three candidates are capable of mediating the strong superexchange interaction found in the coupled binuclear copper site and all three have charge transfer to copper(II) optical features in the 300-500-nm region, the more likely assignment of this 425-nm band, based on known[48] model complexes, appears to be a phenolate-to-copper CT transition.

This study clarifies and supports certain aspects of the spectroscopically effective picture of the coupled binuclear copper active site in hemocyanin (Figure 1). It has shown that the endogenous bridge can be reversibly protonated and displaced, eliminating the strong superexchange coupling, and that there are two distinct and different binding positions, one for the endogenous bridging ligand and a second for exogenous bridging ligands.

Acknowledgment. We are grateful to NIH, Grant AM31450, for support of this research. We thank John Pilbrow for providing the EPR simulation program GNDIMER, Roy Planalp and Luke Schoeniger for technical assistance, and Arturo Porras, David Richardson, Harvey Schugar, and Darlene Spira for helpful discussions.

Registry No. N_3^-, 14343-69-2; Cl^-, 16887-00-6; Br^-, 24959-67-9; copper, 7440-50-8; acetic acid, 64-19-7; fluoride, 16984-48-8; oxygen, 7782-44-7.

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[48] (a) Amundsen, A. R.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6730-6739. (b) Ainscough, E. W.; Bingham, A. G.; Brodie, A. M.; Husbands, J. M.; Plowman, J. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1701-1707.

Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene

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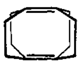
Contribution from the Department of Chemistry, Yale University,
New Haven, Connecticut 06511. Received October 26, 1983

Abstract: Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (**1**), the simplest member of the series of "superphanes", has been prepared by the dimerization of bicyclo[2.2.0]hex-1(4)-ene. The structure of **1** was determined by X-ray crystallography, giving a distance between the double bonds of 2.40 Å. The mechanism of the dimerization is discussed, and the energies of the intermediates are estimated by a combination of ab initio geometry optimizations and molecular mechanics calculations. The properties of **1** are discussed with special emphasis on the interaction between the double bonds. The reactions, including the Cope rearrangement to 2,5-dimethylenetricyclo[4.2.2.0^{1,6}]decane, epoxide formation, and transannular bridging on reaction with bromine are described.

The relative importance of through-bond and through-space interactions[1] has received much study, particularly with regard to interacting π-electron systems in compounds such as norbornadiene,[2] bicyclo[2.2.2]octa-2,5-diene,[2] and the cyclophanes.[3] In this connection, tetracyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (**1**) is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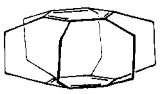
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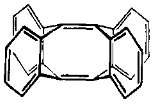
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of special interest since the two double bonds are forced to interact strongly and since it may be considered to be the simplest analogue of superphane (**2**).[4] A tetrabenzo derivative, **3**, has been reported,[5] and it was found that the repulsion between the double bonds led to pyramidalization with an out of plane bending angle of 30.6°. We have been able to prepare **1** by the dimerization of bicyclo[2.2.0]hex-1(4)-ene (**4**) in dilute solution.[6] We now report the details of its formation, along with information on its properties and its reactions.

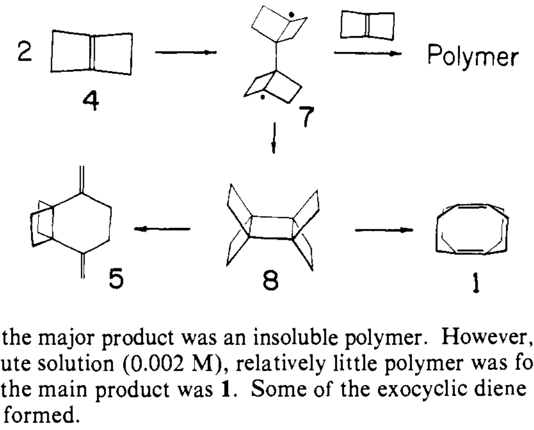
When **4** was allowed to remain in dimethylformamide or pentane solution at around room temperature, it was found to slowly disappear. If the concentration were relatively high (>0.01 M), the major product was an insoluble polymer. However, using a dilute solution (0.002 M), relatively little polymer was formed, and the main product was **1**. Some of the exocyclic diene **5** also was formed.

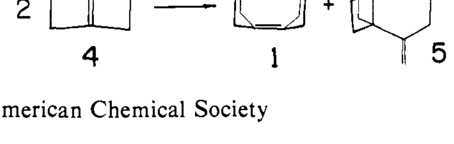
Table I. Kinetics of Dimerization of Bicyclo[2.2.0]hex-1(4)-ene Bicyclo[2.2.0]-hex-1(4)-ene (3)^a

T, °C	10^2k, L mol^{-1} s^{-1}
0.0	1.13 ± 0.06
20.8	3.79 ± 0.20
39.0	19.3 ± 0.9
59.5	53.7 ± 2.7

^{a} $\Delta H^{\ddagger} = 11.5 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -25 \pm 2$ eu.

Scheme I





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[1] Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.

[2] Heilbronner, E.; Maier, J. P. In "Electron Spectroscopy"; Brundle, C. R., Baker, A. D., Eds.; Academic Press: New York, 1977; Vol. I, p 205.

[3] Kovac, B.; Mohranz, M.; Heilbronner, E.; Boekelheide, V.; Hopf, H. *J. Am. Chem. Soc.* **1980**, *102*, 4314.

[4] Sekine, Y.; Boekelheide, V. *J. Am. Chem. Soc.* **1981**, *103*, 1777.

[5] Viavattene, R. L.; Greene, F. D.; Cheung, L. D.; Majeste, R.; Trefonas, L. *J. Am. Chem. Soc.* **1974**, *96*, 4342.

