspective drawing of the final X-ray model of diene disulfone **20**. Hydrogens are omitted for clarity.

Synthesis of *anti*-Sesquinorbornatriene (6). Redirection of the stereochemical course of Diels–Alder cycloadditions to **7** can be achieved with sterically demanding dienophiles, and (*E*)-1,2-bis(phenylsulfonyl)ethylene (**18**)[20] is no exception. Since the total consumption of **7** in the presence of **18** requires 4 days in chloroform solution at 40–50 °C, this [4 + 2] cycloaddition proceeds



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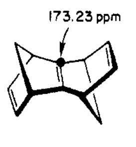
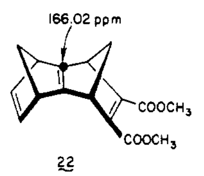
at a much slower rate than that involving **8**. This finding contrasts with the reactivity order observed with a representative number of simpler dienes.[20] Two adducts are formed in ratios ranging from 92:8 (CH_2Cl_2, 5 °C) to 80:20 ($CHCl_3$, 40–50 °C). The predominance of anti isomer **19** was ascertained by ^1H NMR spectroscopy and confirmed by X-ray analysis (Figure 2) to have an internal dihedral angle approaching 180°. Minor product **20**, a *syn*-sesquinorbornene derivative, has proven to be stable toward atmospheric oxygen, although its X-ray crystal structure determination (Figure 3) shows the central double bond to deviate from planarity by 16°. This lack of reactivity compared to **9** may be attributed to the high level of steric compression that would be exerted by the *endo*-(phenylsulfonyl) group upon added pyramidalization of the central carbon atoms resulting from the $sp^2 \rightarrow sp^3$ hybridization change necessitated by epoxidation.

Upon reduction with 8% sodium amalgam in buffered methanol, **19** was indeed converted to **6**. However, variable amounts of a byproduct still containing a phenylsulfonyl group were also produced. The latter substance was identified as **21** on the basis of its ^1H NMR spectrum and especially nuclear Overhauser effect data.

Less contaminated samples of triene **6** were routinely obtained through the use of 1.5% sodium amalgam. Despite the air sensitivity of this hydrocarbon, its ^1H and ^{13}C NMR spectra could be recorded without complication, provided that precautions for the complete exclusion of oxygen were taken. Significantly, the internal sp^2-hybridized carbon atoms of **6** appear still further downfield than those of **5** and, in fact, experience greater deshielding than the corresponding centers in the electronegatively substituted *syn*-sesquinorbornatrienes **22**[15b] and **23**![30]





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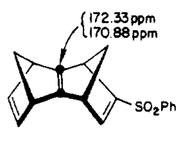
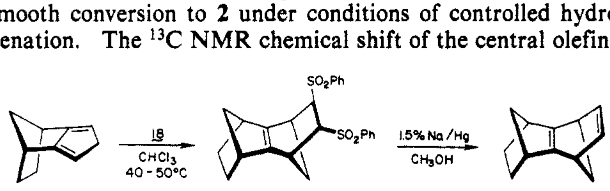
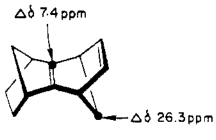


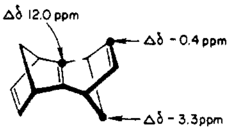
23

Spectral Correlation with *anti*-Sesquinorbornadiene (4). The distinct stereochemical advantage offered by **18** was again utilized in arriving at **4**. Reaction conditions comparable to those deployed earlier resulted in the conversion of isodicyclopentadiene (**11**) during 4 days to disulfone **24** (86% isolated yield). In order to establish the anti configuration of this adduct, its desulfonylation was effected. The resulting diene (**4**) exhibited spectra distinctively different from those of *syn*-sesquinorbornadiene (**3**) and underwent smooth conversion to **2** under conditions of controlled hydrogenation. The ^{13}C NMR chemical shift of the central olefinic carbons in **4** was determined to be 161.28 ppm. The reported value for *anti*-sesquinorbornene (153.86 ppm)[9] again reveals that a significant downfield shift materializes upon introduction of a second double bond (see **25**). The impact on the apical methylene group of the norbornadiene subunit in **4** (26.3 ppm to lower field) is also typical for this structural change.





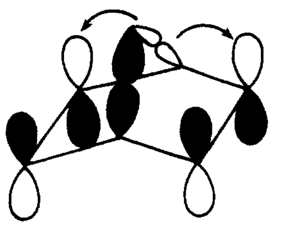
25



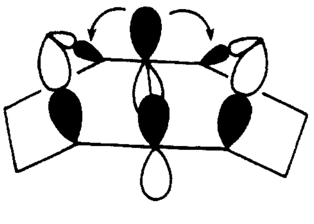
26

The more interesting comparison involves **4** and **6**. The strained internal sp^2-hybridized carbons in the *anti*-triene are deshielded by an additional 12.0 ppm to a chemical shift greater than 1 ppm downfield of the value observed in **5**! Parallel behavior is *not* found in the flanking olefinic or methylene carbons, both of which are shifted *upfield* relative to **4**.

In norbornadiene, the deshielding of the apical methylene carbon[27] is convincingly explained by electron transfer from the σ orbitals of the bridge to the antibonding π orbitals of the double bonds as in A. The prevailing situation is one where two acceptor orbitals interact with one donor orbital. In the trienes **5** and **6**, the acceptor:donor ratio is 3:2. Less electron transfer is consequently possible and the deshielding effect is somewhat reduced.



A



B

The downfield shift associated with the internal olefinic carbons in **5** and **6** can be ascribed to the structural change which certainly introduces bond angle and other strain effects. Furthermore, it can be assumed that interaction of the occupied π orbital of the central double bond with the antibonding orbitals of the neighboring σ bridges operates as well (see, for example, B). Under these circumstances, electron transfer out of the double bond and into the σ system would result. This would lead to a deshielding of the internal bridge carbons.

