

grounds that it requires a disrotatory-disrotatory opening of the bicyclobutane moiety. However, as we will see presently, the extra double bond does not play a purely passive role.

We have shown⁵ that MINDO/3⁶ gives a good account of the course of a variety of pericyclic reactions, both "allowed" and "forbidden", the calculated activation energies usually agreeing with experiment to within ± 5 kcal/mol. We have therefore used it to study the conversion of **1** to **2**.

The reaction was followed by taking the length (r_1 in **1**) of one of the breaking bonds as a reaction coordinate, the energy being minimized with respect to all other geometrical variables for successive increments in r_1 . It soon became apparent that the reaction involves a very unsymmetrical transition state, like that in the corresponding conversion of bicyclobutane (**3**) to 1,3-butadiene (**4**).⁸ In treating such biradicaloid⁹ species by MINDO, it is necessary to include configuration interaction (CI) with the lowest doubly excited configuration.¹⁰ The calculations were therefore carried out including such CI. Figure 1 shows the geometry calculated for **1** and for the transition state for conversion to **2**; it will be seen that one of the breaking bonds remains almost intact in the transition state ($r_2 = 1.60$ Å; see **1**) while the other is greatly weakened ($r_1 = 2.10$ Å).

The reaction is predicted to be extremely exothermic (ΔH , -85 kcal/mol) and the calculated activation energy is low (21.5 kcal/mol). These results certainly account well for the tendency of **1** to detonate.¹¹ The reaction showed none of the characteristics⁴ of "forbidden" reactions, the calculated energy being a smooth function of the reaction coordinate r_1 throughout and no HOMO-LUMO crossing taking place.⁵ We therefore conclude that the conversion of **1** to **2** is an "allowed" process in spite of the fact that the analogous disrotatory-disrotatory conversion of **3** to **4** is "forbidden". We had indeed been unable to establish that **1** is a lumomer⁴ of **2** although it is easily seen⁴ that this is the case for the other benzene isomers, prismane (**5**) and Dewar benzene (**6**).

The fact that **1** \rightarrow **2** is "allowed" whereas **3** \rightarrow **4** (disrotatory-disrotatory) is "forbidden" cannot be explained in terms of orbital correlations between reactants and products because the molecules do not possess enough symmetry. It can, however, be easily interpreted in terms of Evans' principle.³ The transition state for disrotatory-disrotatory **3** \rightarrow **4** is isoconjugate³ with Hückel bicyclobutadiene and so unconditionally antiaromatic. The transition state for **1** \rightarrow **2** on the other hand is isoconjugate with a hydrocarbon that

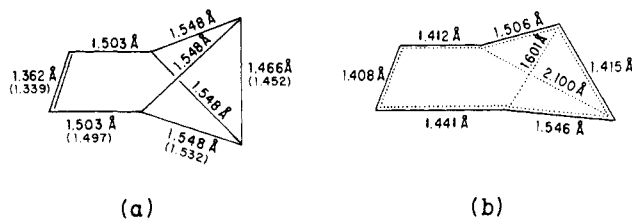


Figure 1. Calculated geometry for (a) benzvalene (**1**) and (b) the transition state for the conversion of benzvalene (**1**) to benzene (**2**).

can be written either as benzene with two meta bridges (**7**) or as cyclobutadiene with two meta bridges (**8**). The situation is analogous to that in the disrotatory conversion of bicyclo[4.2.0]octatriene (**9**) to cyclooctatetraene (**10**) where the transition state is isoconjugate with Hückel benzocyclobutadiene (**11**). Now the aromaticity or antiaromaticity of a ring is reduced by bond alternation,¹² so in cases such as this an appropriate alternation in the lengths of the bonds in the antiaromatic moiety will make the system on balance aromatic. Thus the lengths of the bonds in the four-membered ring of **11** undoubtedly alternate strongly whereas those in the benzene ring are presumably similar in length. In an analogously mixed transition state, similar distortions should likewise favor the contributions of the aromatic moiety. Reactions such as **1** \rightarrow **2** or **9** \rightarrow **10** should therefore be "allowed" and MINDO/3 calculations indicate that neither involves a HOMO-LUMO crossing.¹³