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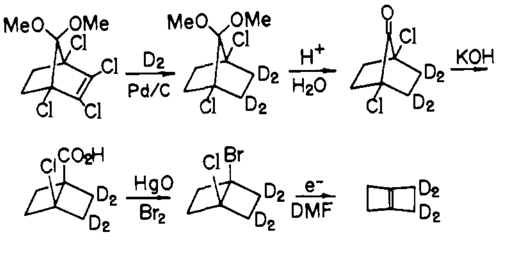
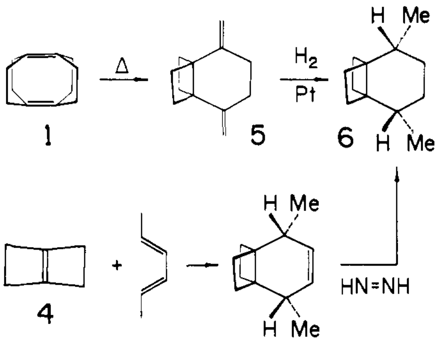
Scheme II



The structure of **1** was apparent from the following data. Analysis shows it to be a dimer of **4**. The ^{13}C NMR spectrum had only two resonances, at 139.2 and 35.6 ppm. The upfield band resulted from a carbon coupled to two hydrogens ($J_{^{13}C-H}$ = 133 Hz) whereas the downfield band was due to a quaternary carbon. The ^{1}H NMR spectrum had two broadened doublets at 2.24 and 3.00 ppm. When **1** was heated (see below) it was converted to **5**. Hydrogenation of **5** gave a dimethylbicyclo[4.2.2]decane (**6**) that was identical with the compound formed by the reaction of **4** with *trans,trans*-2,5-hexadiene followed by reduction.



The disappearance of **4** in dilute solution proceeded via second-order kinetics (Table I). These data suggest that the course of the reaction is as shown in Scheme I. The initial step probably involves the reaction between two molecules of **4** to form the diradical, **7**.[7] This is the first step of many thermally initiated polymerizations.[8] If **4** is in relatively high concentration, it may react with the diradical ultimately leading to polymer. At lower concentrations, a unimolecular reaction of **7** predominates, and it is reasonable to assume that the pentacyclic propellene **8** is an intermediate.

In order to see if **8** might be observed as an intermediate, deuterium-labeled **4** was prepared as shown in Scheme II and the course of the dimerization was followed by ^{2}H NMR spectroscopy in DMF solution. The disappearance of **4**-d_4 was accompanied only by the appearance of deuterium-labeled **1** and **5**, and no signals that might be due to **8** could be observed. This is not surprising since **8** might reasonably be expected to have even lower thermal stability than [2.2.2]propellane,[9] and if this were the case, it would rearrange rapidly under the reaction conditions.

The preference for cleavage of **8** to give **1** rather than **5** as the main product was of interest, since at equilibrium **5** is the predominant species. INDO calculations for **8** and the species formed by stretching one of the propellane bonds showed that the symmetry inversion observed between the HOMO's of normal and stretched [2.2.2]propellane[10] also occurs with **8**. The occupied orbital that had the appropriate symmetry for interacting with the HOMO of the stretched **8** had the larger coefficient for the other propellane bond, leading to the preferred cleavage to **1** rather than to **5**.

Scheme III

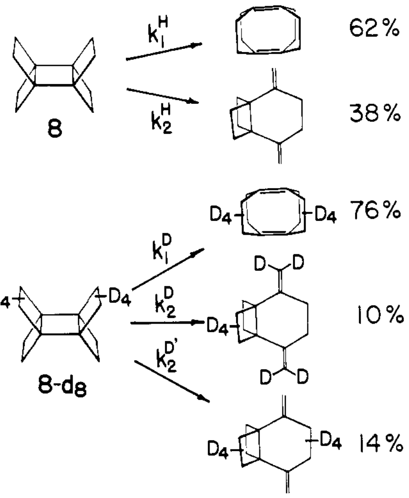


Table II. Equilibrium between the Dienes 1 and 5[a]

T, °C	*K* = 5/1
61.50	0.446
65.50	0.385, 0.401
71.80	0.366, 0.395
76.39	0.342, 0.334
83.25	0.293, 0.291
88.85	0.265, 0.273
91.50	0.267, 0.263
103.95	0.203, 0.196

[a] ΔH = 4.71 ± 0.20 kcal/mol, $\Delta S°$ = 15.7 ± 2.0 eu.

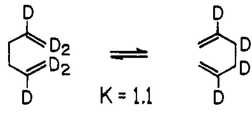
The product ratio in the dimerization of **4**-d_4 was different than that from **4** itself. The reactions may be written as shown in Scheme III. Deuterium substitution should not have a large effect on k_1, and therefore we may assume that $k_1^D \sim k_1^H$. For **8**, the product ratio gives k_1/k_2 = 1.63. Remembering that only half of the bridges in **7**-d_8 are labeled, we may write

$$k_2^H/k_2^D = 0.31k_1^D/k_2^D = (0.31)(76)/10$$

$$k_2^H/k_2^{D'} = 0.31k_1^{D'}/k_2^D = (0.31)(76)/14$$

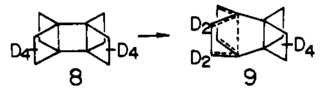
where 0.31 = $2k_2/k_1$ and 76/10 and 76/14 are the product ratios. Thus, k_H/k_D = 1.7, and $k_H/k_{D'}$ = 2.4.

It can be seen that the deuterium prefers an sp^3 center over a vinylic position. This is analogous to the observation of Glatt and Yoger[11] that in the degenerate Cope rearrangement of 1,5-hexadiene, deuterium prefers the methylene position:



The corresponding ratio in the present case is 1.4.

One might at first expect the process described by $k_2^{D'}$ to have a negligible isotope effect. However, if one considers a species such as **9** to lie along the reaction coordinate, there must be intermediate hybridization at the carbons as the propellane bond stretches. This will lead to an isotope effect for either process.



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[7] An alternate mechanism would involve cleavage of the central bond of **7** to give the cyclohexylidenecyclohexane dicarbene, which could then close to form **1**. However, this appears less likely for two reasons. First, secondary carbenes normally undergo a facile hydrogen shift giving an alkene, and the expected triene was not observed. Second, it would not account for the simultaneous formation of **1** and **5**.

[8] Huyser, E. A. "Free-Radical Chain Reactions"; Wiley: New York, 1970; p 338.

[9] Eaton, P. E.; Temme, G., III *J. Am. Chem. Soc.* **1973**, *95*, 7508.

[10] Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 779. Newton, M. D.; Schulman, J. M. *Ibid.* **1972**, *94*, 4391.

[11] Glatt, I.; Yoger, A. *J. Am. Chem. Soc.* **1976**, *98*, 7087.