With certainty, the actual situation cannot be this simple, for **5** and **6** would then be more comparable in their spectral properties. Also, B is a model for **5** but not for **6**. More appropriate to our purposes is consideration of completely delocalized π orbitals such as those that can be derived from the *planar* bicyclohexatriene model[31] (Figures 4 and 5). The six relevant orbitals can be classified according to their symmetry with respect to the σ_v planes. The σ bonds of the two bridges can form the eight delocalized orbitals shown on the right-hand side of Figure 4. The significant point is that HOMO–LUMO interaction capable of allowing electron transfer from the σ framework to the π system does not appear readily feasible because of contrasting symmetry characteristics. In contrast, a similar analysis for norbornadiene (Figure 5) demonstrates that the $\sigma_2 \rightarrow \pi_3$ interaction is not similarly inhibited.

The second aspect concerns electron transfer from the occupied π orbitals to the antibonding σ orbitals. As is evident, every bonding π orbital in the triene enjoys correspondence with an empty σ orbital of proper symmetry. As a consequence, electron transfer of this type should be more efficient than in norbornadiene even if the orbital energies are quite different. This would again lead to an increased shielding of the bridge methylene carbons and an enhanced deshielding of the trigonal carbons. However, **5** and **6** differ unmistakably in their ability to permit operation of these interactions.

The above analysis, while entirely consonant with the observed spectral parameters, requires experimental substantiation. To this end, photoelectron spectroscopic measurements on **3**–**6** will be undertaken in the near future. Although these forthcoming results should shed considerable light on orbital correspondence, the phenomenon of changes in the ^{13}C chemical shift is not significantly related to pyramidalization.

Cycloaddition of 7 at Higher Temperatures. In an effort to accelerate the rate of the Diels–Alder cycloaddition involving **7** and **18**, the reaction was also examined in refluxing toluene solution. Under these circumstances, a disulfone strikingly different than either **19** or **20** was efficiently produced. That addition had actually occurred to the [1,5] hydrogen-shifted isomer of **7** was

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(30) Künzer, H.; Williams, R. V., unpublished findings.

(31) Heilbronner, E.; Bock, H. *The HOMO Model and its Application. Tables of Hückel Molecular Orbitals*; Wiley: New York, 1976; Vol. 3, p 139.

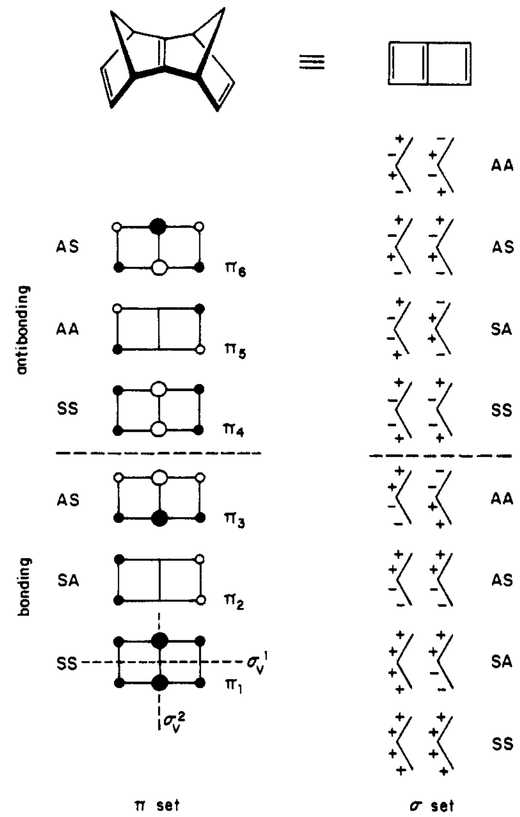


Figure 4. Bicyclohexatriene orbital model.

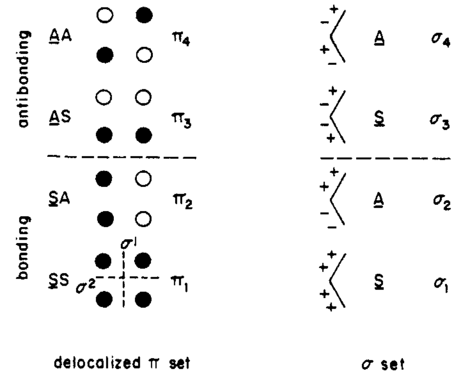
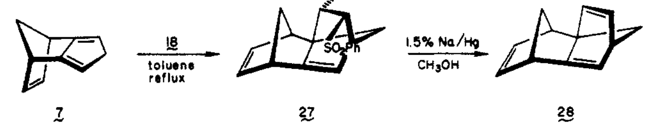


Figure 5. Norbornadiene orbital interactions.

indicated by the appearance of three vinyl protons in the ^{1}H NMR spectrum of the adduct. Comparable observations had previously been noted for isodicyclopentadiene (**11**)[32] and certain of its derivatives.[33] In such cases, the dienophile has engaged in bonding from the exo face and stereoselectively in that manner that avoids projecting a substituent into the area of the methano bridge of the second norbornyl subunit. By analogy, therefore, the new substance should be **27**. This conclusion is in full accord with all the available spectral properties.

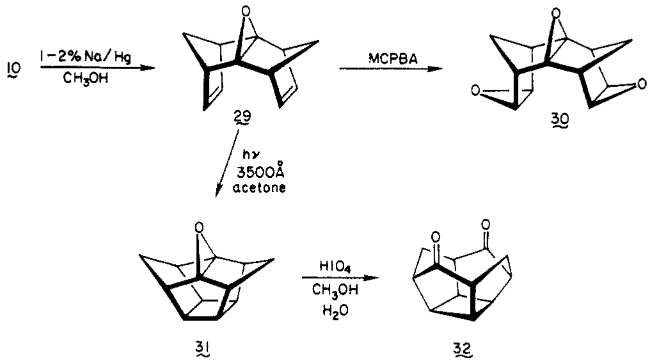


Furthermore, desulfonylation of **27** delivered the interesting triene **28**, the ^{1}H NMR spectrum of which shares many features in common with the known diene of related molecular architecture.[32] Although hydrocarbon **28** is isomeric with **5** and **6**, it does not share their tendency for oxidation in air.

Thus, (*E*)-1,2-bis(phenylsulfonyl)ethylene (**18**) qualifies as a dienophile having a reactivity toward **7** sufficiently low to allow it discriminate extensively in favor of the far less predominant cyclopentadiene isomer, to which it must add with reasonable rapidity.