References and Notes

- (1) This work was supported by the Air Force Office of Scientific Research (Contract No. F44620-71-C-0119) and by the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.
- (2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
- (3) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **11**, 761 (1971).
- (4) M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, *J. Am. Chem. Soc.*, **96**, 5240 (1974).
- (5) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **96**, 5244 (1974).
- (6) MINDO/3 is an improved version of the MINDO⁷ semiempirical SCF MO method: R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294 (1975).
- (7) See N. Bodor, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **94**, 5303 (1972), and earlier MINDO papers cited there.
- (8) M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **97**, 2931 (1975).
- (9) See M. J. S. Dewar and S. Kirschner, *J. Am. Chem. Soc.*, **96**, 5246 (1974).
- (10) R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **94**, 9107 (1972).
- (11) T. J. Katz, E. J. Wang, and N. Acton, *J. Am. Chem. Soc.*, **93**, 3782 (1971).
- (12) M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).
- (13) The calculated¹⁴ activation energy for **9** \rightarrow **10** (22.7 kcal/mol) agreed quite well with experiment¹⁵ (18.8 kcal/mol), this low value also indicating that the reaction is "allowed".
- (14) R. S. Case, M. J. S. Dewar, S. Kirschner, R. Pettit, and W. Siegeir, *J. Am. Chem. Soc.*, **96**, 7581 (1974).
- (15) E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 442 (1964).

Michael J. S. Dewar,* Steven Kirschner

Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Received July 3, 1974

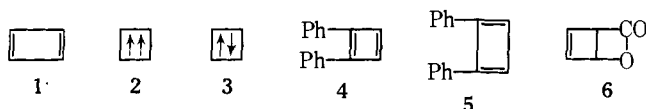
MINDO/3 Study of Cyclobutadiene

Sir:

While the century-old problem concerning the aromaticity of cyclobutadiene (**1**) was solved 10 years ago by Pettit et al.¹ who synthesized **1** and showed it to be antiaromatic as had been predicted by simple MO theory,² a second re-

lated problem remains. Simple MO theory also predicts **1** to have a very low lying triplet state (**2**); is this in fact more stable than the singlet structure (**3**)?

Numerous theoretical studies by ab initio SCF³ and semiempirical SCF⁴ procedures have mostly agreed in predicting the ground state of **1** to be a rectangular singlet, a conclusion strongly supported by the stereospecific addition of **1** to dienophiles⁵ and by the behavior of the vicinal diphenyl derivative of **1** which appears to exist as two valence tautomers, **4** and **5**, separated by quite a high activation barrier.⁶ On the other hand **1** has recently been obtained^{3c,7,8} in inert gas matrices at low temperatures by photolysis of photo- α -pyrone (**6**), and its infrared spectrum and that of a pyrone (**6**), and its infrared spectrum and that of a dideuterio derivative indicate strongly that the species so obtained has D_{4h} symmetry. If so, current theory^{3,4} would seem to require this to be the triplet **2**.



We recently reported⁹ a detailed study of the $(CH)_4$ system using an improved version (MINDO/3¹⁰) of the MINDO semiempirical SCF MO method¹¹ and this investigation has now been extended to the corresponding triplet states. Since the results for **2** suggest a novel and interesting resolution of the apparent conflict concerning the multiplicity of **1**, we are reporting them at this stage.

The calculations were carried out by the "half-electron" method¹², the geometries being found by minimizing the energy with respect to all geometrical variables using a modified gradient method.^{13,14} The heats of formation (ΔH_f , kcal/mol) and geometries of **2** and **3** were as follows: singlet (**3** rectangular), ΔH_f , 94.4, CC bond lengths 1.533, 1.342 Å; triplet (**2**; square), ΔH_f , 100.3, CC bond lengths 1.433 Å. Thus MINDO/3 agrees with the earlier calculations^{3,4} in predicting **1** to have a singlet ground state. The present value for the heat of formation, together with that from the earlier π approximation,⁴ leads to an estimated strain energy in **3** of 49.9 kcal/mol.

A square singlet structure for **1** is predicted to lie well above the square triplet (by 13.1 kcal/mol). The intersection of the singlet and triplet surfaces therefore lies above **2** in energy. Since spin-orbit coupling must be unimportant in **1**, the singlet and triplet wave functions cannot mix to any great extent in the vicinity of the intersection. Conversion of **2** to **3** should therefore require activation, the transition state corresponding to the lowest point along the intersection of the singlet and triplet surfaces.

We have developed a program for locating and following such singlet-triplet intersections. In this way the transition state for conversion of **2** to **3** was located and found to lie 2.3 kcal/mol above **2**. A study of the skeletal vibrations of triplet **1** showed moreover that the conversion involves only one of the normal modes for which we calculate $\nu = 1210 \text{ cm}^{-1}$, $h\nu = 3.5 \text{ kcal/mol}$.¹⁵ Conversion of **2** to **3** should therefore require at least 3.5 kcal/mol of activation.¹⁶

The conversion of **2** to **3** could therefore be very slow at the low temperatures used in the matrix isolation experiments,^{7,8} particularly since there is likely to be a serious mismatch between the vibrational levels of **2** and **3** and a correspondingly low probability for the intersystem crossing.¹⁷ The species obtained by Lin and Krantz,⁷ and by Chapman et al.,⁸ could then have been the triplet—but excited triplet, not the ground state. Indeed, this conclusion seems to be entirely consistent with the photochemical procedures used by them. Not only may **1** have been formed

from triplet excited **6**, in which case it would have been obtained initially as the triplet **2**, but also any singlet (**3**) could well have been photodecomposed to acetylene which was in fact a major by-product.^{18,19}

Acknowledgment. This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by the Robert A. Welch Foundation through Grant F-126. The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.