Table III. Results of ab Initio Calculations[a]

compound	energy, hartrees	ΔH_f, kcal/mol
bicyclo[2.2.0]hex-1(4)-ene (4)	−231.36506	95 (93)[b]
pentacyclo[4.2.2.$2^{2,5}$.$0^{2,5}$]dodecane (8)	−462.81628	131
tricyclo[4.2.2.$2^{2,5}$]dodeca-1,5-diene (1)	−462.94480	54
tricyclo[4.2.2.$2^{2,5}$]dodecane (10)	−465.35146	−9

[a] All energies were calculated by using the 4-31G basis set and the STO-3G optimized geometries. [b] Based on large basis set calculation.[17]

Table IV. Results of Molecular Mechanics Calculations

compound	ΔH_f, kcal/mol	
	MM2[a]	best estimate[b]
tricyclo[4.2.2.$2^{2,5}$]dodeca-1,5-diene (**1**)	69.1	54
2,5-dimethylenetricyclo[4.2.2.$0^{1,6}$]decane (5)	64.0	59
pentacyclo[4.2.2.$2^{2,5}$]dodecane (8)	92.8	131
1.1′-bibicyclo[2.2.0]hexane (11)	61.7	62
tetracyclo[4.2.2.2.^{2,5}$0^{2,6}$]dodecane (19)	9.2	9
tetracyclo[4.2.2.2.^{2,5}$0^{1,6}$]dodecane (20)	44.4	44
tricyclo[4.2.2.$0^{2,5}$]dodecane (**10**)	−11.2	−11
bicyclo[2.2.0]hexane	26.8	29.9[c]
[2.2.2]propellane	46.3	65[d]

[a] Based on Allinger's MM2 force field. [b] Adjusted to fit all data including ab initio calculations; see text. [c] Observed value, based on heat of hydrogenation of bicyclo[2.2.0]hexane.[21] [d] Calculated value based on a large basis set ab initio calculation.[17]

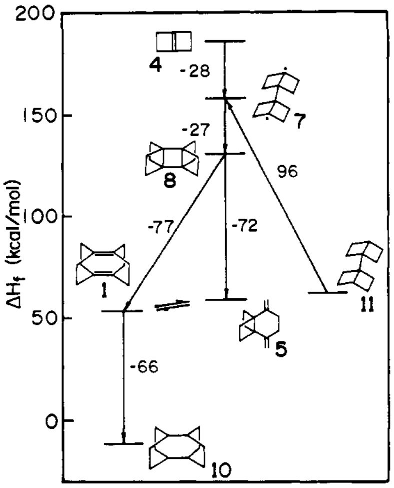

Figure 1. Calculated energies of compounds involved in the conversion of **4** to **1**.

Then, the actual bond cleavage step will lead to a further discrimination between H and D in the process leading to **5**.

We are interested in the energies of the compounds involved in the sequence that leads from **4** to **1** and **5**. Direct calorimetric measurements are impractical for most of the compounds, but the observation that the conversion of **1** and **5** led to an equilibrium mixture allowed us to determine the difference in energy between these compounds. The equilibrium constant was determined as a function of temperature via ^{1}H NMR spectroscopy giving the data listed in Table II. They lead to $\Delta H_r = 4.7 \pm 0.2$ kcal/mol, and $\Delta S = 15 \pm 2$ ea. Thus, the reaction has an unfavorable enthalpy of reaction and is entropy driven.

The entropy change is easily understood. The more symmetrical compound, **1**, has a symmetry number of 4 whereas **5** has $\sigma = 2$. This leads to a change in entropy of 1.4 eu. Of more importance, **1** would be expected to be relatively rigid whereas **5** should have a number of low-frequency vibrations which will give significant contribution to its entropy. Molecular mechanics calculations led to $\Delta S = 10$ eu,[12] in good agreement with the observed difference in entropy.

The enthalpies of formation of the remaining compounds were estimated by combining results from ab initio MO calculations and molecular mechanics. The MO calculations are useful in giving relative energies of compounds since the error due to neglect of electron correlation approximately cancels when energies of reaction are calculated.[13] These calculations have been successfully applied to a variety of small ring compounds.[14] Molecular mechanics calculations are useful for relatively unstrained hydrocarbons and in these cases give enthalpies of formation with an uncertainty of ~1 kcal/mol.[15] It also may be applied to larger molecules having low symmetry for which ab initio calculations become relatively impractical. Molecular mechanics is less satisfactory for highly distorted compounds such as **1** and **8**. Thus, the two computational techniques are in this case complementary.

Because of the size of the molecules, geometry optimization in the MO calculations on the C_{12} compounds was practical only using the STO-3G basis set. This usually gives reasonable geometries[13] but very poor relative energies between alkenes and alkanes.[13,14] Therefore, the final energies were calculated using the split-valence 4-31G basis set and the STO-3G optimized geometries. The energies are listed in Table III.

The conformation of **1** may be based on boat cyclohexanes (D_{2h} symmetry) (**1a**) or twist-boats (D_2 symmetry) (**1b**). The geometry optimization was started from both conformations. The structure of **1b** moved steadily toward that of **1a**. The calculated structure had a distance between double bonds of 2.399 Å. In order to see if the structure had been calculated correctly, and to precisely determine the distance between the double bonds, which is of importance in understanding the photoelectron spectrum,[16] an X-ray crystal structure determination was carried out. The details of the structure will be presented in the following paper.[17] For the present purpose, it is important to note that the observed structure had D_{2h} symmetry and a cross-ring distance of 2.395 Å, in very good agreement with the calculated structure. It may also be compared with the cross-ring distance of 2.42 Å found in the tetrabenzo derivative of **1**.[3]

In order to have a better basis for estimating the energies of the compounds, the energy of the hydrogenation product of **1**, tricyclo[4.2.2.2]dodecane (**10**) also was calculated. Here, a D_{2h} conformation was assumed since molecular mechanics calculations suggest that the D_{2h} and D_2 conformers have very similar energies,[18] and the use of a higher symmetry considerably facilitates the molecular orbital calculations. This relatively unstrained compound was chosen as a reference compound for the C_{12} series, and the enthalpy of formation obtained via molecular mechanics is given in Table IV.[19] This calculation should give a reliable value since the enthalpy of formation of bicyclo[2.2.2]octane may be calculated satisfactorily.[15]

The enthalpies of formation of all of the compounds may now be estimated. Using the group equivalents we have derived for converting ab initio energies to enthalpies of formation,[20] we obtain the values given in Table III. The ΔH_f for **4** is close to that obtained by using a larger basis set (93 kcal/mol),[14] and the ΔH_f for **10** is in good agreement with that estimated via molecular mechanics (MM2), −11 kcal/mol. Having a value for ΔH_f of **1**,

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(12) The calculations were carried out by using the program and parameters of Boyd (Chang, S.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3109).

