Stereoselection in [4 + 2] Cycloadditions to *anti,anti*-2,3-Diethylidenenorbornane and -norbornene. Crystal Structure Analysis of Double Bond Deformation in the Adducts[1]

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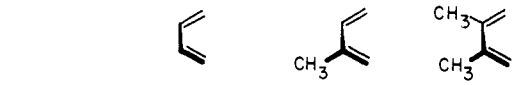
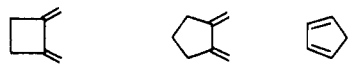
Abstract: Diels–Alder addition of *anti,anti*-2,3-diethylidenenorbornane (**4**) to *N*-phenylmaleimide, *p*-benzoquinone, phenyl vinyl sulfone, and dimethyl acetylenedicarboxylate (DMAD) gave exclusively products resulting from below-plane dienophile capture. In contrast, *N*-methyltriazolinedione (MTAD) added to **4** with overwhelmingly preferred above-plane stereoselection. Where the less reactive norbornene analogue **5** is concerned, below-plane stereoselectivity begins to fall off when DMAD is involved (94% endo). However, reaction with MTAD led to a 55% endo/45% exo product distribution. Extensive use was made of X-ray crystallography for product characterization. These data permitted full analysis of static π-bond deformation to be made in five adducts. The findings are discussed in relation to σ/π interaction and orbital tilting in these exocyclic dienes.

Past experience has shown that Diels–Alder reactivity differences in substituted 1,3-butadienes[3] depend in large part on the magnitude and direction of the s-cis/s-trans conformational equilibrium.[4] The distance separating C_1 and C_4 in the diene also contributes in a major way to the cycloaddition rate,[5] a factor well-known to underlie the preeminent position of cyclopentadiene as a highly reactive 4π partner.[6] Dihedral angle alterations appear to be of much less decisive importance.[7]

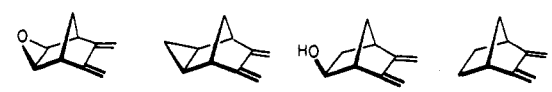


3a
k_{rel} 1 3 11
(MA, C_6H_6, 25°C)



5
k_{rel} 1 59 23,715
(MA, dioxane, 30°C)

When *geometric* variances in the diene structure are greatly minimized or eliminated, the more subtle consequences of long-range *electronic* effects make their appearance.[8,9] For example, when diene units are grafted onto otherwise rigid and structurally similar norbonyl frameworks, significant reactivity differences are observed. Although the kinetic inequalities are not as large on



9 1 35 44 178
k_{rel}
(TCNE, toluene, 20°C)

an absolute scale, they are nevertheless meaningful because the customarily influential factors discussed above have been virtually equalized. Modifications in the electronic properties of the pendant *s-cis*-butadiene moiety are currently thought to be the source of these reactivity differences. More specifically, hyperconjugative interaction of the particular norbornane part structure with the adjacent π system so alters the energies and/or shape of the diene frontier orbitals that Diels–Alder reactivity is appreciably affected. The situation has been compared in nature to the ability of cyclopropane,[10] cyclobutane,[11] and bent cyclohexane rings[12] to interact with neighboring π networks.

Our interest in this area stems from the fact that high π facial stereoselectivity is observed in Diels–Alder cycloadditions to norbornyl- and norbonenyl-fused dienes whose structural features are conductive to revealing dienophile capture from above or below the π plane.[13-16] It is obviously required that a stereochemical

(1) Electronic Control of Stereoselectivity. 19. For part 18, see: Green, K. E.; Paquette, L. A. *J. Org. Chem.*, in press.
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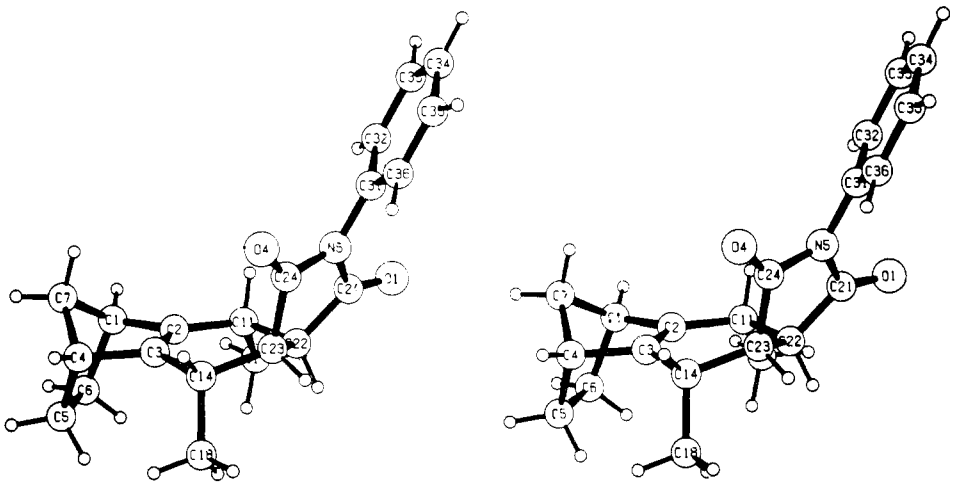
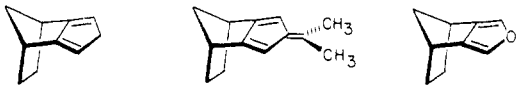


Figure 1. X-ray stereoview of 6 showing the molecular conformation in the crystal.

marker be incorporated into the 4π component, and five-ring annulation as in **1–3** has met this need quite satisfactorily. We



1 2 3

have interpreted the findings that **1–3** enter into kinetically controlled cycloaddition almost always[14c,15,17] from below the diene π surface (syn to the ethano bridge) as suggestive evidence for orbital mixing between bicyclic σ and diene π_s electrons with resultant tilting of the π orbitals. Other explanatory arguments have also been advanced.[15,16,18]

The end-to-end junction of terminal diene centers with a single atom bridge is recognized to promote high Diels–Alder reactivity. Does heightened reactivity also bring enhanced stereoselectivity? The experiments to be reported here that involve the diethylidene compounds **4** and **5** bear on this important question. Also to be

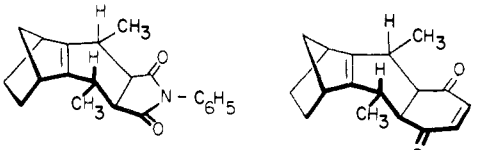
4 5

presented are detailed structural features of several cycloadducts.

Results

Substrate Synthesis and Cycloaddition Chemistry. The α-diketones corresponding to **4** and **5** had previously been prepared from dichlorovinylene carbonate and cyclopentadiene.[19] Individual Wittig reaction of these substances with ethyltriphenylphosphonium iodide produced a mixture of isomers from which the desired diene and triene could be isolated by a tandem HPLC–VPC sequence. The stereochemical purity of the products was evident from ^1H and ^{13}C NMR (six lines) analysis. That the methyl groups were both exo oriented followed from the predominance of these less sterically congested symmetric isomers in the reaction mixtures.