[4]Peristylane-2,4-dione. Previously, one of the present authors reported a synthesis of diketone **32** in connection with the first successful acquisition of [4]peristylane derivatives.[34] Presently, the readiness with which **10** can be produced suggested an alternate, more expedient route to **32**. To this end, **10** was also desulfonylated to generate diene epoxide **29**. This crystalline substance has given no tendency for rearrangement under neutral conditions. In this respect, it differs appreciably from norbornadiene monoepoxides, which are noted to be exceedingly prone to structural isomerization.[35] Further epoxidation of **29** with *m*-chloroperbenzoic acid afforded trisepoxide **30**, whose high symmetry is attested to by its four-line ^{13}C NMR spectrum.

Diene epoxide **29** prepared in this manner need not be purified prior to irradiation with 3500-Å lamps in a Rayonet reactor. These photocyclization conditions result in clean conversion to the strained cage molecule **31**. Upon exposure to periodic acid in aqueous methanol, **31** experiences cleavage to target compound **32**. This five-step sequence constitutes a particularly brief route to [4]peristylane-2,4-dione.



Experimental Section

Cycloaddition of Tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene with 8. A Schlenk filtration apparatus was fitted with two 50-mL, one-necked flasks. A magnetic stirring bar was previously placed in that flask destined to be the reaction vessel. The entire apparatus was flushed with argon while being flame dried. Rapidly, the cooled flask was charged with (*Z*)-1,2-bis(phenylsulfonyl)ethylene (3.7 g, 12 mmol), dry deoxygenated tetrahydrofuran (20 mL), and triene **7** (1.6 g, 12 mmol). The entire vessel was wrapped in aluminum foil, and the reaction mixture was stirred for 2 days at room temperature under an argon atmosphere. The precipitated adduct was separated by suction filtration and subsequently dried at 0.3 torr for 1 h in the Schlenk apparatus. There was obtained 4.3 g (82%) of **9** as white crystals, which turn brown on heating to 215 °C and melt to a red liquid at 222 °C. Storage under argon was employed to offset possible air oxidation: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00–7.52 (series of m, 10 H), 6.47 (t, J = 1.8 Hz, 2 H), 3.33 (br, s, 2 H), 3.20 (br s, 2 H), 2.73 (d, J = 2.0 Hz, 2 H), 2.60 ($^1/_2$ABq, J = 9.9 Hz, 1 H), 2.13 ($^1/_2$ABq, J = 6.7 Hz, 1 H), 1.93 ($^1/_2$ABq, J = 6.7 Hz, 1 H), 1.62 ($^1/_2$ABq, J = 9.9 Hz, 1 H); ^{13}C NMR (20 MHz, $CDCl_3$) δ 161.24, 141.12, 139.15, 133.52, 128.93, 128.49, 70.65, 63.87, 48.34, 47.03, 44.19; MS, m/z calcd ($M^+ - SO_2Ph$) 297.0949, obsd 297.0968.

Epoxidation of 9. A 100-mL, three-necked flask fitted with a magnetic stirring bar was flame dried in a stream of argon and charged with

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(32) (a) Subramanyam, R.; Bartlett, P. D.; Iglesias, G. Y. M.; Watson, W. H.; Galloy, J. *J. Org. Chem.* **1982**, *47*, 4491. (b) Paquette, L. A.; Williams, R. V.; Carr, R. V. C.; Charumilind, P.; Blount, J. F. *Ibid.* **1982**, *47*, 4566.

(33) Paquette, L. A.; Charumilind, P.; Gallucci, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 7364.

(34) (a) Paquette, L. A.; Browne, A. R.; Doecke, C. W.; Williams, R. V. *J. Am. Chem. Soc.* **1983**, *105*, 4113. (b) Engel, P.; Fischer, J. W.; Paquette, L. A. *Z. Kristallogr.* **1984**, *116*, 225. (c) Paquette, L. A.; Fischer, J. W.; Browne, A. R.; Doecke, C. W. *J. Am. Chem. Soc.* **1985**, *107*, 686.

(35) See, for example: (a) Meinwald, J.; Labana, S. S.; Labana, L. L.; Wahl, G. H. *Tetrahedron Lett.* **1965**, 1789. (b) Padwa, A.; Koehn, W. *J. Org. Chem.* **1973**, *38*, 4007. (c) Gilbert, J. C.; Smith, K. R. *Ibid.* **1976**, *41*, 3883. (d) Chapleo, C. B.; Roberts, S. M.; Newton, R. F. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2088. (e) Baxter, A. D.; Javed, T.; Wakefield, B. J.; Hollerton, J.; Newton, R. F.; Roberts, S. M. *Ibid.* **1985**, 1803.

deoxygenated argon-saturated dichloromethane (60 mL) and disulfone **9** (1.3 g, 3.0 mmol). This solution was cooled to 0 °C, and *m*-chloroperbenzoic acid (0.8 g, 4.5 mmol) was added. After being stirred for 4 h at 0 °C, the reaction mixture was treated with water and the separated organic phase was washed with saturated sodium bicarbonate solution (3×) and water (1×) before drying. Solvent evaporation left a white solid, recrystallization of which from dichloromethane–hexane afforded 1.0 g (74%) of pure **10** as white crystals which turn brown above 204 °C and melt to a red liquid at 224 °C: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 7.99–7.56 (series of m, 10 H), 6.40 (t, J = 1.9 Hz, 2 H), 3.73 (d, J = 2.6 Hz, 2 H), 2.99 (br s, 2 H), 2.84 (br s, 2 H), 2.26 (dd, J = 10.8, 1.0 Hz, 1 H), 2.02–1.96 (m, 2 H), 1.42 (dd, J = 8.0, 1.0 Hz, 1 H); ^{13}C NMR (20 MHz, $\mathrm{CDCl_3}$) δ 140.80, 140.30, 133.80, 129.15, 128.55, 67.15, 65.35, 54.47, 44.63, 44.13, 36.10; MS, m/z calcd ($\mathrm{M^+ - C_6H_5SO_2}$) 313.0864, obsd 313.0873.