(13) Pople, J. A. *Mod. Theor. Chem.* **1977**, *4*, 1.

(14) Wiberg, K. B.; Wendoloski, J. *J. Am. Chem. Soc.* **1982**, *104*, 5679. Wiberg, K. B. *Ibid.* **1983**, *105*, 1227. Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.*, in press.

(15) Burkert, U.; Allinger, N. L. *ACS Monogr.* **1982**, *No. 177*.

(16) Honneger, E.; Heilbronner, E.; Wiberg, K. B. *J. Electron Spectrosc. Relat. Phenomen.* **1983**, *31*, 369.

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(18) Osawa, E. *J. Am. Chem. Soc.* **1979**, *101*, 5523.

(19) Allinger's MM2 program and parameters[15] were used.

(20) Wiberg, K. B. *J. Comput. Chem.*, to be published.

Table V. Kinetics of the Cope Rearrangement of Tricyclo[4.2.2.2^{2,5}]dodecadiene (1)[a]

T, °C	10^4k, s^{-1}
76.2	2.40 ± 0.11
87.1	9.65 ± 0.55
94.5	19.1 ± 0.5
100.0	37.2 ± 2.6

[a] $\Delta H^{\ddagger} = 28.7 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger} = 6.8 \pm 4.5$ eu.

that for **5** is fixed by the observed energy difference, leading to $\Delta H_f = 59$ kcal/mol.

The energies of some of the compounds as calculated by molecular mechanics are given in Table IV. The less strained compounds present no difficulty, but the MM2 energies of the more highly strained propellanes appear to be considerably underestimated. This is not surprising since the geometries and hybridization are quite different than those of the compounds for which MM2 was parameterized.

The calculated enthalpy of formation of bicyclo[2.2.0]hexane is in reasonable accord with the observed energy,[21] and therefore the calculated value for 1,1′-bibicyclo[2.2.0]hexane (**11**) should be satisfactory. If a bridgehead C–H bond dissociation energy of 100 kcal/mol and a H–H dissociation energy of 104 kcal/mol are used, ΔH_f of the diradical **7** would be approximately 158 kcal/mol. These energies are summarized in Figure 1.

It can be seen that all of the steps illustrated in Scheme I are highly exothermic, including the formation of the diradical **7** and the pentacyclic propellane **8**. Presumably, this is the reason for the efficient conversion of **4** to **1**.

The rate of the Cope rearrangement of **1** to **5** is also of interest since it must proceed via a boat activated complex. The rate constants were determined at several temperatures giving the data summarized in Table V. The activation parameters were $\Delta H^{*} = 28.7$ kcal/mol ($E_a = 28$ kcal/mol) and $\Delta S^{*} = 6$ eu. The degenerate Cope rearrangement of 1,5-hexadiene proceeds via the favored chair activated complex[22] and has $E_a = 36$ kcal/mol. When forced to react via a boat activated complex, the activation energy increased to 45 kcal/mol,[22,23] which is considerably larger than found for the rearrangement of **1**.

The high activation energy for the boat activated complex is believed to be due to repulsion between the center carbons of the two three-carbon fragments in the activated complex, whereas this interaction is absent in the chair activated complex.[22] The unique feature of **1** is that the repulsion is built into the ground state, leading to a smaller energy difference between the diene and its activated complex.

The interaction between the double bonds of **1** has been of special interest to us. One of the useful ways in which to examine such an interaction is via photoelectron spectroscopy.[1-4] The photoelectron spectrum of **1** has been examined and gave two well-resolved bands at 8.6 and 9.3 eV, followed by a broad band resulting from the overlap of σ-ionization bands.[16] On the basis of the molecular orbital calculations for **1**, it was concluded that the 8.6-eV band represented the overlap of the accidentally almost degenerate in-phase (S-π) and out-of-phase (A-π) combinations of the two double bonds and that the 9.3-eV band resulted from a σ-orbital composed of four bonding σ-allyl groups that were mutually antibonding (Figure 2).

The two π-ionization potentials should depend on the distance between the double bonds.[16] In order to explore this dependence, we have calculated the molecular orbital energy levels as a function of the distance between the double bonds, keeping the bond lengths found for the calculated equilibrium structure. The results are shown in Figure 3. It can be seen that S-π decreases in energy as the distance is decreased, in accord with its cross-ring bonding character. At larger distances, A-π lies at a lower energy than S-π because of the through-bond interaction with the σ* orbitals of the two-carbon bridges. However, as the distance becomes smaller, the energy of A-π rises rapidly as a result of its cross-ring antibonding character. At the distance found for **1**, the two molecular orbitals have essentially the same energy. In contrast to the change in energy of the π MO's, the high-lying σ-orbital is quite insensitive to the cross-ring distance. It may be noted that the highest occupied MO of the reduced hydrocarbon **10** corresponds to the σ-orbital in Figure 2.

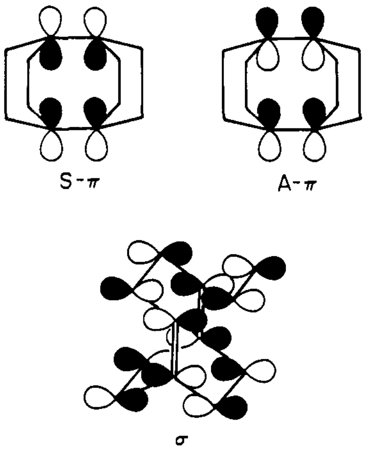

Figure 2. Three highest occupied molecular orbitals of the diene **1**.

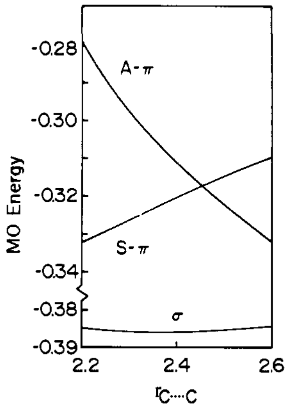

Figure 3. Change in energy of the three highest occupied molecular orbitals of **1** as a function of the distance between the double bonds.