When benzene solutions of **4** and *N*-phenylmaleimide were allowed to stand at room temperature, slow reaction was observed. After 13 days, a single crystalline adduct was obtained in 91.5% isolated yield. The specific course of dienophile stereoselection could not be convincingly established on spectroscopic grounds alone. However, all ambiguities were removed by X-ray crystal structure analysis, which confirmed the product to be **6**, with dienophile capture occurring from *below* the diene plane (Figure 1).



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In the case of *p*-benzoquinone, **4** was transformed during 10 days at room temperature in chloroform solution exclusively into **7**. For the majority of the Diels–Alder reactions examined in this study, small scale NMR tube experiments were conducted alongside the preparative scale runs. The only distinguishable difference in the dual cycloadditions was the requisite change to the deuterated solvent equivalent. In no instance was formation of a product different from the one isolated observed. Consequently, the more rapid kinetically controlled formation and cycloreversion of an isomeric adduct, at least to spectroscopically detectable levels, can be ruled out. As with **6**, the stereochemical nature of **7** could not be ascertained directly. However, the interconversion of **7** with **13** (vide infra) by means of selective catalytic hydrogenation confirmed the operation of below-plane stereoselection.

Phenyl vinyl sulfone[20] added smoothly to **4** in refluxing toluene solution during 8 days to deliver **8** (97%). The exo orientation of the phenylsulfonyl substituent as well as the syn disposition of the ethano bridge and methyl groups were confirmed by X-ray analysis (Figure 2). Thus. the proclivity of moderately and weakly

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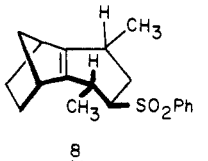

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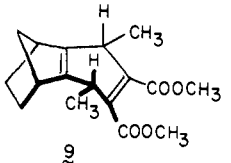

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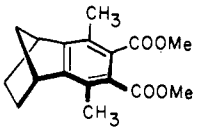

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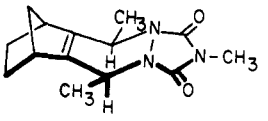

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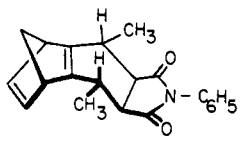
reactive dienophiles to add to **4** from the endo direction conforms to the pattern established earlier by **1**.

To investigate the stereochemical behavior of **4** under conditions where earlier transition states are thought to be involved,[21] more reactive 2π partners such as dimethyl acetylenedicarboxylate (DMAD) and *N*-methyltriazolinedione (MTAD) were next studied. With DMAD, a reasonable reaction rate was observed at room temperature in chloroform solution. Under these conditions, consumption of starting materials was seen to be virtually complete after 16 h, during which time the formation of a lone adduct was seen (^{13}C NMR). During the purification of this substance, partial air oxidation to **10** occurred. Our ignorance over the combined shielding effects of the two flanking double bonds on the methyl groups in the nonaromatized cycloaddend, caused in part by the availability of several conformations to each stereoisomer, again forced recourse to X-ray analysis. The experimentally determined three-dimensional structure of **9** in the solid state is reproduced in Figure 3.

Reaction of **4** with MTAD proceeded very rapidly at −70 °C in dichloromethane solution to furnish a homogeneous product (100%). The configuration of this crystalline solid was deduced from its independent formation by controlled catalytic hydrogenation of **18**, the structural features of which are entirely secure (vide infra). In this particular instance, therefore, above-plane stereoselection is overwhelmingly preferred, quite in contrast to the π-facial reaction mode followed by **1**.

Because triene **5** is less reactive than **4**, longer reaction times were typically required for its Diels–Alder reactions to proceed to completion. Where *N*-phenylmaleimide and *p*-benzoquinone were concerned, adduct formation was arrested after 5 (100%) and 7 weeks (94%), respectively, at room temperature. That **12** and **13** share a common configurational relationship with their



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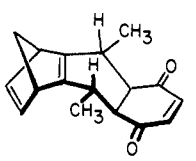

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dihydro counterparts **6** and **7** was ascertained by catalytic reduction. Because **13** crystallized in a more suitable form for X-ray analysis than did **7**, it was selected as the candidate for structure elucidation. A stereoview of **13** is seen in Figure 4.

Phenyl vinyl sulfone acted on **5** to give **14** (96%), the controlled hydrogenation of which furnished **8**. On the other hand, DMAD added to the triene to give two products in a 94:6 ratio. The major product (**15**), which could be easily purified, was converted in conventional fashion to **9**. Accordingly, endo π-facial stereoselectivity continues to be favored in this example.

In the least stereoselective process uncovered, triene **5** added 1 equiv of MTAD to yield a 55:45 mixture of two urazoles. The isomers were separated by high-pressure liquid chromatography (HPLC) and the more highly crystalline minor component was

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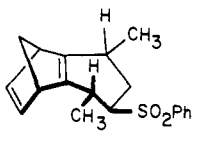

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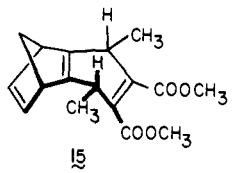

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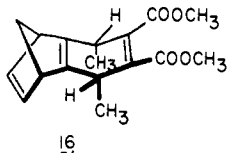

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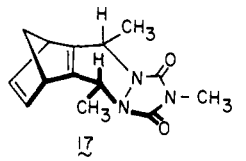
both reduced to give **11** and subjected to X-ray analysis, which revealed it to be **18** (Figure 5). (Crystallographic data for



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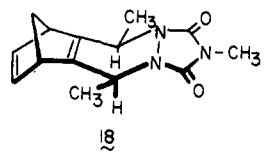
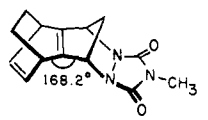


18

cycloadducts **6**, **8**, **9**, **13**, and **18** are given in Table I.)

Static π-Bond Deformation in the Adducts. Several years ago, Fukui advanced the proposition that the exo stereoselectivity observed in addition reactions to norbornene and norbornadiene arises because of π-orbital distortion toward the exo face.[22] More recent theoretical studies have not arrived at precisely the same conclusion. Instead, the local asymmetry about the double bonds in these molecules is thought to generate small, but significant, endo pyramidalization in the ground state.[18,23,24] Others consider the exo stereoselectivity to be a transition-state phenomenon.[25] Prior to the present series of investigations,[14] X-ray methods had been applied to six compounds (**19**,[13f] **20**,[17] **21**,[27] **22**,[26] **23**,[27] and **24**[17]) that have the common structural characteristic (excluding



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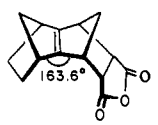

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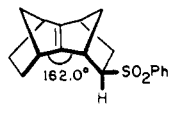

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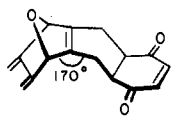

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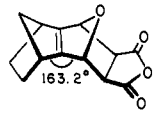