Anal. Calcd for $\mathrm{C_{24}H_{22}O_5S_2}$: C, 63.42; H, 4.88. Found: C, 63.29; H, 5.01.

syn-Sesquinorbornatriene (5). The quantity of **9** obtained by reaction of **7** (350 mg, 2.7 mmol) with **8** (832 mg, 2.7 mmol) was immediately dissolved in freshly distilled deoxygenated methanol (30 mL). While under a blanket of argon, the slurry was mechanically stirred while 2% sodium amalgam (from 400 mg of sodium and 30 g of mercury) was added portionwise. After 10 h of vigorous stirring at room temperature, the organic layer was separated and extracted with oxygen-free pentane. The combined pentane layers were dried and freed of solvent under an inert atmosphere to give 200 mg (47%) of **5** as an oxygen-sensitive clear oil which quickly yellowed on standing at room temperature. It is particularly important that all the transfers described above be performed under oxygen-free conditions. The *syn*-triene was also conveniently prepared by method A described below for the synthesis of the *anti*-triene.

For **5**: IR ($\mathrm{CH_2Cl_2}$, cm^{-1}) 3090–2800, 1370, 790; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 6.34 (t, J = 1.6 Hz, 4 H), 3.48 (t, J = 1.6 Hz, 4 H), 2.18 ($^1/_2$ABq, J = 6.0 Hz, 2 H), 2.02 ($^1/_2$ABq, J = 6.0 Hz, 2 H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 172.14, 140.32, 69.12, 50.02; MS, m/z calcd ($\mathrm{M^+}$) 156.0939, obsd 156.0986.

Cycloaddition of Isodicyclopentadiene with 8. A solution of **11** (1.32 g, 10 mmol) and **8** (3.08 g, 10 mmol) in deoxygenated tetrahydrofuran (20 mL) was stirred under an atmosphere of argon for 2 days at room temperature. During this time, a white precipitate formed. The reaction mixture was concentrated to dryness to leave a residue consisting of **12** and **13** in a ratio of 1:1.2 (300-MHz ^{1}H NMR analysis). These components were readily separated by MPLC on silica gel (elution with chloroform–ethyl acetate, 20:3) to give 1.7 g of **12** and 2.1 g of **13** (total adduct yield of 86%). Both isomers were further purified by recrystallization from acetone.

For **12**: mp 237 °C dec; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 8.01–7.54 (series of m, 10 H), 3.32 (br s, 2 H), 3.22 (d, J = 2.0 Hz, 2 H), 2.86 (br s, 2 H), 2.59 (d, J = 9.6 Hz, 1 H), 1.66–1.59 (m, 3 H), 1.30 (dm, J = 8.3 Hz, 1 H), 1.01 (d, J = 8.3 Hz, 1 H), 0.59 (dd, J = 7.8, 2.3 Hz, 2 H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 154.88, 141.10, 133.79, 129.22, 128.74, 68.15, 50.68, 47.50, 46.97, 42.71, 25.72; MS, m/z calcd ($\mathrm{M^+ - SO_2C_6H_5}$) 299.1106, obsd 299.1115.

Anal. Calcd for $\mathrm{C_{24}H_{24}O_4S}$: C, 65.43; H, 5.49. Found: C, 65.47; H, 5.48.

For **13**: mp 232 °C; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 8.05–7.53 (series of m, 10 H), 4.22 (br s, 2 H), 3.16 (br s, 2 H), 3.06 (br s, 2 H), 2.45 (dm, J = 7.9 Hz, 1 H), 1.82 (dm, J = 7.1 Hz, 2 H), 1.65–1.43 (m, 3 H), 1.08 (dd, J = 7.3, 2.2 Hz, 2 H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 152.24, 141.44, 133.34, 128.89, 128.76, 71.63, 55.39, 52.38, 47.08, 42.98, 27.07; MS, m/z calcd ($\mathrm{M^+}$) 440.1160, obsd 440.1127.

Anal. Calcd for $\mathrm{C_{24}H_{24}O_4S}$: C, 65.43; H, 5.49. Found: C, 65.45; H, 5.49.

Epoxidation of 12. A cold (0 °C), magnetically stirred solution of **12** (220 mg, 0.5 mmol) in dichloromethane (5 mL) was treated with 1.5 equiv of *m*-chloroperbenzoic acid in one portion. The reaction mixture was stirred at 0 °C for 1.5 h and treated with water. Following workup in the predescribed manner, the crude epoxide was recrystallized from acetone to provide 176 mg (77%) of pure **14** as white crystals melting at 278 °C with decomposition; ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 8.02–7.56 (series of m, 10 H), 4.30 (d, J = 2.9 Hz, 2 H), 3.12 (br s, 2 H), 2.59 (br s, 2 H), 2.19 (dd, J = 10.9, 1.0 Hz, 1 H), 1.98 (dt, J = 10.9, 1.5 Hz, 1 H), 1.81 (dm, J = 9.4 Hz, 1 H), 1.60 (dm, J = 10.0 Hz, 2 H), 1.42 (dd, J = 10.0, 2.5 Hz, 2 H), 0.62 (d, J = 9.4 Hz, 1 H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 140.45, 133.83, 129.18, 128.55, 69.06, 57.06, 45.41, 40.45, 39.05, 35.13, 27.36; MS, m/z calcd ($\mathrm{M^+ - SO_2C_6H_5}$) 315.1055, obsd 315.1001.

Anal. Calcd for $\mathrm{C_{24}H_{24}O_5S_2}$: C, 63.14; H, 5.30. Found: C, 62.84; H, 5.36.

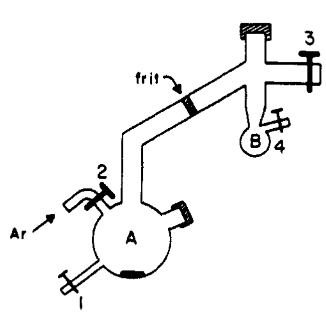

Figure 6. Reaction vessel.

syn-Sesquinorbornadiene (3). The sodium amalgam-mediated desulfonylation of **12** (572 mg, 1.3 mmol) was performed as described for *anti*-sesquinorbornatriene (method A) with 30 g of 1.5% amalgam in 20 mL of deoxygenated methanol. There was isolated 65 mg (32%) of **3**: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 6.37 (br s, 2 H), 3.28 (br s, 2 H), 2.87 (br s, 2 H), 2.07 ($^1/_2$ABq, J = 6.0, 1.2 Hz, 1 H), 1.96 ($^1/_2$ABq, J = 6.1, 0.9 Hz, 1 H), 1.32–1.27 (m, 3 H), 1.01 (dd, J = 8.0, 1.0 Hz, 1 H), 0.37 (dd, J = 7.0, 1.3 Hz, 2 H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 157.35, 137.90, 69.68, 48.03, 47.28, 42.02, 20.19; MS, m/z calcd ($\mathrm{M^+}$) 158.1096, obsd 158.1096.

