via a diradical intermediate such as VIII or some dipolar intermediate. The reaction proceeds very fast at 0° which seems more consistent with a concerted process rather than a two-step process, at least one involving some high-energy radical intermediate such as VIII.

The above data, together with those obtained earlier, all point to a singlet ground state for cyclobutadiene and, since there is general agreement among the various theoretical treatments recently produced that the most stable state of a square configuration should be a triplet state, we consider then that the data also point to a rectangular configuration for the ground state of the molecule.

(17) The authors thank the National Science Foundation, the Petroleum Research Foundation, administered by the American Chemical Society, the U. S. Army (Durham, N. C.), and the Robert A. Welch Foundation for financial assistance. We also thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

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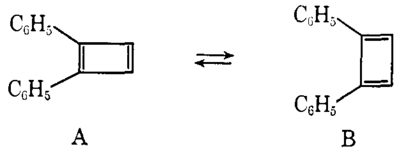
On the Possible Rectangular Nature of Cyclobutadiene

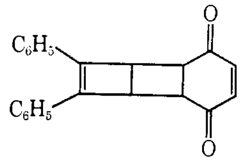
Sir:

The majority of experimental evidence available to date indicates that cyclobutadiene possesses a singlet electronic ground state.[1] This is in agreement with the calculations of Dewar and Gleicher[2] whose theoretical treatment also predicts that the singlet state has the four carbon atoms disposed at the corners of a rectangle, rather than a square, with the molecule having alternating short double bonds and long single bonds. If this geometry is correct, it follows that two isomers of *ortho*-disubstituted cyclobutadienes could exist. The present paper presents data which are consistent with the postulate that two isomeric and interconvertible *o*-diphenylcyclobutadienes exist as indicated in eq 1.

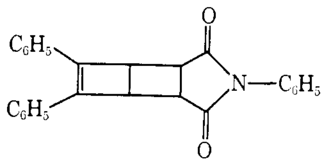


(1)

Assuming for the moment that the equilibrium 1 does exist, then because of the sensitivity of Diels–Alder additions to steric effects it would be expected that isomer B (1,4-diphenylcyclobutadiene) would be more reactive as a diene than isomer A (1,2-diphenylcyclobutadiene). In agreement with this we find that liberation of *o*-diphenylcyclobutadiene, through oxidative degradation of its iron tricarbonyl complex,[3] in the presence of benzoquinone yields only the Diels–Alder adduct I and in high yield.[4] The structure of compound I (yellow crystals, mp 173°) follows from its nmr spectrum which consists of absorptions at τ 2.62 (multiplet, area 10), 3.50 (singlet, area 2), 5.82 (complex, area 2), and 6.23 (complex, area 2).[5] Using N-phenylmaleimide which, like benzoquinone, is rated as a moderately active dienophile[6] again gives rise only to the symmetrical adduct II. Compound II (white crystals, mp 203°) exhibits absorptions centered at τ 2.70 (complex, area 15), 5.91 (area 2), and 6.25 (area 2), the latter absorptions appearing as an A_2B_2 system. Compounds I and II would result from Diels–Alder addition to the isomeric form B and inspection of the nmr spectrum of the total crude reaction product in each case fails to reveal the presence of any adduct which would follow from addition of the dienophiles with isomer A.