23

24

24) of being substantially bent about the central double bond. The downward tilt in these compounds varies from 11.8° in **19**, 16.4° in **20**, 18.0° in **21**, and 16.8° in **23** to 10° in **22** and 0.1° in **24**. An equal number of more diverse, yet related, structural types have been comparably elucidated in our more recent work.[14] Although the factors responsible for this π-bond nonplanarity have not yet been unequivocally identified,[18,28,29] some have moved rapidly to accept these findings as confirmatory experimental

(22) (a) Inagaki, S.; Fukui, K. *Chem. Lett.* **1974**, 509. (b) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.
(23) Wipff, G.; Morokuma, K. *Tetrahedron Lett.* **1980**, 4445.
(24) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, 2435.
(25) See ref 36 (Schleyer, P. v. R.; Maier, W.) and 37 (Gleiter, R.; Böhm, M.) in: Huisgen, R. *Pure Appl. Chem.* **1981**, *53*, 171.
(26) Pinkerton, A. A.; Schwarzenbach, D.; Stibbard, J. H. A.; Carrupt, P.-A.; Vogel, P. *J. Am. Chem. Soc.* **1981**, *103*, 2095.
(27) Hagenbuch, J.-P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1819.
(28) Wagner, H.-U.; Szeimies, G.; Chandrasekhar, J.; Schleyer, P. v. R.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 1210.
(29) Gleiter, R.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, 927.

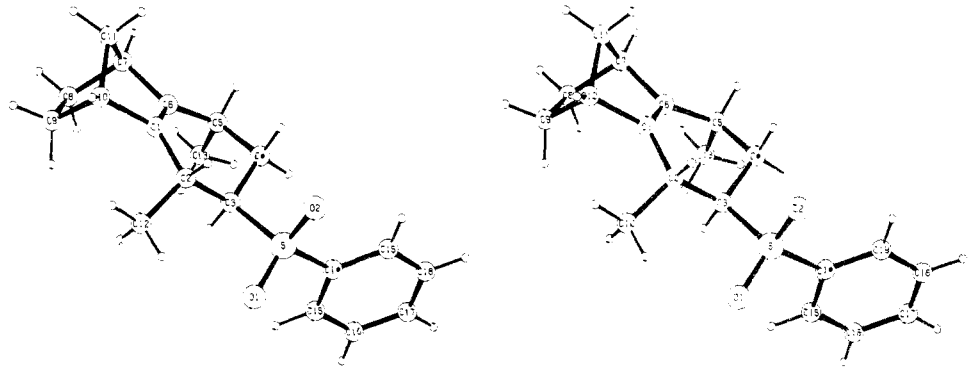


Figure 2. X-ray stereoview of **8** showing the molecular conformation in the crystal.

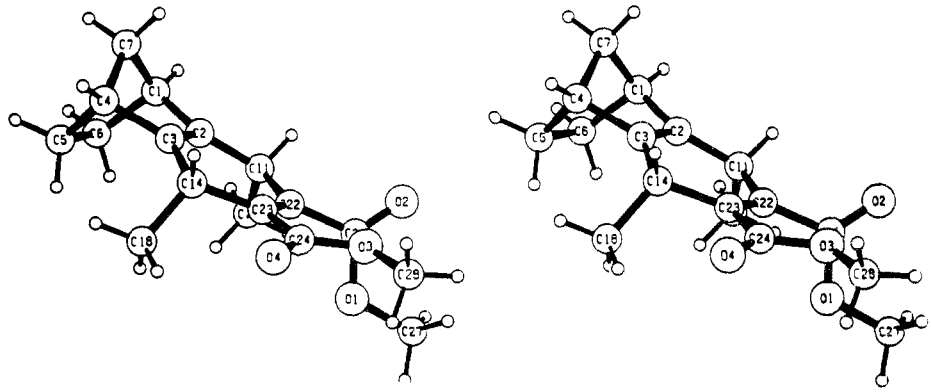


Figure 3. X-ray stereoview of **9** showing the molecular conformation in the crystal.

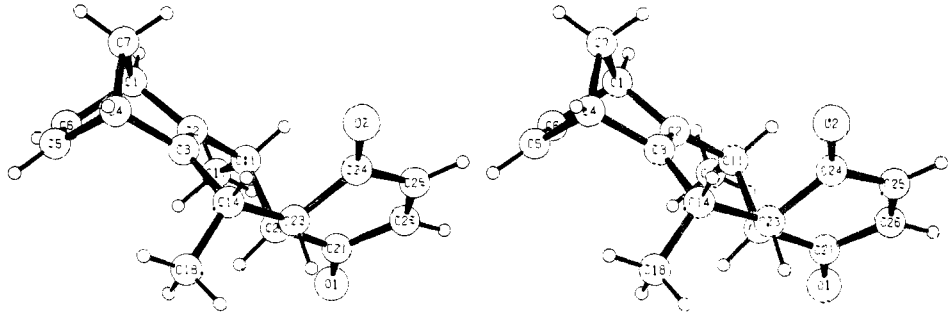


Figure 4. X-ray stereoview of **13** showing the molecular conformation in the crystal.

Table I. Crystallographic Data for Selected Cycloadducts[a]

	6	8	9	13	18
formula	$C_{21}H_{23}NO_2$	$C_{19}H_{24}O_2S$	$C_{17}H_{22}O_4$	$C_{17}H_{18}O_2$	$C_{14}H_{17}N_3O_2$
space group	$P\bar{1}$	$P2_1/a$	$P2_1/c$	$P2_1/c$	$P4_2bc$
a, Å	7.869 (1)	10.985 (4)	15.351 (3)	5.533 (1)	17.911 (2)
b, Å	10.335 (2)	15.502 (3)	6.241 (2)	10.661 (2)	
c, Å	12.238 (1)	10.295 (2)	16.292 (4)	22.656 (5)	8.340 (1)
α, deg	72.73 (1)				
β, deg	81.92 (1)	100.81 (3)	93.09 (2)	92.63 (2)	
γ, deg	71.24 (1)				
Z	2	4	4	4	8
D_{calcd}, g cm^{-3}	1.188	1.221	1.237	1.265	
reflctns measd	2425	3139	2092	1132	981
reflctns obsd[b]	2273	2794	1816	1026	834
R (R_w)	0.043 (0.060)	0.039 (0.048)	0.046 (0.055)	0.048 (0.057)	0.041 (0.041)
cryst size, mm	0.40 × 0.45 × 0.75	0.25 × 0.25 × 0.8	0.20 × 0.25 × 0.55	0.15 × 0.25 × 0.30	0.10 × 0.10 × 0.55
max θ, deg	57	70	57	48	57
least-squares refinement	full matrix	full matrix	full matrix	full matrix	full matrix

[a] All structures were solved by a multiple-solution procedure (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* 1971, A27) (Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination)). [b] Reflections were regarded as significant if $I > 2.5\sigma(I)$.

evidence for inherent pyramidalization in bridge bicyclic olefins.[17,26]