Cycloaddition of Tricyclo[5.2.1.0^{2,6}]deca-2,5,8-triene with 18. A solution of **7** (1.3 g, 10 mmol) and (*E*)-1,2-bis(phenylsulfonyl)ethylene (3.08 g, 10 mmol) in deoxygenated chloroform (30 mL) was stirred under argon at 40–50 °C for 4 days. The clear reaction mixture was concentrated on a rotary evaporator to leave a pale-yellow oil which solidified on cooling. This product was recrystallized from acetone to give white crystals (3.6 g, 82%). Medium-pressure liquid chromatography on silica gel (gradient elution with dichloromethane–ether) was successful in separating **19** (80%) from **20** (20%). Reactions conducted in $\mathrm{CH_2Cl_2}$ solution at 0 °C (10 days; 50% reaction) gave a product ratio of 92:8.

For major product **19**: mp 163–164 °C (from dichloromethane–ether); ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$) δ 7.95–6.87 (series of m, 10 H), 6.74 (dd, J = 4.9, 3.0 Hz, 1 H), 6.64 (dd, J = 4.9, 2.8 Hz, 1 H), 4.44 (dd, J = 5.2, 3.4 Hz, 1 H), 4.07 (dd, J = 5.2, 2.1 Hz, 1 H), 3.86 (m, 1 H), 3.37 (m, 1 H), 3.17 (m, 1 H), 3.08 (m, 1 H), 2.95 (dt, J_t = 1.5 Hz, 1 H), 2.36 (dm, J_d = 5.8 Hz, 1 H), 2.24 (dq, J = 8.8, 1.2 Hz, 1 H), 1.38 (dq, J = 8.8, 1.5 Hz, 1 H); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 7.96–7.50 (series of m, 10 H), 6.82 (m, 2 H), 4.33 (dd, J = 5.2, 3.4 Hz, 1 H), 3.77 (dd, J = 5.2, 1.8 Hz, 1 H), 3.70 (m, 1 H), 3.51 (m, 1 H), 3.47 (m, 1 H), 3.41 (m, 1 H), 2.62 (dt, J_t = 1.5 Hz, 1 H), 2.33 (dq, J = 5.8, 1.5 Hz, 1 H), 2.20 (dq, J = 8.9, 1.5 Hz, 1 H), 1.57 (dq, J = 8.9, 1.8 Hz, 1 H); ^{13}C NMR (125 MHz, $\mathrm{CDCl_3}$) δ 165.49, 164.15, 144.89, 144.81, 140.40, 139.00, 133.98, 133.66, 129.35, 129.17, 128.58, 128.08, 78.59, 68.87, 68.52, 54.37, 50.96, 48.62, 47.30, 46.94.

Anal. Calcd for $\mathrm{C_{24}H_{22}O_4S_2}$: C, 65.73; H, 5.06. Found: C, 65.48; H, 4.90.

For minor product **20**: mp 169–171 °C (from dichloromethane–ether); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 7.95–7.44 (series of m, 10 H), 6.90 (dd, J = 4.9, 3.0 Hz, 1 H), 6.52 (dd, J = 4.9, 3.0 Hz, 1 H), 4.20 (dd, J = 5.8, 3.0 Hz, 1 H), 3.71 (br s, 1 H), 3.65 (br s, 1 H), 3.48 (br s, 1 H) 3.42 (br s, 1 H), 3.26 (dd, J = 6.1, 1.8 Hz, 1 H), 2.20 (dm, 1 H), 2.09 (dt, J_t = 1.5 Hz, 1 H), 2.05 (dm, J = 6.1 Hz, 1 H), 1.75 (dm, J = 9.2 Hz, 1 H).

Anal. Calcd for $\mathrm{C_{24}H_{22}O_4S_2}$: C, 65.73; H, 5.06. Found: C, 65.70; H, 5.00.

anti-Sesquinorbornatriene (6). Method A. The apparatus illustrated in Figure 6 is flame dried while flushed with argon. Flask A is charged with dry, deoxygenated, argon-saturated methanol (20 mL) and disulfone **19** (657 mg, 1.5 mmol). Sodium amalgam (1.5% w/w, 30 g) was added during the first hour of reaction. After 3 h of vigorous magnetic stirring, the reaction mixture had become a clear solution. The mercury was drained off through stopcock 1. Solvent was evaporated under vacuum (0.3 torr) via stopcock 3. Flask B was cooled to −78 °C, and the volatile hydrocarbon product was collected by heating flask A gently with a heat gun. During this procedure, vacuum was pulled through stopcock 4. Following removal of traces of solvent, the triene **6** collected amounted to 92 mg (39%). This material, a colorless crystalline solid, is air sensitive: ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$) δ 6.83 (t, J = 1.6 Hz, 4 H), 3.53 (t, J = 1.6 Hz, 4 H), 2.27 ($^1/_2$ABq, J = 5.3 Hz, 2 H), 2.03 ($^1/_2$ABq, J = 5.3 Hz, 2 H); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$) δ 173.23, 143.88, 77.53, 50.42; MS, m/z calcd ($\mathrm{M^+}$) 156.0939, obsd 156.0927.

Method B. A 100-mL, round-bottomed flask was charged with sodium dihydrogen phosphate (3 g), sodium amalgam (8% w/w, 3.30 g, 11.5 mg-atom), and methanol (25 mL). The mixture was warmed to ca. 50 °C and swept with a stream of argon. Disulfone **19** (500 mg, 1.14 mmol) was added and the reaction mixture was sonicated at 40–45 °C for 1 h. Rapid extraction with cold, degassed pentane (2 × 30 mL) was followed by drying over anhydrous sodium sulfate and concentration on a rotary evaporator. The resulting oil (93 mg) was contaminated with ca. 10% of the partially reduced sulfone **21**.