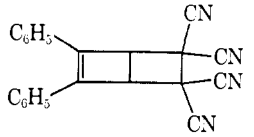


I

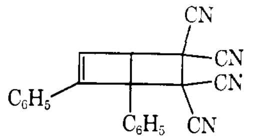


II

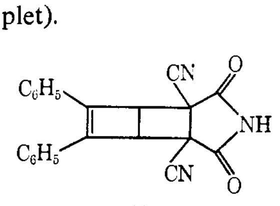
The reaction however takes a different course when extremely reactive dienophiles are employed. With tetracyanoethylene[6] *o*-diphenylcyclobutadiene cleanly yields the two adducts III and IV in the ratio 1:7, respectively.[4] The major isomer, IV (white crystals, mp 112°), apart from the ten aromatic protons at τ 2.48, exhibits one olefinic proton at τ 2.84 (doublet, J = 1.0 cps) and one allylic proton at τ 5.12 (doublet). The isomeric adduct III (white crystals, mp 202°) displays nmr absorptions at τ 2.55 (complex multiplet, area 10) and 5.13 (singlet, area 2). Almost identical behavior is seen with dicyanomaleimide which is an even more reactive dienophile than tetracyanoethylene.[7] Addition of dicyanomaleimide to *o*-diphenylcyclobutadiene produces the two isomeric adducts V and VI again in a ratio of 1:7, respectively. Compound V (white crystals, mp 248°) has absorptions at τ 2.6 (multiplet, area 10) and 5.31 (singlet, area 2) while compound VI (white crystals, mp 115°) displays nmr absorptions at τ 3.10 (area 1, doublet), 5.20 (area 1, doublet), and 2.80 (area 10, multiplet).



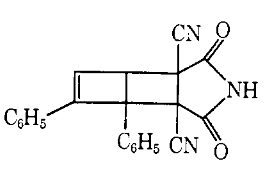
III



IV



V



VI

The most direct explanation of the above results is that *o*-diphenylcyclobutadiene exists as an equilibrium mixture of the two isomers A and B. With moderately active dienophiles the rate of interconversion of A and B is fast compared to the Diels–Alder addition and the

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[1] P. Reeves, J. Henery, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5888 (1969).

[2] M. J. S. Dewar and G. J. Gleicher, *ibid.*, 87, 3255 (1965).

[3] G. G. Emerson, L. Watts, and R. Pettit, *ibid.*, 87, 131 (1965).

[4] The nmr spectrum of the total crude reaction product reveals no significant absorptions other than those due to the indicated product.

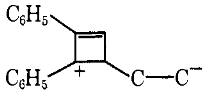
[5] The elemental analysis of this and each of the other new compounds reported are in agreement with those expected from the proposed structure. The stereochemistry of the Diels-Alder adducts reported has not been determined.

[6] J. Sauer, H. Wiest, and A. Mielert, *Chem. Ber.*, 97, 3183 (1964).

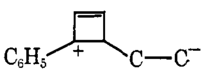
[7] J. Sauer and B. Schroder, *Angew. Chem. Intern. Ed. Engl.*, **4**, 711 (1965).

reaction with the dienophile proceeds *via* the more reactive isomer, namely B. However with the extremely reactive dienophiles the rate of interconversions is relatively slow and the two types of adducts are observed. Unless tetracyanoethylene and dicyanomaleimide accidentally have the same relative reactivity, it follows that the equilibrium constant for eq 1 is approximately 7 in favor of isomer A.[8]

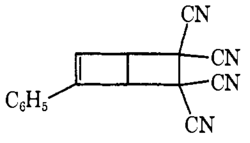
If cyclobutadiene were square and only one 1,2-diphenyl derivative existed then it could be argued that the different types of adducts result from a switch in mechanism from a concerted Diels–Alder reaction with benzoquinone and N-phenylmaleimide to a dipolar or diradical type addition with tetracyanoethylene and dicyanomaleimide. With tetracyanoethylene the intermediate 1,2-diphenylallyl cation (or radical) derivative VII would then be required to close preferentially to yield the isomer IV; such also would be required with dicyanomaleimide and it would be then held accidental that both reagents yield the same distribution of isomeric adducts. We are however inclined to reject this alternative explanation. In other molecules when given a choice between 1,2 and 1,4 addition, tetracyanoethylene prefers to react in the normal concerted Diels–Alder manner.[9] In particular we find that with 2,3-diphenylbutadiene, tetracyanoethylene adds completely in a 1,4 manner and no evidence of 1,2 addition can be found.[4] Furthermore this argument would suggest that addition to phenylcyclobutadiene should also proceed *via* the allylic cation (or radical) VIII and that this would also then be expected to ring close in a manner analogous to VII. However, this is not the case. We find that tetracyanoethylene reacts with phenylcyclobutadiene to produce predominantly, if not exclusively, the adduct IX;[10] this is the isomer to be expected on the basis of a normal Diels–Alder addition to phenylcyclobutadiene.