References and Notes

- (1) L. Watts, J. P. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3255 (1965).
- (2) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3345 (1952); *Tetrahedron Suppl.*, **8**, 75 (1966).
- (3) (a) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968); (b) R. J. Buenker and S. D. Peyerimhoff, *J. Am. Chem. Soc.*, **91**, 4342 (1969); (c) A. Krantz, C. Y. Lin, and M. D. Newton, *ibid.*, **95**, 2744 (1973).
- (4) M. J. S. Dewar, M. C. Kohn, and N. Trinajstić, *J. Am. Chem. Soc.*, **93**, 3437 (1971).
- (5) (a) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 623 (1966); (b) R. Pettit, *Pure Appl. Chem.*, **17**, 253 (1969).
- (6) (a) P. Reeves, T. Devon, and R. Pettit, *J. Am. Chem. Soc.*, **91**, 5890 (1969); (b) P. Reeves, Ph.D. Dissertation, The University of Texas in Austin, 1969.
- (7) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972).
- (8) O. L. Chapman, D. De Ier Court, R. Roth, and T. Pacansky, *J. Am. Chem. Soc.*, **95**, 1337 (1973).
- (9) R. C. Bingham, M. J. S. Dewar, and H. W. Kollmar, *J. Am. Chem. Soc.*, in press.
- (10) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, to be submitted for publication.
- (11) N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969); M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1969); N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *ibid.*, **2929**; N. Bodor, M. J. S. Dewar, and D. H. Lo, *ibid.*, **94**, 5303 (1972).
- (12) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Am. Chem. Soc.*, **90**, 1953 (1968); M. J. S. Dewar and N. Trinajstić, *J. Chem. Soc. A*, 1220 (1971).
- (13) M. J. S. Dewar, H. W. Kollmar, D. H. Lo, H. Metiu, P. J. Student, and P. Weiner, to be submitted for publication.
- (14) In the case of open shell systems the gradient cannot be found by finite difference using a constant bond order matrix.¹³ The gradients were calculated by finite difference from full SCF calculations. This procedure was still faster than SIMPLEX.
- (15) To optimize our estimate of the vibration frequency, we scaled the MINDO/3 value using the calculated and observed frequencies for acetylene.
- (16) Note that zero point energies are automatically included in MINDO/3 estimates of energies, due to the procedure used in the parametrization. We established that the conversion of **2** to **3** cannot occur by tunneling through the barrier as a result of zero point vibrations.
- (17) Cf. L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 102 (1972).
- (18) The conversion of singlet excited **1** to acetylene is an "allowed" process which should occur readily since the ground state reaction is only weakly endothermic (ΔH , 21 kcal/mol according to MINDO/3). The analogous reaction of **2** to give acetylene plus triplet excited acetylene is extremely exothermic so **2** should have been stable under the conditions used^{7,8} to prepare **1** from **6**.
- (19) A referee has suggested that Cl should be included in calculating square singlet **1**. This is true in ab initio SCF treatments but not in MINDO/3. Cl must be included²⁰ in MINDO/3 calculations for biradicals in which the radical centers are widely separated, to allow for the special correlation effects corresponding to separation of the "unpaired" electrons. In **1**, however, the "unpaired" electrons occupy similar regions of space so the correlation effects should be little greater than in normal molecules. A similar situation arises in the orthogonal "biradical" form of ethylene that forms the transition state for rotation about the C=C bond. Here MINDO/3 without Cl gives an excellent estimate of the barrier²¹ while inclusion of Cl leads to one that is much too low. Since inclusion of Cl leads²² to an energy for square singlet **1** that is still marginally higher than that of the triplet, we feel certain that the singlet is in fact much higher.
- (20) See R. C. Bingham and M. J. S. Dewar, *J. Am. Chem. Soc.*, **94**, 9107 (1972).
- (21) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975); calcd 63.9; obsd 65.0 kcal/mol.
- (22) Unpublished work by Dr. C. E. Doubleday, Jr.

Michael J. S. Dewar,* Herbert W. Kollmar

Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Received July 28, 1974