Further extraction of the reaction mixture with dichloromethane (2 × 20 mL) and rotary plate silica gel chromatography on silica gel (elution with ethyl acetate in petroleum ether) afforded 100 mg (19%) of **21**, mp 111–112 °C (from ether): ^{1}H NMR (200 MHz, CDCl$_3$) δ 7.96–7.52 (series of m, 5 H), 6.97 (m, 2 H), 3.74 (m, 1 H), 3.64 (m, 1 H), 3.55 (m, 1 H), 3.22 (m, 1 H), 3.14 (m, 1 H), 2.79 (dm, 1 H), 2.35 (dm, J = 5.5 Hz, 1 H), 2.18 (dm, 1 H), 1.51 (dm, J = 12.2 Hz, 1 H), 1.43 (dm, J = 7.9 Hz, 1 H).

Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.45; H, 6.08. Found: C, 72.15; H, 6.11.

Cycloaddition of Isodicyclopentadiene with 18. A solution of **11** (420 mg, 3.2 mmol) and (*E*)-1,2-bis(phenylsulfonyl)ethylene (1.0 g, 3.2 mmol) in deoxygenated, argon-saturated chloroform (8 mL) was stirred at 40–50 °C for 4 days under an atmosphere of argon. The clear reaction mixture was concentrated in vacuo and the solid residue was recrystallized from acetone to give 1.2 g (86%) of **24**, mp 191 °C: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.94–7.53 (series of m, 10 H), 4.30 (dd, J = 5.0, 3.5 Hz, 1 H), 3.80 (dd, J = 5.0, 1.9 Hz, 1 H), 3.34 (d, J = 1.0 Hz, 1 H), 3.16 (dd, J = 3.2, 1.3 Hz, 1 H), 3.06 (br s, 1 H), 2.94 (br s, 1 H), 2.31 (dd, J = 8.9, 1.0 Hz, 1 H), 1.84 (dt, J = 8.1, 1.8 Hz, 1 H), 1.75 (br d, J = 8.2 Hz, 2 H), 1.60 (m, 1 H), 1.31 (dd, J = 8.0, 1.0 Hz, 1 H), 1.04 (m, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 155.71, 153.79, 140.52, 139.32, 133.88, 133.58, 129.30, 129.14, 128.64, 128.27, 68.61, 68.55, 55.53, 52.43, 45.66, 45.19, 43.48, 41.66, 27.03, 26.25; MS, m/z calcd (M$^+$) 440.1116, obsd 440.1165.

Anal. Calcd for $C_{24}H_{24}O_4S_2$: C, 65.43; H, 5.49. Found: C, 65.40; H, 5.53.

***anti*-Sesquinorbornadiene (4).** The sodium amalgam-mediated desulfonylation of **24** (572 mg, 1.3 mmol) was performed as described previously for **19** (method A) with 25 g of 1.5% amalgam in deoxygenated methanol (20 mL): ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.89 (t, J = 1.8 Hz, 2 H), 3.34 (t, J = 1.6 Hz, 2 H), 3.11 (br s, 2 H), 2.32 ($^1/_2$ABq, J = 5.7 Hz, 1 H), 2.11 ($^1/_2$ABq, J = 5.7 Hz, 1 H), 1.66 (m, 2 H), 1.21 ($^1/_2$ABq, J = 7.9, 2.0 Hz, 1 H), 1.11 ($^1/_2$ABq, J = 8.0 Hz, 1 H), 0.98 (m, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 161.28, 144.29, 80.79, 49.33, 47.95, 43.60, 25.54; MS, m/z calcd (M+$^{)}$ 158.1096, obsd 158.1096.

***anti*-Sesquinorbornene (2) from 4.** A sample of **4** was prepared from 572 mg (1.3 mmol) of **24** and 30 g of the sodium amalgam in 20 mL of deoxygenated argon-saturated methanol as described above. A slight modification was introduced in that about 5 mL of methanol was collected with the diene in flask B which now housed a magnetic stirring bar. The apparatus was flushed with argon, platinum oxide (5 mg) was introduced, and the argon atmosphere was supplanted by hydrogen via three evacuate-fill cycles. Stirring of the mixture was maintained for 20 min, whereupon the catalyst was separated by filtration and the solvent was carefully evaporated. The crude product was seen to contain a small amount of *anti*-sesquinorbornane (^{1}H NMR analysis). Crystallization from 0.5 mL of cold acetone afforded 25 mg of **2**, whose physical properties are in accord with published data: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.81 (br s, 4 H), 1.68 (d br s, J = 6.5 Hz, 4 H), 1.33 ($^1/_2$ABq, J = 7.4 Hz, 2 H), 1.27 ($^1/_2$ABq, J = 7.4 Hz, 2 H), 1.09 (dd, J = 6.9, 2.1 Hz, 4 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 153.83, 54.52, 41.39, 26.61.

High-Temperature Cycloaddition of 7 to 18. A suspension of **18** (924 mg, 3.0 mmol) in toluene (10 mL) was heated overnight at the reflux temperature in a slow stream of argon. Triene **7** (390 mg, 3.0 mmol) was then introduced, and heating was continued for 12 h. The solvent was removed on a rotary evaporator, and the solid residue was recrystallized from acetone to give 1.0 g (80%) of **27** as white crystals, mp 196 °C: ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.98–7.51 (series of m, 10 H), 6.2 ($^1/_2$ABq, J = 5.4, 3.1 Hz, 1 H), 6.13 ($^1/_2$ABq, J = 5.4, 3.1 Hz, 1 H), 5.67 (d, J = 2.6 Hz, 1 H), 4.26 (dd, J = 5.3, 3.8 Hz, 1 H), 4.08 (dd, J = 5.3, 2.1 Hz, 1 H), 3.43 (br s, 1 H), 3.33 (br s, 1 H), 3.04 (br s, 1 H), 2.12 ($^1/_2$ABq, J = 9.1 Hz, 1 H), 1.79 (br s, 2 H), 1.45 ($^1/_2$ABq, J = 9.1, 2.0 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 160.05, 140.51, 140.21, 138.10, 136.66, 133.97, 133.73, 129.35, 129.17, 128.58, 128.26, 118.76, 70.96, 67.88, 67.69, 51.73, 50.41, 46.97, 43.76, 43.35; MS, m/z calcd (M$^+$) 438.0959, obsd 438.0960.