Another common result of an interaction between double bonds is a shift in the first electronic transition. The UV spectrum of **1** had λ_{max} 205 (ϵ = 19 000) and 235 nm (shoulder, $\epsilon \sim 1500$, cyclohexane). A shoulder at about 230 nm and end absorption has been reported for a number of dienes that are forced to interact through space.[24] The band at 205 nm is probably the olefinic π–π* transition, which has been shifted to longer wavelengths by alkyl substitution and possibly also be the angular distortion at the double bond. We plan to examine the spectrum in more detail in the gas phase.

We may now turn to the reactions of **1**. An increase in strain energy caused by molecular distortion frequently leads to high reactivity in a Diels–Alder reaction, whereas simple alkenes are normally relatively unreactive. The reaction between **1** and cyclopentadiene proceeded rapidly at room temperature and gave a bis adduct, **12**, which was a mixture of syn and anti isomers. When a limited amount of cyclopentadiene was used, a mixture of **12** and a mono adduct, **13**, was obtained.

When exposed to oxygen, **1** was converted into a new compound (**14**) that contained two oxygens but had no carbonyl band in the infrared spectrum. The ^{1}H and ^{13}C NMR spectra indicated that

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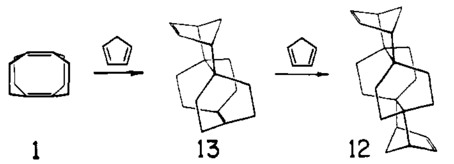
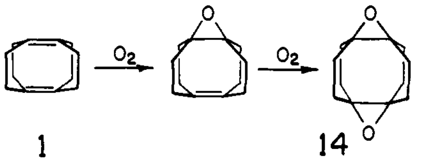


1 13 12

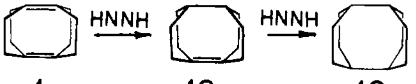
it had the same symmetry as **1**, suggesting that it might be the diepoxide. An X-ray structure determination confirmed this structure.[17,25] When **1** was exposed to oxygen for a limited time, and cyclopentadiene was added, a monoepoxide, mono-Diels–Alder adduct **15** was formed, indicating that the epoxidation proceeded in a stepwise fashion.



1 14

Reaction with triplet oxygen appears to be a common occurrence for strained alkenes. Bicyclo[3.3.1]non-1-ene,[26] tricyclo-[4.2.1.$0^{2,5}$]non-2(5)-ene,[27] and 2,3,4,4-tetramethylbicyclo-[3.2.1]octa-2,6-diene[28] reacted with oxygen, and in the latter case, the corresponding epoxide was isolated as the product. Humulene was converted to its epoxide with triplet oxygen,[29] and 1,2-dialkoxy-1-haloethenes were converted to alkoxyhaloacetates, presumably via an epoxide intermediate.[30] Ketenes and strained acetylenes also react with triplet oxygen.[31] Despite the number of examples of this type of reaction, the mechanism does not appear to have received serious study.

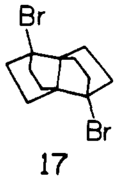
The reduction of **1** to **10** could be effected using either Wilkinson's catalyst or diimide. The monoene **16** could be isolated



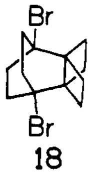
1 16 10

from the diimide reduction indicating that the reaction proceeded in a stepwise fashion. The reduction using the catalyst is of interest since tetrasubstituted alkenes are normally not reduced.[32] The stepwise nature of the reactions discussed above suggests that some strain is relieved when one of the double bonds has reacted. However, all three reactions are characteristic of strained alkenes, and therefore a significant amount of the original strain must still be present. We should like to measure the heats of hydrogenation of both **1** and **16**.

The diene **1** rapidly reacted with 1 equiv of bromine to give a dibromide in which both double bonds had been eliminated, as indicated by the ^{13}C spectrum. A transannular reaction might reasonably be expected on the basis of the reactions of 1,5-cyclooctadiene and related compounds and could lead to either **17** or **18**. It was not readily possible to distinguish between these



17

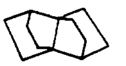


18

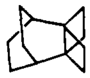
structures on the basis of spectroscopic data, and as a result the structure was determined by X-ray crystallography.[17] This showed the correct structure to be **17**.

In the case of the structurally related 1,5-cyclooctadiene, Uemura et al.[33] found that bromine reacts to give only 1,2- and 1,4-addition products. However, both chlorine and iodine reacted to give products derived from transannular 1,5-bridging in addition to 1,2- and 1,4-addition.

The structure of **17** is interesting in that it corresponds to the fusion of two norbornane units along their 1,7-bonds. The energy of the parent hydrocarbon **19** was estimated (Table IV) and



19



20

indicated that considerable strain is relieved on the conversion of **1** to **17** ($\Delta H \sim 45$ kcal/mol for the conversion of **1** to **19**). The alternate 1,4-addition giving **18** would lead to the ring system **20**. Its energy also was estimated (Table IV). The ΔH_f of **20** is considerably larger than that of **19**, and this difference in energy may be a major factor in leading to 1,5-bridging in the present case.

Another common reaction of strained alkenes is silver complex formation.[33] When **1** was treated with a limited quantity of aqueous silver nitrate solution, an insoluble 1:1 complex was formed. This complex dissolved in aqueous silver nitrate to give a water-soluble 2:1 complex (**21**) of Ag^+ with **1**, which had an NMR spectrum slightly shifted from that of **1** (2.71 and 3.08 ppm for **21**, 2.24 and 3.00 ppm for **1**). The insoluble nature of the 1:1 complex suggests that it may be polymeric with one Ag^+ complexed with one of the double bonds of each of two molecules of **1**.