While it is remarkable that π-bond deformations of the preceding type had not been previously uncovered, there clearly exists a need for structural information on a larger array of norbornene and norbornadiene derivatives. Close examination of **19**–**24**, for example, reveals four of these compounds to be *syn*-sesquinorbornenes or closely allied substances; only **22** can be considered to possess lessened structural intricacy, although it is hardly low

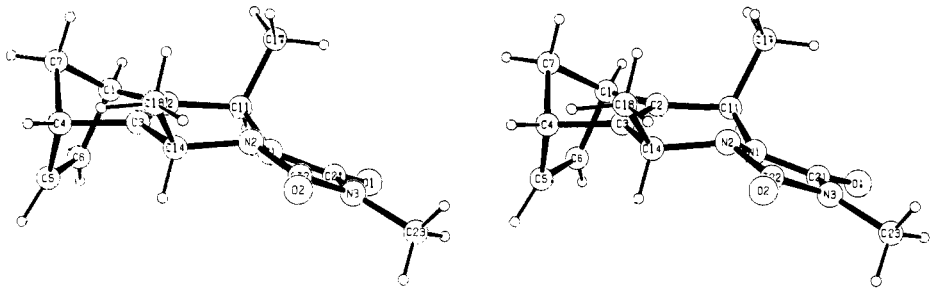


Figure 5. X-ray stereoview of **18** showing the molecular conformation in the crystal.

level. The planar nature of *anti*-sesquinorbornene **24** and related molecules[14] may stem from a canceling effect between the two ring systems sharing a common double bond.

For reasons discussed earlier in this paper, a series of adducts having norbornene and norbornadiene components were made available, and their three-dimensional structures were determined by X-ray analysis (Figures 1–5). For the most part, these molecules share a lower degree of complexity than **19–24** and consequently serve as useful probes of the pyramidalization question.

The molecular structure of **6** is presented as a stereoview in Figure 1. The final atomic parameters, bond lengths and angles, and selected torsion angles are reported in Tables II–V (supplementary material). The two planes of special interest are (C_1, C_2, C_3, C_4) and (C_{11}, C_2, C_3, C_{14}). Each set of four atoms is planar within experimental error, but there is a dihedral angle of 6.3° between these two planes, the "folding" occurring along the double bond in a downward (endo) direction. Although the cyclohexene ring is somewhat folded, a significant displacement of the methyl groups toward quasi-axial positions persists. This conformational arrangement may result from the combined π distortion about the norbornene double bond and relative positioning of the fused succinimide unit on the six-membered ring.

The benzoquinone adduct **13** (Figure 4) shares many intrinsic structural similarities with **6**. Its informative atomic parameters, bond lengths, valence angles, and interplanar angles are given in Table XIII–XVI. Of particular note is the dihedral angle deformation between the planes defined by (C_1, C_2, C_3, C_4) and (C_{11}, C_2, C_3, C_{14}), which, in this instance, has fallen to 4.8°. This statistically significant difference could arise from the fact that two six-membered rings are now mutually cis fused. Other factors may, of course, also be responsible. In this connection, the norbornadiene character of **13** might exert small changes not feasible by virtue of the norbornene nature of **6**. Significantly, however, neither compound is seen to possess important intramolecular contacts that could be relieved by π-bond deviations from planarity.

An examination of the molecular framework of **18** (Figure 5) provided insight into the question of possible π-bond geometry changes with altered (above-plane) dienophile capture. As the experimental data contained in Tables XVII–XX indicate, **18** features a distortion that is not symmetrically distributed. That is, atom pairs (C_{11}, C_{14}) and (N_1, N_2) are displaced unequally and in opposite directions from the plane through atoms C_2 and C_3 and the midpoint of C_1 and C_4 (plane I in the output). The planes calculated for **18** are as follows: I, M14 = midpoint (C_1, C_4, C_2, C_3); II, M11-14 = midpoint (C_{11}, C_{14}, C_2, C_3); III, (C_3, C_1, C_2, C_{11}); IV, (C_2, C_4, C_3, C_{14}); V, (C_3, C_1, C_{11}); and VI, (C_2, C_4, C_{14}). In this adduct, the nonplanarity about the internal double bond and the resultant asymmetry are best illustrated by the displacement of various atoms from plane I. Thus, C_1 and C_4 are 0.02 Å from the plane in opposite directions (required to be equal because their midpoint is one of the three defined points for this plane). More relevantly, C_{11} and C_{14} are both displaced on the same side of the plane, opposite to the side of apical C_7, but not by an equal amount. The marked asymmetry involving N_1 and N_2 is also to be especially noted. The latter is only 0.17 Å from the plane while the former is 0.78 Å removed. In brief, the conformation of **18** lacks the mirror symmetry that one might normally expect.

Plane II is analogous to plane I and is calculated from atoms C_2 and C_3 and the midpoint of C_{11} and C_{14}. The dihedral angle between planes I and II is taken as the measure of nonplanarity about the C_2–C_3 double bond. Since each plane involves C_2, C_3, and one midpoint, the intersection of the plane must be along the C_2–C_3 bond. In **18**, this angle is 8.1°.

Planes III and IV are calculated for the center atoms C_2 (plane III) and C_3 (plane IV) and the three neighbor atoms about each central atom. It is evident that these two sets of atoms are not planar, the measured values exceeding the anticipated deviations from the plane of lesss than 0.01 Å. Planes V and VI are the same as III and IV, except that the central atom has been omitted from each. In plane V, we see that C_2 is 0.07 Å out of the plane of its three neighbors, displaced to the same side as C_7; for plane VI, C_3 is 0.05 Å out of the plane of its neighbors.

Since sulfone **8** is derived from an acyclic dienophile, it differs from the three preceding compounds by lacking an additional fused ring. As Figure 2 clearly shows, the steric demands of the phenylsulfonyl group for equatorial status induce appropriate flexing of the cyclohexene ring. The resulting conformational alignment orients the C_{12} methyl substituent equatorially, while its C_{13} counterpart is projected into a quasi-axial environment. The combination of these effects is not considered to be the source of the 4.5° out-of-plane downward "folding" about the central double bond (see Tables VI–IX).

There is a further difference in **9** that is related to its 1,4-dihydrobenzene nature. The additional double bond in the pendant six-membered ring serves to flatten this segment of the molecule to an extent greater than any of the other substitution plans (Figure 3). Nonetheless, bond lengths and angles about the norbornene π system in **9** are not greatly perturbed by this structural change (Tables X–XII), the departure from planarity being 6.9° in the endo direction. Since this value closely parallels that observed for the other adducts, small geometric and ring strain changes around the periphery appear to have little influence upon the geometry in the vicinity of the central double bond.