Triene 28. Reaction of **27** (570 mg, 1.3 mmol) with 30 g of 1.5% sodium amalgam in deoxygenated methanol (20 mL) according to the predescribed procedure furnished 97 mg (47%) of **28**: ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.89 (dd, J = 5.3, 3.2 Hz, 1 H), 6.50 (d, J = 5.2 Hz, 1 H), 6.14 (t, J = 1.7 Hz, 2 H), 5.95 (dd, J = 2.8, 1.1 Hz, 1 H), 3.49 (m, 1 H), 3.31 (br s, 1 H), 3.07 (br s, 1 H), 2.10 (dt, J = 8.6, 1.6 Hz, 1 H), 2.01 (dq, J = 8.6, 1.0 Hz, 1 H), 1.89 (dt, J = 5.5, 1.2 Hz, 1 H), 1.69 (dd, J = 5.5, 1.7 Hz, 1 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 164.71, 145.49, 142.32, 136.21, 135.35, 123.91, 74.85, 71.22, 53.38, 52.02, 43.11, 42.21; MS, m/z calcd (M$^+$) 156.0939, obsd 156.0938.

Epoxydiene 29. A 100-mL, three-necked flask containing a stirring paddle was flame dried in a stream of nitrogen. After the flask cooled, dry methanol (15 mL), disodium hydrogen phosphate (1 g), epoxy disulfone **10** (454 mg, 1 mmol), and 3 g of a total 20 g of 1.3% sodium amalgam were placed therein. The remaining amalgam was added during the following 6 h of reaction time during which vigorous mechanical stirring was maintained. Water (20 mL) and dichloromethane (30 mL) were added, and the organic phase was washed twice with water and dried. Solvent evaporation left a colorless oil that solidified in the refrigerator. This material was purified by sublimation at 40–50 °C and 0.3 torr to give 79 mg (46%) of **29** as colorless crystals, mp 75 °C: ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.08 (br s, 4 H), 3.03 (br s, 4 H), 2.15 ($^1/_2$ABq, J = 7.6 Hz, 2 H), 1.27 ($^1/_2$ABq, J = 7.6 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 143.56, 76.70, 51.77, 45.69; MS, m/z calcd (M$^+$) 172.0888, obsd 172.0890.

Trisepoxide 30. A cold (0 °C), magnetically stirred mixture of **29** (20 mg, 0.12 mmol), sodium bicarbonate (84 mg), and dichloromethane (8 mL) was treated with *m*-chloroperbenzoic acid (173 mg, 1 mmol). The reaction mixture was stirred at 0 °C for 4 h and processed with an aqueous workup. The organic phase was washed 3 times with saturated sodium carbonate solution and dried. Solvent evaporation left a white solid, recrystallization of which from ethyl acetate afforded 17 mg (70%) of **30**, mp 240–245 °C dec: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.40 (br s, 4 H), 3.00 (br s, 4 H), 1.52 ($^1/_2$ABq, J = 9.6 Hz, 2 H), 1.37 ($^1/_2$ABq, J = 9.6 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 64.02, 53.53, 42.49, 22.09; MS, m/z calcd (M$^+$) 204.0786, obsd 204.0805.

Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.28; H, 5.91.

Photocyclization of 29. An unpurified sample of **29** obtained from desulfonylation of **10** (454 mg, 1 mmol) was dissolved in acetone (10 mL) and irradiated for 8.5 h in a Pyrex tube with 3500-Å lamps in a Rayonet reactor. Following solvent evaporation, the residue was chromatographed on silica gel (elution with dichloromethane). Further purification by VPC (SE-30, 160 °C) gave 52 mg (30%) of **31** as colorless crystals, mp 126 °C: ^{1}H NMR (300 MHz, CDCl$_3$) δ 2.57 (m, 4 H), 2.23 (br s, 4 H), 1.55 ($^1/_2$ABq, J = 11.0 Hz, 2 H), 1.30 ($^1/_2$ABq, J = 11.0 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 63.97, 39.58, 38.65, 33.95; MS, m/z calcd (M$^+$) 172.0888, obsd 172.0902.

[4]Peristylane-2,6-dione (32). A solution of **31** (50 mg, 0.3 mmol) and periodic acid (140 mg, 0.6 mmol) was reacted in a manner directly paralleling the procedure described in ref 34. The reaction time was 20 h. Recrystallization of the crude product from hexane containing a small amount of ethyl acetate gave **32** (43 mg, 76%) as white crystals melting above 300 °C: ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.49–3.46 (m, 4 H), 2.70–2.65 (br m, 4 H), 2.31 (d, J = 13.1 Hz, 2 H), 2.15–2.04 (m, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 225.48, 53.67, 42.58, 41.73.

X-ray Crystallographic Analysis of 10. This epoxy disulfone ($C_{24}H_{24}O_5S_2$) crystallized in a monoclinic system, space group $P2_1/a$, with a = 12.540 (4) Å, b = 16.021 (5) Å, c = 10.365 (4) Å; β = 100.7 (3)°; V = 2046.1 Å^3; Z = 4; and D_{calcd} = 1.480 g cm^{-3}.

A total of 3805 reflections were recorded on a Philips PW 1100 diffractometer in the θ–2θ scan mode to a θ of 25° using Mo Kα monochromatized radiation (λ = 0.7107 Å). The 3548 unique reflections (R = 0.07) were used to solve the structure with MULTAN 80 programs. The non-hydrogen atoms were refined anisotropically with block diagonal least squares. The hydrogen atoms were found on a ΔF map and refined isotropically. The conventional R factor for the 1228 observed reflections ($I > 3\sigma(I)$) was 0.064.

X-ray Crystallographic Analysis of 19. This disulfone ($C_{24}H_{22}O_4S_2$) crystallized in the monoclinic system, space group $P2_1/a$, with a = 16.116 (5) Å, b = 12.573 (4) Å, c = 10.304 (4) Å; β = 95.1 (3)°; V = 2079.6 Å^3; Z = 4; and D_{calcd} = 1.400 g cm^{-3}.

A total of 3743 reflections were collected, of which 3559 were considered unique (R = 0.013). A Philips PW 1100 four-circle diffractometer was employed in the θ–2θ scan mode to 2θ = 50° with Mo Kα radiation (λ = 0.7107 Å). The structure was again phased by MULTAN 80 programs and refined by block-diagonal least squares. The non-hydrogen atoms were anisotropic; the hydrogen atoms were found on a ΔF map and refined isotropically. The final conventional R factor for the 1401 reflections considered observed with $I > 3\sigma(I)$ was 0.052.