Experimental Section

1,4-Dichloro-7,7-dimethoxybicyclo[2.2.1]heptane-*2,2,3,3-d*$_4$. To a Parr hydrogenation flask were added 50.0 g of 1,2,3,4-tetrachloro-7,7-dimethoxybicyclo[2.2.1]hept-2-ene, 140 mL of ethyl acetate, 0.72 g of 10% Pd on carbon, and 54.0 g of triethylamine (stored over sodium hydroxide). The mixture was treated with deuterium at 60 psi in a Parr hydrogenation apparatus, and the reaction was complete within 12 h. The salts were removed by filtration, and the solid was washed with 300 mL of ethyl acetate. The combined solution was concentrated by using a rotary evaporator giving a light yellow oil. It was dissolved in 200 mL of ethyl ether, and washed with 100 mL of 1 N hydrochloric acid followed by 50 mL of saturated sodium chloride solution. After drying over magnesium sulfate, the ether solution was concentrated giving 39 g (~100%) of 1,4-dichloro-7,7-dimethoxybicyclo[2.2.1]heptane-*2,2,3,3-d*$_4$. Distillation (100 °C at 6 mm) gave a solid, mp 59–60 °C.

1,4-Dichlorobicyclo[2.2.1]heptan-7-one-*2,2,3,3-d*$_4$. To a stirred solution of 40.0 g of 1,4-dichloro-7,7-dimethoxybicyclo[2.2.1]heptan-*2,2,3,3-d*$_4$ in 560 mL of methylene chloride (dried over molecular sieves) were added 126 mL of concentrated sulfuric acid in a slow but continuous stream. The mixture was stirred for 7–8 h at room temperature. The two-phase system was separated, and the acid layer was extracted twice with 150-mL portions of dry methylene chloride. The combined methylene chloride solution was swirled with a few grams of basic alumina and stored in a freezer overnight. After filtering, the solution was concentrated by using a rotary evaporator giving 25.3 g of a yellow solid (79%). The crude solid was triturated with dry ether to give 13.4 g of purified ketone. The ether solution was concentrated and the residue recrystallized from ether to give 1.9 g of the ketone. The remainder was a mixture of ketone and hydrate. This mixture was dissolved in toluene, and water was removed by azeotropic distillation. The solution was concentrated and the residue was recrystallized from ether to give 3.4 g of the ketone. The total yield of pure ketone was 16.8 g (53%), mp 154–156 °C.

4-Chlorobicyclo[2.2.0]hexane-1-carboxylic-*2,2,3,3-d*$_4$ Acid. A solution of 13.4 g (0.073 mol) of 1,4-dichlorobicyclo[2.2.1]heptan-7-one-*2,2,3,3-d*$_4$ in 250 mL of dry tetrahydrofuran (distilled from sodium benzophenone ketyl) was treated with 17.4 g of sodium hydroxide which had been reduced to a powder in a drybox. The addition was carried out at 0 °C with vigorous stirring, and the base was added in two portions

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with a 45-min interval. Vigorous stirring was continued for 12 h at 0 °C. The mixture was then treated with 86 mL of cold (0 °C) 6 N hydrochloric acid over a 1-h period. The layers were separated, and the organic layer was concentrated giving a solid residue. The aqueous layer was extracted 3 times with 80-mL portions of ethyl ether, and the combined ethereal solution was added to the above residue. It was extracted 4 times with 80-mL portions of sodium bicarbonate solution, which had been cooled to 0 °C. Each 80-mL portion of the bicarbonate solution was drained into a 2-L flask containing 184 mL of 1 N hydrochloric acid. Additional concentrated hydrochloric acid was added to bring the pH to zero while cooling to 0 °C. The precipitate was filtered giving after air drying 10.8 g (94%) of the acid. Recrystallization from ether raised the melting point to 148–50 °C (lit.[34] mp 143–144 °C for the unlabeled compound).

1-Bromo-4-chlorobicyclo[2.2.0]hexane-*2,2,3,3-d*$_4$. A 100-mL three-necked round-bottomed flask was equipped with a stirrer, an efficient condenser, and a dropping funnel. The reaction vessel was kept under a positive pressure of nitrogen, and 2.87 g (13.3 mmol) of red mercuric oxide, 2.13 g of magnesium sulfate, and 18 mL of methylene chloride (dried over molecular sieves) were added. A solution of 3.37 g (20.5 mmol) of the chloroacid and 1.44 mL of bromine in 55 mL of methylene chloride was added over a 30-min period. Then, the reaction vessel was heated by using a 40 °C oil bath for 3 h. The reaction mixture was cooled to room temperature and stirred, and 1 mL of saturated sodium bisulfite solution was added to remove excess bromine. The methylene chloride solution was decanted. The solids were triturated with 50 mL of methylene chloride, and the combined organic solution was washed with two 20-mL portions of saturated sodium bicarbonate solution. After it was dried over magnesium sulfate, the solution was concentrated by using a rotary evaporator. The crude product was dissolved in a minimum of pentane and chromatographed on 10 g of basic alumina (nonactivated). It was eluted with 80 mL of pentane. Concentration gave 2.92 g (71%) of the white crystalline chloro bromide, mp 59–60 °C (lit.[34] mp 59 °C for the unlabeled compound). The procedure may be scaled up without modification to prepare 20 g of the chlorobromide.

Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (1). An electrolysis cell was filled with 350 mL of 0.1 N tetraethylammonium bromide (TEAB, recrystallized and dried before use) in dry dimethylformamide (distilled after stirring over barium oxide for 12 h). It was equipped with a large platinum gauze working electrode, a stirrer, and an anode compartment formed from a porous ceramic cup containing electrolyte (TEAB) and electrolyte solution along with a graphite felt electrode. A mercury electrode was used as the reference. After preelectrolysis to remove electroactive species, the cell was cooled in a −30 °C refrigerated bath, and 1.56 g (8 mmol) of 1-bromo-4-chlorobicyclo[2.2.0]hexane was added with stirring. Electrolysis was carried out under a nitrogen atmosphere using a potential of −1.8 to −2.0 V vs. the mercury pool electrode. The initial current was on the order of 200–300 mA, and electrolysis was carried out until the current dropped to ~30 mA (about 8 h). The temperature in the cell was maintained between −20 and −30 °C.