Our analysis of these five adducts indicates that norbornene derivatives exhibit bent double bonds on the order of 4.5–10°, whereas *syn*-sesquinorbornene systems experience distortions approximately twice as large in the same direction. The space groups and packing interactions differ rather widely for both **19–24** and the present set of adducts. Although dissimilar crystal lattice effects and intermolecular interactions certainly exist, no contacts appear short enough to cause π-bond deformations of this magnitude. *The origins of olefin nonplanarity must therefore be inherent to such carbocyclic frameworks.* However, the question of whether this phenomenon is the result of geometric constraints[30] or prevailing homoconjugative and hyperconjugative interactions[31] cannot be considered fully resolved at present. Nevertheless, the structural findings do conform to recent ab initio calculations that predict double bond deformations of 3.4–4.9° for norbornene and 1.7–2.3° for norbornadiene.[18,23,24]

The presence of a distorted π bond in **18** is of particular interest

(30) (a) Greenhouse, R.; Borden, W. T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 1664. (b) Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. M. *Ibid.* **1974**, *96*, 4342. (c) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (d) Shea, K. J. *Tetrahedron* **1980**, *39*, 1683 and references cited therein.

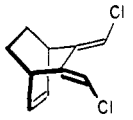
(31) (a) Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. (b) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1. (c) Gleiter, R. *Angew. Chem.* **1974**, *86*, 770. (d) Heilbronner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936.

in the present context, since it provides suggestive evidence that suitable structural bending is achieved in the adducts of **4** and **5** irrespective of the course of π-facial stereoselection that is followed by the dienophile.

Discussion

The stereochemical findings described here reveal that diene **4** enters into Diels–Alder reactions from its endo surface except when the highly reactive *N*-methyltriazolinedione reagent is involved. In this last instance, cycloaddition proceeds from above the π plane. In the case of the less reactive triene **5**, endo stereoselectivity begins to fall off when DMAD is utilized; furthermore, 100% exo stereoselection is now not attained with MTAD, only 45% of **18** being produced.

In an earlier report, Avenati and Vogel described the stereochemical outcome of tetracyanoethylene addition to **25**–**28**.[32]



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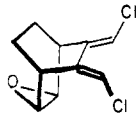

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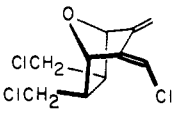

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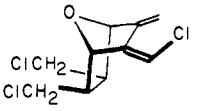
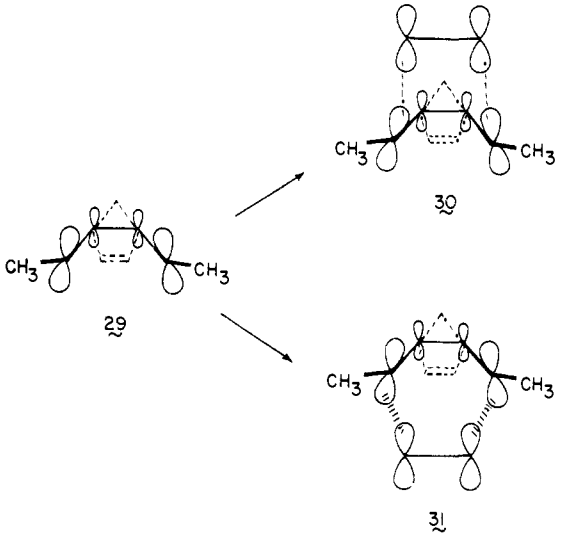


28

While the two dichloro-substituted dienes reacted preferentially from their endo face, addition to **27** and **28** proceeded with exo stereoselectivity. Because the chlorine substituents so markedly alter the shapes and energies of the π orbitals present in these systems, a full analysis of this cycloaddition behavior is seriously complicated.

In contrast, the use of methyl substituents as stereochemical markers does not create electronic perturbations of comparable magnitude. As in the case of their cyclopentadiene counterparts,[14] the subjacent π orbital in **4** and **5** is concentrated in the exocyclic double bonds and experiences disrotatory tilting with respect to the molecular plane as in **29** because of substantial admixing of



29 **30** **31**

high-lying norbornyl σ electrons.[33] Since the faces of these dienes are not, to a first approximation, differentiated by geometric or steric factors, this strong σ admixing would appear to be the important factor underlying the observed stereoselectivity.[34] Because of the higher levels of antibonding interaction (the result of improved overlap between two filled orbital pairs) that materialize in the transition state for exo addition (**30**),[14,34] endo stereoselectivity is usually favored. The present results conform nicely to this trend, except when highly reactive dienophiles such as DMAD and MTAD are involved.

The latter two reagents frequently do not conform to the distinctive stereochemical characteristics of less reactive 2π donors. What is responsible for this sometimes maverick behavior? One possible complication is with our model, which is founded on direct analysis of the shapes of the frontier and subjacent orbitals in the unperturbed diene (triene) and dienophile. The resulting static, time-independent profile is presently forced upon us by limitations in computer time and costs.

DMAD and MTAD are recognized to be highly polarizable reagents that, in addition, possess a pair of electrons orthogonal to those about to engage in bonding. It becomes entirely likely that an extended dynamical view of their Diels–Alder reaction with **4** and **5** would reveal the onset of pronounced electronic perturbations in direct opposition to the ground-state interaction pattern.[35] Until a full time-independent analysis can be made of the coupling between all components along each step of the reaction pathway, the interplay between polarizability and eventual π-facial stereoselectivity must be viewed as an open question. Notwithstanding, the face selectivity exhibited toward **4** and **5** by dienophiles possessing a single double bond conforms well to our π-orbital tilting hypothesis. It is now quite clear that dienes grafted onto norbornyl or norbornenyl frameworks need not be cyclic (i.e., cyclopentadiene, furan, etc.) to strongly favor endo dienophile capture.

Experimental Section

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 467 spectrophotometer. The ^{1}H NMR spectra were determined with Varian EM-390 and Bruker HX-90 instruments, and apparent splittings are given in all cases. The ^{13}C NMR spectra were obtained with a Bruker WP-80 spectrometer. Mass spectra were measured on an AEI-MS9 spectrometer at an ionizing energy of 70 eV. Microanalytical determinations were performed at the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

***anti*,*anti*-2,3-Diethylidenenorbornane (4).** Into a 3-L three-necked flask was placed sodium hydride (33.12 g of 50% in mineral oil, 0.692 mol) and the solid was washed 3 times with dry pentane. The flask was evacuated and blanketed 3 times with nitrogen. Anhydrous dimethyl sulfoxide (350 mL) was introduced by syringe, and the resulting mixture was heated at 80 °C with stirring for several hours until hydrogen evolution ceased. Following cooling to room temperature, a solution of ethyltriphenylphosphonium iodide (289 g, 0.692 mol) in warm dimethyl sulfoxide (1750 mL) was added. The blood-red solution was stirred for 15 min before 34.3 g (0.276 mol) of bicyclo[2.2.1]heptane-2,3-dione[18] dissolved in 400 mL of the same solvent was slowly introduced (warming). When addition was complete, the mixture was heated at 60–68 °C for 22 h and poured into 1500 mL of ice water. The product was extracted into petroleum ether (2 × 1500 mL), and the combined organic phases were washed with 50% aqueous dimethyl sulfoxide (400 mL) and brine (300 mL). After the solution was dried, the solvent was slowly removed by distillation at atmospheric pressure and the residue was distilled (bp 68–72 °C (12 mm)) to give 16.4 (40%) of isomeric diene mixture.