X-ray Crystallographic Analysis of 20. This disulfone ($C_{24}H_{22}O_4S_2 \cdot C_2H_5OH$) crystallized in the triclinic system, space group $P1$, with a = 12.247 (4) Å, b = 10.677 (4) Å, c = 10.144 (4) Å; α = 114.8 (3)°, β = 96.7 (3)°, γ = 97.7 (3)°; Z = 2; V = 1171.0 Å^3; and D_{calcd} = 1.373 g cm^{-3}.

A total of 3707 unique reflections were collected on a Philips PW 1100 four-circle diffractometer to 2θ = 50° using the θ–2θ scan mode and Mo Kα radiation (λ = 0.7107 Å). The structure was phased with MULTAN 80 programs and refined anisotropically for non-hydrogen atoms using full-matrix least squares. The hydrogen atoms were found on a ΔF map and refined isotropically. The ethyl alcohol molecule is disordered about the origin. The final conventional R factor for the 2962 reflections considered observed with $I > 3\sigma(I)$ was 0.071.

Acknowledgment. We are grateful to the National Institutes of Health for the financial support of this work (Grant CA-12115) and to Prof. Harald Günther for a helpful exchange relating to ^{13}C NMR shift theory.

Supplementary Material Available: Bond lengths and bond angles for **10**, **19**, and **20**, as well as fractional coordinates and anisotropic thermal parameters for each compound (9 pages). Ordering information is given on any current masthead page.

Novel Peri-Condensed Weitz-Type Donors: Synthesis, Physical Properties, and Crystal Structures of 3,10-Dithiaperylene (DTPR), 1,6-Dithiapyrene (DTPY), and Some of Their CT Complexes

Kazuhiro Nakasuji,*[1a] Hirohisa Kubota,[1a] Tomoyuki Kotani,[1a] Ichiro Murata,*[1a] Gunzi Saito,[1b,d] Toshiaki Enoki,[1b] Kenichi Imaeda,[1b] Hiroo Inokuchi,[1b] Masako Honda,[1c] Chuji Katayama,[1c] and Jiro Tanaka[1c]

Contribution from the Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan, the Institute for Molecular Science, Okazaki 444, Japan, and the Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464, Japan. *Received October 1, 1985*

Abstract: 3,10-Dithiaperylene (DTPR, **1a**), 1,6-dithiapyrene (DTPY, **2a**), and their diphenyl derivatives, Ph_2DTPR (**1b**) and Ph_2DTPY (**2b**), were prepared as examples of molecular design for condensed type donors with two sulfur atoms. The electrochemistry indicates that these heterocycles are actually two-stage redox systems with low oxidation potentials, indicating large enhancement of the donor ability. They may be aptly termed peri-condensed Weitz-type donors. We obtained relatively high conductive (compressed powder samples) CT complexes utilizing these donors and TCNQ-type acceptors. In addition, especially noteworthy is the high conductivity of $Ph_2DTPR\text{-}DDQ_{0.75}$ (σ = 0.5 S cm^{-1}) despite the fact that the complex consists of neither TTF-type donor nor TCNQ-type acceptor. In addition, these heterocycles gave stable iodine complexes, in accord with the relatively low values of their oxidation potentials. The conductivities of these iodine complexes of compressed powder samples are the same order of magnitude with that of the iodine complex of perylene. The crystal structures of Ph_2DTPR, $Ph_2DTPR\text{-}ClO_4$, DTPY, and $(Ph_2DTPY)_2\text{-}I_3$ show columnar stacks of donor molecules. Significant differences in bond lengths between the neutral and cationic forms are observed.

I. Introduction

Most of the charge-transfer (CT) complexes with high electrical conductivity are formed from the component donor molecules based on 1,3- or 1,2-dichalcogenole skeleton such as tetrathiafulvalene (TTF) or tetrathiotetracene (TTT), respectively.[2] One way to the development of this chemistry and physics is to explore a new class of donors which do not contain such dichalcogenole rings so as to extend the range of molecular conductors.[3,4] Recently, Wudl and co-workers synthesized a new condensed organosulfur π-donor, 3,4:3',4'-bibenzo[*b*]thiophene (BBT) designed as *an isoelectronic heterocycle with perylene in the neutrtal state*.[4]

Our molecular design strategy for new organic electron donors is the replacement of two of the sp^2 carbon atoms in a polycyclic arene by two polarizable chalogens. This might produce a heterocycle with an increased donor ability, since *the two electron oxidation state, the dication, of the resulting molecule is isoelectronic with the original arene.* We now report examples of such a molecular design for new condensed π-donors and some studies of their CT complexes.

II. Results and Discussion

A. Synthesis and Physical Properties. We have synthesized 3,10-dithiaperylene (DTPR, **1a**) and its 2,11-diphenyl derivative (Ph_2DTPR, **1b**) as our initial targets among many possible isomers, selecting perylene as the basic skeleton. Reductive coupling of ketones **3**[5] with $TiCl_4\text{-}Zn$[6] in THF gave **4a** (60%) and **4b** (74%), which were converted to **5a** (40%) and **5b** (70%) by photochemical dehydrocyclization with 400-W high pressure Hg lamp. Dehydrogenation of the cyclized products **5** with *N*-chlorosuccinimide[7] in CH_2Cl_2 at −30 °C afforded the desired products, DTPR (**1a**, 40%) as yellow leaflets and Ph_2DTPR (**1b**, 36%) as red needles. Very recently, Bechgaard and his co-workers[8] have reported the crystal structure and solid state properties of the CT complex of 1,6-dithiapyrene (DTPY, **2**) with TCNQ which shows metallic conducting behavior down to 4 K. Since DTPY also falls under the same category of our molecular design, we have studied some of the properties of DTPY and its 3,8-diphenyl derivative (Ph_2DTPY, **2b**) independently. According to the Tilak procedure, DTPY (**2a**)[9] and Ph_2DTPY (**2b**) were prepared in improved yields (22 and 20% from the disulfides **6**, respectively), which make the

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[1] (a) Osaka University. (b) Institute for Molecular Science. (c) Nagoya University. (d) Present address: The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minatoku, Tokyo 106, Japan.

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