After the electrolysis was completed, the solution was warmed in a 55 °C bath for 1 h under a nitrogen atmosphere. It was then cooled in a dry-ice/acetone bath and extracted with 500 mL of cold pentane. The pentane solution was washed with two 100-mL portions of 1 N hydrochloric acid at 0 °C. The pentane solution was dried over magnesium sulfate, filtered, and concentrated at 0 °C to give 340 mg (53%) of a white waxy solid consisting mainly of **1** with a minor amount of **5** and polymer. The material was treated with just enough pentane to dissolve it; the flask was flushed with argon and placed in a freezer. The pentane solution was separated by decantation to give 136 mg of pure **1**. It did not have a definite melting point, but on heating a change occurred at 80 °C, after which it rearranged to **5**: ^{1}H NMR (CDCl$_3$, 250 MHz) δ 2.24, 3.00 (bd, J = 7 Hz); ^{13}C NMR (CDCl$_3$) δ 35.6 (s), 139.2 (t, J = 133 Hz). The structure was determined by X-ray crystallography.[17]

2,7-Dioxapentacyclo[7.1.0.2^{3,6}.2^{1,8}.0^{6,8}]tetradodecane (14). A pentane solution of **1** was prepared as described above. It was mixed with 300 mL of chloroform, stirred, and treated with oxygen (passed over its surface) for ~20 h. Concentration gave 0.5 g of a white solid, which was mainly the epoxide. Trituration with ether gave nearly pure material. After recrystallization from chloroform/ether, it had mp 302 °C (sealed tube). ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.77, 1.80 (endo H, 8 H); 2.14, 2.17 (exo H, 8 H); ^{13}C NMR (CDCl$_3$, 67.88 MHz, off-resonance decoupled) δ 27.08 (t), 62.14 (s). The structure was determined by X-ray crystallography.[17]

In another experiment, the electrolysis solution (above) was stirred at room temperature overnight exposed to air. An excess of cyclopentadiene was then added. The DMF solution was extracted with pentane, and the pentane solution was washed with saturated sodium bicarbonate solution, dried over magnesium sulfate, and concentrated under reduced pressure. Analysis by gas chromatography on a 2 ft × 1/4 in. 30% SE30 column at 190 °C showed the presence of a new compound as a major product (~50%). It was identified as the monoepoxide, monocyclopentadiene adduct (**15**): mass spectrum, parent, m/z calcd for $C_{17}H_{22}O$ 242.1671, found 242.1667; ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.15 (2 H, t, J = 1.8 Hz), 2.25–2.40 (4 H, m), 2.22 (2 H, t, J = 1.8 Hz), 1.45–2.00 (13 H, complex m), 1.22 (1 H, dt, J = 8.9, 1.8 Hz); ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 136.5, 64.3, 57.8, 46.5, 45.0, 34.5, 31.4, 27.3, 26.7.

1,5-Dibromotetracyclo[4.2.2.2^{2,5}.0^{2,6}]dodecane (17). A pentane solution of **1**, prepared as described above, was treated under nitrogen at 0 °C with a solution of 1 mL of bromine in 100 mL of chloroform until the bromine color persisted. Excess bromine was removed with saturated aqueous sodium bisulfite. Removal of the solvent gave 0.75 g (63%) of a yellow solid. Trituration with ether gave 0.68 g of the dibromide as a white solid, mp 303 °C (sealed tube). ^{1}H NMR (CDCl$_3$, 270 MHz) δ 1.41 (m, 4 H), 1.98 (m, 4 H), 2.40 (m, 4 H), 2.76 (4 m, 4 H); ^{13}C NMR (CDCl$_3$ 67.88 MHz) 67.0, 60.3, 45.3, 28.0 ppm. The structure was determined by X-ray crystallography.[17]

Reaction of Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (1) with Cyclopentadiene: Heptacyclo[12.2.2.2^{6,9},1^{2,5}.1^{10,13}.0^{1,6}.0^{9,4}]docosa-6,14-diene (12). To a solution of 175 mg (1.1 mmol) of **1** in 20 mL of pentane were added 0.6 mL (7 mmol) of freshly distilled cyclopentadiene. After 3.5 h at room temperature, the solvent was removed under reduced pressure to give a white solid. It was washed with two small portions of pentane to remove dicyclopentadiene and dried under reduced pressure to give 178 mg (61%) of **12** as a mixture of syn and anti isomers. One of the isomers was considerably more soluble in pentane than the other, allowing the less soluble isomer (**12a**) to be obtained in pure form, mp 216–219 °C. ^{1}H NMR (500 MHz) δ 1.07 (2 H, dt, J = 8.6, 1.7 Hz), 1.35–1.47 (8 H, m), 1.67–1.77 (6 H, m), 1.96–2.07 (8 H, m), 6.16 (4 H, t, J = 1.7 Hz); ^{13}C NMR (22.5 MHz) 139.6, 59.3, 44.8, 44.7, 33.1, 30.8 ppm. Mass spectrum, parent, m/z calcd for $C_{22}H_{28}$ 292.2191, found 292.2149. The other isomer has a similar ^{1}H NMR spectrum and is characterized by δ 6.1 (t, J = 1.8 Hz) and 2.1–2.3 (m).

When 0.25 mmol of **1** was treated with 0.56 mmol of cyclopentadiene, two compounds were formed in a 2:1 ratio. They could be separated by gas chromatography using a 5 ft × $^1/_4$ in. 1.5% OV-101 column at 140 °C. The major component was the mono adduct, pentacyclo-[8.2.2.2^{2,5}1^{6,9}0^{5,10}]heptadeca-1-ene (**13**), and the minor component was the bis adduct **12**. **13**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.99 (2 H, t, J = 1.7 Hz), 2.71–2.82 (2 H, m), 2.45–2.68 (4 H, m), 1.80–2.17 (12 H, m), 1.73 (1 H, bd, J = 8.6 Hz), 1.10 (1 H, dt, J = 8.6, 1.7 Hz). Anal. C, H.

When a chloroform solution of **13** was exposed to air for 24 h, the NMR spectrum indicated that it had been converted to the monoepoxide **15**.

Reduction of Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (1). (a) Diimide. A mixture of 137 mg (0.86 mmol) of **1** and 0.3 g (1.5 mmol) of potassium azodicarboxylate in 25 mL of dry methylene chloride was cooled to −78 °C under argon and treated with stirring with 2 mL of acetic acid in 10 mL of methylene chloride over a 2-h period. The solution was warmed to 0 °C, and an additional 1 mL of acetic acid in 10 mL of methylene chloride was added over a 0.5-h period. After stirring overnight at room temperature, 40 mL of water was added and the layers were separated. The aqueous layer was washed with two 20-mL portions of methylene chloride. The combined organic solution was washed with saturated sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent gave a crude product, which was separated by gas chromatography on a 10 ft by $^1/_4$ in. 5% Carbowax 20M on Chrom P (80/100) column at 115 °C, giving 18 mg of the monoene **16** and 26 mg of the saturated hydrocarbon **10**.