The isomers were chromatographically separated on a Waters Prep 500 high-pressure liquid chromatograph (silica gel) with the aid of band shaving techniques (elution with petroleum ether). The fractions containing **4** were again carefully evaporated, and final purification was achieved by VPC (2 ft × 0.25 in. 15% SE-30, 180 °C): IR (cm^{-1}, neat) 3035, 2958, 2915, 2863, 1442, 938, 870, 810, 795; ^{1}H NMR ($CDCl_3$) δ 5.45 (q, J = Hz, 2 H), 3.05 (m, 2 H), 1.7 (d, J = 6 Hz, 6 H), 1.6–1.4 (m, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 145.16, 107.34, 40.10, 39.13, 28.10, 14.12; mass spectrum, m/e (M^+) calcd 148.1252, obsd 148.1257.

(32) Avenati, M.; Vogel, P. *Helv. Chim. Acta* **1982**, *65*, 204.

(33) As has proven customary for these systems, the highest occupied MO shows no evidence for tilting by INDO and MINDO/3 methods, presumably because its energy level is too far removed from the high-lying σ electrons of the bicyclic moiety. We thank Professor R. Gleiter and Dr. M. Böhm for their help in arriving at the π orbital profiles of **4** and **5**.

(34) Gleiter, R.; Paquette, L. A. *Acc. Chem. Res.* submitted for publication.

(35) It is not clear whether orbital distortion (Burgess, E. M.; Liotta, C. L. *J. Org. Chem.* **1981**, *46*, 1703) is the proper phenomenon to invoke here, since tilting may remain important and no allowance has previously been made for this component of the overall interaction.

Anal. Calde for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.97; H, 10.93.

***anti,anti*-5,6-Diethylidene-2-norbornene (5).** A 15.0 g (0.123 mol) sample of bicyclo[2.2.1]hept-2-ene-5,6-dione[18] was treated as described above (50 °C for 16 h) with 14.8 g (0.308 mol, 50% in oil) of sodium hydride and 128.8 g (0.308 mol) of ethyltriphenylphosphonium iodide in dimethyl sulfoxide (595 mL). Distillation afforded 8.23 g (45.8%) of isomeric trienes, bp 90–94 °C (15 mm). High-pressure liquid chromatography in the predescribed manner followed by preparative VPC purification delivered **5** as a colorless liquid: IR (cm^{-1}, neat) 3058, 2992, 2962, 2920, 2855, 1440, 1375, 1335, 1305, 895, 808, 795, 730; ^1H NMR ($CDCl_3$) δ 6.2 (m, 2 H), 5.6 (q, J = 6 Hz, 2 H), 3.6 (m, 2 H), 1.7 (d, J = 6 Hz, 6 H), 1.4 (m, 2 H); ^{13}C NMR (ppm, $CDCl_3$) 141.33, 136.18, 109.67, 50.88, 45.34, 14.27; mass spectrum, m/e (M^+) calcd 146.1095, obsd 146.1099.

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.52; H, 9.62.

1,2,3,4,5,6,7,8-Octahydro-5,8-dimethyl-*N*-phenyl-1,4-methanonaphthalene-6,7-dicarboximide (6). A solution of **4** (106 mg, 0.721 mmol) and *N*-phenylmaleimide (125 mg, 0.721 mmol) in benzene (10 mL) was stirred under nitrogen at room temperature for 13 days. Evaporation of solvent afforded 221 mg (91.5%) of a single adduct, which was homogeneous by TLC and by ^1H and ^{13}C NMR. Although TLC purification on silica gel (elution with 4:1 petroleum ether–ethyl acetate) resulted in partial decomposition of this material, pure adduct was obtained as colorless crystals from ether–petroleum ether: mp 98.5–99.0 °C; IR (cm^{-1}, KBr) 2955, 1710, 1490, 1375, 1195, 1170, 1160; ^1H NMR ($CDCl_3$) δ 7.5–7.1 (m, 5 H), 2.8 (m, 6 H), 1.8–1.0 (series of m, 6 H), 1.35 (d, J = 6 Hz, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 178.51, 141.62, 132.25, 129.09, 128.31, 126.42, 48.89, 46.80, 45.00, 30.10, 26.65, 21.51; mass spectrum, (m/e (M^+) calcd 321.1729, obsd 321.1736.

Anal. Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21. Found: C 78.25; H, 7.33.

1,2,3,4,8a,9,10,10a-Octahydro-9,10-dimethyl-1,4-methanoanthracene-5,8-dione (7). A solution of **4** (98.5 mg, 0.666 mmol) and benzoquinone (71.9 mg, 0.666 mmol) in chloroform (5 mL) was stirred under nitrogen at room temperature for 10 days. Evaporation of solvent yielded 153 mg (89%) of a single adduct homogeneous by TLC and by ^1H and ^{13}C NMR. Pure **7** was obtained by TLC purification on silica gel (elution with 9:1 petroleum ether–ethyl acetate) and recrystallization from ether–petroleum ether as pale yellow needles: mp 114–115 °C; IR (cm^{-1}, KBr) 2960, 2860, 1680, 1450, 1255; ^1H NMR ($CDCl_3$) δ 6.6 (s, 2 H), 2.7 (m, 6 H), 1.8–0.8 (series of m, 6 H), 1.05 (d, J = 6 Hz, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 199.54, 141.46, 139.64, 53.58, 48.55, 44.48, 29.67, 26.78, 17.84; mass spectrum, m/e (M^+) calcd 256.1463, obsd 256.1472.

Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.74; H, 7.88.

1,2,3,4,5,6,7,8-Octahydro-5,8-dimethyl-6-(phenylsulfonyl)-1,4-methanonaphthalene (8). A solution of **4** (162 mg, 1.09 mmol) and phenyl vinyl sulfone (184 mg, 1.09 mmol) in toluene (15 mL) was heated at the reflux temperature under nitrogen for 8 days. Evaporation of solvent yielded 336 mg (97%) of a single adduct (TLC and NMR analysis). Recrystallization from petroleum ether–ethyl acetate gave **8** as colorless crystals: mp 120–120.5 °C; IR (cm^{-1}, KBr) 2960, 2950, 2870, 1445, 1280, 1140; ^1H NMR ($CDCl_3$) δ 7.8 (m, 2 H), 7.5 (m, 3 H), 3.1–2.3 (series of m, 5 H), 1.9–1.4 (m, 4 H), 1.3–0.8 (series of m, 4 H), 1.2 (d, J = 6.0 Hz, 3 H), 0.9 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 143.80, 140.60, 138.55, 133.41, 128.99, 128.75, 65.63, 48.50, 44.51, 30.29, 28.15, 26.84, 26.60, 19.75, 19.17.

Anal. Calcd for $C_{19}H_{24}O_2S$: C, 72.11; H, 7.64. Found: C, 71.91; H, 7.96.