VII

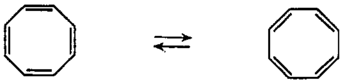


VIII



IX

Although perhaps not imperative we consider that the above results are more consistent with the hypothesis that cyclobutadiene is rectangular in its ground state, in which case this molecule would then fit in with the pattern that has now emerged for other cyclic polyenes. Those cyclic polyenes which possess $(4n + 2)\ \pi$ electrons are "aromatic" and possess equal carbon–carbon bonds while those having $4n\ \pi$ electrons are "nonaromatic" and have alternating short double bonds and long single bonds. Anet, *et al.*,[11] have recently shown that the inversion of cyclooctatetraene from one tub form to the other proceeds faster than the rearrangement of the double bonds within the molecule. If it can be assumed that the inversion of the tub form proceeds *via* a planar structure then it follows that the planar cyclooctatetraene exists as an irregular octagon and that equilibrium 2, which is entirely analogous to 1, should also exist. Recent X-ray data confirm that [16]annulene, another member of the $4n$ series, also possesses alternating short double and long single bonds.[12]



(2)

It is of interest to note that when complexed to a transition metal *via* the entire conjugated system, the cyclobutadiene and cyclooctatetraene ligands now adopt a square[13] and regular octagon[14] configuration, respectively. This change in shape presumably arises because of the back donation of electrons from the metal to the antibonding orbitals of the ligands, these levels being of lower energy when the carbon–carbon distances become equal.

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(8) Using the data of Sauer, *et al.* (ref 6), as a basis for the diene reactivity of cyclobutadiene one obtains a value in the vicinity of 5 kcal/mol for the orbital-symmetry forbidden interconversion of the rectangular forms of cyclobutadiene. This neglects any effects due to the phenyl groups.

(9) J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, **84**, 2210 (1962). The only established exceptions of which we are aware is the case of dimethylenecyclobutene where the normal Diels–Alder reaction would be required to yield a derivative of cyclobutadiene (A. T. Blomquist and Y. C. Meinwald, *ibid.*, **81**, 667 (1959); R. Criegee, *Angew. Chem.*, **74**, 703 (1962)) and where large amounts of strain energy are involved (C. A. Stewart, *J. Amer. Chem. Soc.*, **84**, 117 (1962)).

(10) Phenylcyclobutadieneiron tricarbonyl was prepared by addition of lithiocyclobutadieneiron tricarbonyl to cyclohexenone followed by dehydration and dehydrogenation. The total crude product in the addition of phenylcyclobutadiene to tetracyanoethylene shows ethylenic hydrogen absorptions centered at τ 3.82 and two allylic hydrogen absorptions at τ 5.11 and 5.61 in the ratio 1:1:1. Similar stereochemical results are seen with other monosubstituted cyclobutadienes, *e.g.*, the methyl-, ethyl-, isopropyl-, and iodo derivatives.

(11) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Amer. Chem. Soc.*, **86**, 3576 (1964).

(12) S. M. Johnson and I. C. Paul, *ibid.*, **90**, 6555 (1968).

(13) J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 3254 (1965).

(14) H. Dietrich and H. Dierks, *Angew. Chem. Intern. Ed. Engl.*, **5**, 899 (1966).

(15) The authors thank the National Science Foundation, The Petroleum Research Foundation, the U. S. Army (Durham, N. C.), and the Robert A. Welch Foundation for financial assistance. We also thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

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Unique Intermolecular and Intramolecular Exchange Reactions of Hexaborane(10)

Sir:

The apparent inconsistency between the X-ray diffraction study of crystalline hexaborane(10) and boron-11 nmr studies on the neat liquid or its solutions in inert solvents has long been known. In the crystalline solid (Figure 1)[1-3] hexaborane(10) has four different types of borons; two are unique and situated on the mirror plane (1, 2) and two pairs (3 and 6, 4 and 5) are related by the mirror plane. The boron-11 nmr consists of

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(1) K. Eriks, W. N. Lipscomb, and R. Schaeffer, *J. Chem. Phys.*, **22**, 754 (1954).

(2) F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert, Jr., and W. N. Lipscomb, *ibid.*, **28**, 56 (1958).

(3) Nomenclature and numbering follow the "Rules for Nomenclature of Boron Compounds," *Inorg. Chem.*, **7**, 1945 (1968).