Tricyclo[4.2.2.2^{2,5}]dodec-1-ene (**16**) had an ^{1}H NMR spectrum that consisted of an ABCD pattern (500 MHz, δ 2.70 (A), 2.35 (B), 1.92 (C), 1.85 (D); J_{AB} = 11, J_{AD} = 11, J_{BC} = 11, J_{BD} = 3, J_{CD} = 11 Hz as shown by decoupling A and B) along with a cross-ring AB′ coupling (3 Hz). In addition, there was a singlet at δ 1.54 (bridgehead). All the bands were broadened by other small couplings that could not be resolved. ^{13}C NMR (22.5 MHz, CDCl$_3$) δ 28.7, 31.0, 35.4, 140.0; mass spectrum, parent, m/e calcd 162.1409, found 162.1407.

Tricyclo[4.2.2.2^{2,5}]dodecane (**10**) had mp 305–317 °C (sealed tube) after softening at 240–245 °C (reported, 242–248 °C):[35] ^{1}H NMR (270 MHz, CDCl$_3$) δ 1.43 (8 H, bd, J = 9 Hz), 1.91 (4 H, bs), 1.98 (8 H, bd, J = 9 Hz); ^{13}C NMR (22.5 MHz, CDCl$_3$) 30.0, 24.3 ppm.

(b) Wilkinson's Catalyst. To 11.6 mg of **1** in 2 mL of degassed benzene-d_6 was added 1 mL of a prereduced saturated solution of Wil-

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kinson's catalyst in benzene-d_6. The solution was treated with hydrogen while it was stirred, and after 2 h the NMR spectrum of the solution indicated complete reduction. The solvent was removed, and the product was dissolved in pentane. It was passed through a small amount of nonactivated basic alumina. Removal of the solvent followed by sublimation gave pure **10**.

Silver Complex. A sample 21.2 mg (0.13 mmol) of recrystallized diene **1** was dissolved in 3 mL of pentane and was treated with a solution of 45.5 mg (0.27 mmol) of silver nitrate in 1 mL of water with vigorous stirring. The pentane and water were removed by freeze drying giving 58.5 mg of a gray powder. The ^{1}H NMR spectrum in D_2O solution (250 MHz, DSS ref) had bands at δ 2.71 (bd, J = 8 Hz) and 3.08 (bd, J = 8 Hz), and the ^{13}C spectrum had bands at δ 3.64 and 128.1. A pure sample was obtained by triturating the solid with methanol and removing the methanol from the solution under reduced pressure. Anal. Calcd for $C_{12}H_{16}(AgNO_3)_2$ Ag: 43.2%. Found: 44.2%.

In another experiment, 48 mg of **1** (0.30 mmol) was dissolved in 7 mL of pentane, and a solution of 105 mg (0.62 mmol) of silver nitrate in 2.5 mL of water was added dropwise with stirring. A white precipitate was formed. It was separated and washed with pentane (48 mg). Anal. Calcd for $C_{12}H_{16}AgNO_3Ag$: 32.7%. Found: 31.8%. The 1:1 adduct was insoluble in water but was soluble in aqueous silver nitrate solution giving the 2:1 adduct as shown by its NMR spectrum. The aqueous solution was freeze dried giving a gray powder, which was a mixture of the bis silver adduct and silver nitrate.

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Structure, Bonding, and Intramolecular Interactions in Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene and Related Compounds

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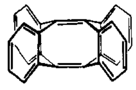
Contribution from the Department of Chemistry, Yale University,
New Haven, Connecticut 06511. *Received October 26, 1983*

Abstract: The structure of tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (**1**) has been determined by X-ray crystallography. The nature of the interaction between the double bonds of **1** was examined by comparing the observed geometry with that calculated by an ab initio procedure and by molecular mechanics. The effect of distortion on electron densities was examined by calculation using the wave function for **1**. Similar effects on other strained alkenes were examined. The effect of converting the double bonds to three-membered rings was examined via the crystallographic study of the diepoxide formed by the reaction of **1** with oxygen. The distortion produced by cross-ring bridging was examined by a crystallographic study of the dibromide formed from **1**, as well as by molecular mechanics calculations.

The double bonds of tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (**1**)[1] are constrained to interact through space, and there may also be important through-bond interactions. In investigating these interactions, it is important to know accurately the distance between the double bonds.[2] This was determined by an X-ray crystallographic analysis.

An ORTEP diagram of the molecular structure of **1** is shown in Figure 1. The molecule is crystallographically centrosymmetrical and consists of two olefinic groups linked by four bridging $-CH_2CH_2-$ groups. Final positional and thermal parameters from the structural analysis are listed in Table I. Interatomic distances and angles are listed in Table II. The double bond, C_1-C_2, at 1.354 (1) Å is slightly longer than a normal double bond (e.g., C=C in C_2H_4 = 1.33 Å)[3] but compares very favorably with the C=C length, 1.35 Å, found in the related molecule 9,9,10,10-tetradehydrodianthracene (**2**).[4] The lengths of the four sp^3–sp^2 C–C single bonds, C_1-C_3, C_1-C_5, C_2-C_4, and C_2-C_6, are all very similar and range from 1.516 (1) to 1.521 (1) Å. However, the two independent sp^3–sp^3 C–C single bonds, C_3-C_4 and C_5-C_6, 1.595 (1) and 1.596 (1) Å, respectively are considerably longer than the normal value of 1.54 Å. All the hydrogen atoms were located and refined in the analysis. All C–H bond distances are normal and span the relatively narrow range 0.981–1.038 Å.


1


2

The intramolecular distance between the two double bonds in **1** is 2.395 (1) Å. The corresponding distance in **2** is 2.42 Å. Both of these distances are about 1.0 Å less than the π–π C···C van der Waals contact of 3.4 Å found for simple aromatic compounds.[5] It can safely be assumed that at this distance the interaction lies far into the repulsive region of the potential function. We have estimated that the strain energy of **1** is 44 kcal/mol.[1] The inherent strain in **1** appears primarily in the form of two molecular distortions: (1) the elongation of the C–C single bonds in the bridging CH_2CH_2 groups and (2) the nonplanarity of the double bonds

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