Dimethyl 1,2,3,4,5,8-Hexahydro-5,8-dimethyl-1,4-methanonaphthalene-6,7-dicarboxylate (9). A solution of **4** (169 mg, 1.14 mmol) and dimethyl acetylenedicarboxylate (266 mg, 1.87 mmol) in 5 mL of chloroform was stirred under a nitrogen atmosphere at room temperature for 5 days. The solvent was evaporated and excess DMAD removed at 70 °C and 0.4 torr. A single adduct (^{13}C NMR analysis) was produced in quantitative yield. When attempts were made to purity this material by TLC on silica gel (elution with 15% ethyl acetate in petroleum ether), some aromatization was encountered. There was isolated 187 mg (56%) of **9** and 102 mg (31%) of **10**.

For **9**: mp 65–66 °C; IR (cm^{-1}, KBr) 2950, 2860, 1745, 1720, 1615, 1430, 1295, 1260; ^1H NMR ($CDCl_3$) δ 3.75 (s, 6 H), 3.33 (m. 2 H), 2.75 (br s, 2 H), 1.8–1.0 (m, 8 H), 1.15 (d, J = 6.5 Hz, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 168.80, 140.40, 139.09, 52.04. 49.08, 44.52, 34.03, 26.94, 20.44; mass spectrum, m/e (M^+) calcd 290.1518, obsd 290.1527.

Anal. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64. Found: C, 70.53; H, 7.72.

For dimethyl 1,2,3,4-tetrahydro-5,8-dimethyl-1,4-methanonaphthalene-6,7-dicarboxylate (**10**): mp 51.5–52.5 °C; IR (cm^{-1}, KBr) 2940, 2860, 1730, 1430, 1285, 1200; ^1H NMR ($CDCl_3$) δ 3.8 (s, 6 H), 3.5 (br s, 2 H), 2.3 (s, 6 H), 2.0–1.0 (series of m, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 169.44, 149.24, 130.01, 126.32, 52.14, 48.08, 42.04, 25.73, 15.92; mass spectrum, m/e (M^+) calcd 288.1361, obsd 288.1369.

Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.81; H, 6.99. Found: C, 70.83; H, 7.05.

1,4,5,6,7,8-Hexahydro-*N*,1,4-trimethyl-5,8-methanophthalazine-2,3-dicarboximide (11). A solution of **4** (62.7 mg, 0.424 mmol) in 5 mL of dichloromethane was stirred under nitrogen at −78 °C while a solution of *N*-methyltriazolinedione in dichloromethane was added by syringe until the pink color just persisted. The reaction mixture was allowed to warm to room temperature and the solvent was evaporated to provide 11 as the only adduct in quantitative yield. Recrystallization from ether–petroleum ether gave the analytical sample as colorless prisms: mp 86.0–86.5 °C; IR (cm^{-1}, KBr) 2970, 2880, 1765, 1700, 1470, 1395, 1370, 1285, 1270; ^1H NMR ($CDCl_3$) δ 4.2 (q, J = 6.6 Hz, 2 H), 3.0 (s, 3 H), 2.85 (m, 2 H), 1.8–0.9 (series of m, 6 H), 1.57 (d, J = 6.6 Hz, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 153.36, 138.94, 50.15, 48.20, 42.28, 25.92, 24.80, 18.35; mass spectrum, m/e (M^+) calcd 261.1477, obsd 261.1484.

Anal. Calcd for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33. Found: C, 64.15; H, 7.34.

1,4,5,6,7,8-Hexahydro-5,8-dimethyl-*N*-phenyl-1,4-methanonaphthalene-6,7-dicarboximide (12). A solution of **5** (235 mg, 1.61 mmol) and *N*-phenylmaleimide (279 mg, 1.61 mmol) in benzene (7 mL) was stirred under nitrogen for 5 weeks. Evaporation of solvent left a single adduct in quantitative yield, which proved homogeneous by TLC and NMR spectroscopy. During the course of TLC purification on silica gel (elution with 4:1 petroleum ether–ethyl acetate) some decomposition and air-oxidation was encountered. In addition to pure **12** (214 mg), there was also isolated some monoepoxide (32 mg), which was not further characterized.

For **12**: mp 134–135 °C; IR (cm^{-1}. KBr) 2960, 2920, 1715, 1590, 1495, 1445, 1390, 1190; ^1H NMR ($CDCl_3$) δ 7.4–7.1 (m, 5 H), 6.65 (br s, 2 H), 3.3 (br s, 2 H), 3.05 (q, J = 8 Hz, 2 H), 2.8 (br s, 2 H), 1.85 (br s, 2 H), 1.1 (d, J = 8 Hz, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 178.61, 148.37, 142.30, 132.25, 129.04, 128.31, 126.37, 71.08, 52.29, 46.36, 30.39, 19.52; mass spectrum, m/e (M^+) calcd 319.1572, obsd 319.1580.

Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63. Found: C 78.80; H, 6.78.

1,4,8a,8,10,10a-Hexahydro-9,10-dimethyl-1,4-methanoanthracene-5,8-dione (13). A solution of **5** (231 mg, 1.58 mmol) and benzoquinone (171 mg, 1.58 mmol) in chloroform (10 mL) was stirred for 7 weeks under nitrogen at room temperature. Upon evaportion of the solvent, 343 mg (85%) of adduct and 34 mg of unreacted benzoquinone were isolated (the latter by selective sublimation, therefore 94% recovery). The adduct, which was shown to be a single isomer by the usual criteria, was obtained as yellow needles by recrystallization from ether–petroleum ether: mp 128.5–129.5 °C; IR (cm^{-1}, KBr) 3050, 2980, 2955, 2940, 1680, 1600, 1545, 1450; ^1H NMR ($CDCl_3$) δ 6.7 (t, J = 8 Hz, 2 H), 6.6 (s, 2 H), 3.35 (m, 2 H), 2.7 (m, 4 H), 1.9 (br s, 2 H), 0.9 (d, J = 7 Hz, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 199.66, 148.80, 142.92, 139.70, 71.12, 53.40, 51.83. 29.80, 15.90; mass spectrum m/e (M^+) calcd 254.1307, obsd 254.1315.

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.15; H, 7.19.

1,4,5,6,7,8-Hexahydro-5,8-dimethyl-6-(phenylsulfonyl)-1,4-methanonaphthalene (14). A solution of **5** (134 mg, 0.916 mmol) and phenyl vinyl sulfone (154 mg, 0.916 mmol) in toluene (15 mL) was heated at the reflux temperature under nitrogen for 5 days. Upon solvent evaporation, a single adduct (278 mg, 96%) was obtained. Purification by TLC on silica gel (elution with 4:1 petroleum ether–ethyl acetate) gave **14** as colorless crystals: mp 95–96 °C; IR (cm^{-1}, KBr) 3085, 2980, 2940, 2870, 1450, 1295, 1135. 1080; ^1H NMR ($CDCl_3$) δ 8.0–7.4 (m, 5 H), 6.68 (m, 2 H), 3.25 (br s, 2 H), 3.0–2.2 (series of m, 4 H), 2.0–1.4 (m, 3 H), 1.1 (d, J = 6.0 Hz, 3 H), 0.8 (d, J = 6.3 Hz, 3 H); ^{13}C NMR (ppm, $CDCl_3$) 150.79, 147.54, 142.93, 142.83, 138.70, 133.46, 129.09, 128.90, 70.93, 65.64, 51.80, 30.10, 28.21, 17.87, 17.19; mass spectrum, m/e (M^+) calcd 314.1340, obsd 314.1349.

Anal. Calcd for $C_{19}H_{22}O_2S$: C, 72.57; H, 7.05. Found: C, 72.61; H, 7.11.

Dimethyl 1,4,5,8-Tetrahydro-5,8-dimethyl-1,4-methanonaphthalene-6,7-dicarboxylate (15). A solution of **5** (276 mg, 1.89 mmol) and dimethyl acetylenedicarboxylate (280 mg, 1.97 mmol) in 5 mL of chloroform was stirred at room temperature under a nitrogen atmosphere for 10 days during which time an additional 222 mg of DMAD was introduced. The solvent was evaporated and excess DMAD removed at 70 °C and 0.4 torr. NMR analysis of the residue (100% yield) showed it to consist of two isomers in a 94:6 ratio. TLC purification and recrystallization from petroleum ether succeeded in providing the pure major isomer; the minor component has not yet been isolated in a pure state.

For **15**: mp 75.5–76.0 °C; IR (cm^{-1}, KBr) 2985, 2930, 1730, 1720, 1620, 1430. 1260; ^1H NMR ($CDCl_3$) δ 6.7 (br s, 2 H), 3.8 (s, 6 H), 3.5–3.3 (m. 4 H), 1.9 (br s, 2 H), 1.0 (d, J = 6.5 Hz, 6 H); ^{13}C NMR

(ppm, $CDCl_3$) 168.80, 147.25, 142.34, 139.09, 70.74, 52.09, 51.46, 34.08, 18.25; mass spectrum, m/e (M^+) calcd 288.1361, obsd 288.1369.

Anal. Calcd for $C_{17}H_{10}O_4$: C, 70.81; H, 6.99. Found: C, 70.83; H, 7.05.

1,4,5,8-Tetrahydro-*N*,1,4-trimethyl-5,8-methanophthalazine-2,3-dicarboximide (17 and 18). A solution of **5** (410 mg, 2.80 mmol) in dichloromethane (10 mL) was stirred under nitrogen at −70 °C while a solution of *N*-methyltriazolinedione in dichloromethane was introduced via syringe until a slight color persisted. The resulting solution was allowed to warm to room temperature and the solvent was evaporated to give a quantitative yield of adducts **18** (45%) and **17** (55%). This mixture was separated by HPLC on a Waters Prep 500 instrument with petroleum ehter–ethyl acetate (3:1) as eluent. The individual isomers were subsequently recrystallized from ether–petroleum ether and obtained as colorless crystalline solids.

For **18**: mp 138–140 °C; IR (cm^{-1}, KBr) 3020, 2980, 2940, 1760, 1720, 1690, 1475; ^1H ($CDCl_3$) δ 6.8 (m, 2 H), 4.3 (q, J = 6 Hz, 2 H), 3.5 (m, 2 H), 3.05 (s, 3 H), 2.1 (m, 2 H), 1.55 (d, J = 6 Hz, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 153.17, 147.15, 142.83, 73.31, 52.48, 49.86, 24.81, 18.06; mass spectrum; m/e (M^+) calcd 259.1321, obsd 259.1325.

Anal. Calcd for $C_{14}H_{17}N_3O$: C, 64.87; H, 6.61. Found: C, 64.84; H, 6.61.

For **17**: mp 131–132 °C; IR (cm^{-1}, KBr) 3060, 2950, 2930, 2860, 1760, 1715, 1465; ^1H NMR ($CDCl_3$) δ 6.8 (m, 2 H), 4.7 (q, J = 6 Hz, 2 H), 3.5 (m, 2 H), 3.05 (s, 3 H), 2.1 (m, 2 H), 1.25 (d, J = 6 Hz, 6 H); ^{13}C NMR (ppm, $CDCl_3$) 153.07, 146.38, 142.73, 71.27, 51.85, 50.83, 24.81; mass spectrum, m/e (M^+) calcd 259.1321, obsd 259.1327.

Catalytic Hydrogenation Experiments. General Procedure. A sample of the appropriate triene adduct was dissolved in ethyl acetate and a small quantity of platinum oxide or 5% palladium–carbon was added. With vigorous stirring, the mixture was hydrogenated at atmospheric pressure and reduction was arrested upon uptake of 1 mol of hydrogen. The solution was filtered through Celite and the filtrate was evaporated. The residual solid in every case proved identical by mixture melting point and ^1H NMR with the corresponding diene adduct.

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Supplementary Material Available: Tables of final atomic parameters, bond lengths, bond angles, torsion angles, and final anisotropic thermal parameters for **6**, **8**, **9**, **13**, and **18** (Tables II–XXV) (21 pages). Ordering information is given on any current masthead page.

A Stable Br^+ Complex. A Twisted Bicyclo[2.2.2]octane Derivative. Synthesis and Structure of Bis(quinuclidine)bromine(I) Tetrafluoroborate

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Abstract: A stable complex of Br^+, bis(quinuclidine)bromine(I), has been prepared, and the structure of its tetrafluoroborate salt has been determined by single-crystal X-ray diffraction techniques. Bis(quinuclidine)bromine(I) tetrafluoroborate crystallizes in the chiral space group T^4-$P2_13$ of the cubic system with four formula units in a cell of dimension a = 12.029 (4) Å; the ions are situated on C_3 axes. The structure was described by 84 variables, and at convergence of the full-matrix, least-squares refinement the values of R and R_w (on F, 453 data for which $F_o^2 > 3\sigma(F_o^2)$) are 0.024 and 0.027. The N–Br–N grouping of the cation is strictly linear, but the two Br–N bond lengths, 2.156 (2) and 2.120 (2) Å, are quite different. The conformation of the quinuclidines around the Br atom is neither staggered nor eclipsed; one quinuclidine is rotated relative to the other about the C_3 axis by about 30°. The quinuclidine cages are themselves twisted so that the two N–C–C–C torsion angles are 12.8 (4)° and −4.8 (5)°. The rms libration of the quinuclidine cages about the C_3 axis, estimated from a rigid-body thermal-motion analysis, is between 5.2° and 6.2°.

Since the discussions of Noyes and Stieglitz,[2] halogen cations of the type X^+ have received a great deal of attention, particularly as electrophiles in halogenation reactions; there is, however, no strong evidence for their existence as discrete ions in condensed phases. This is not surprising if one considers X^+ to be analogous to H^+, which is generally situated on some basic site. The X^+ ions have been the subject of several critical reviews.[3]

Although I^+ and Br^+ cannot be prepared as discrete ions, they can be stabilized in amine complexes with coordination number II. Several bis(amine)iodine(I) and -bromine(I) complexes have been investigated by various spectroscopic techniques,[4-8] and the evidence supports a linear N–X–N arrangement.

Bis(amine)halogen(I) complexes are important practically as new, stable sources of active halogen and theoretically as probes of the electronic structure about the central halogen.[9,10] These

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