Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 76-17572) and the U.S. Public Health Service (Grant GM 22620-01).

References and Notes

(1) We use the term "individual-carbon resonance" to designate a peak that arises either from a single carbon of a protein or from two or more equivalent carbons (such as the two δ carbons of a tyrosine or phenylalanine residue whose phenyl ring is undergoing fast internal rotation about the C^{β}–C^{γ} bond).
(2) E. Oldfield, R. S. Norton, and A. Allerhand, *J. Biol. Chem.*, **250**, 6368 (1975).
(3) E. Oldfield, R. S. Norton, and A. Allerhand, *J. Biol. Chem.*, **250**, 6381 (1975).
(4) E. Oldfield and A. Allerhand, *J. Biol. Chem.*, **250**, 6403 (1975).
(5) A. Allerhand, R. F. Childers, and E. Oldfield, *Biochemistry*, **12**, 1335 (1973).
(6) A. Allerhand, R. F. Childers, and E. Oldfield, *Ann. N.Y. Acad. Sci.*, **222**, 764 (1973).
(7) E. Oldfield and A. Allerhand, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 3531 (1973).
(8) See, for example, D. J. Nelson, S. J. Opella, and O. Jardetzky, *Biochemistry*, **15**, 5552 (1976).
(9) R. S. Norton, A. O. Clouse, R. Addleman, and A. Allerhand, *J. Am. Chem. Soc.*, **99**, 79 (1977).
(10) The ^1H irradiation (at 270 MHz) had a peak field strength of about 0.8 G. For fully proton-decoupled spectra, it was centered 7 ppm downfield from Me_4Si, and had a random-noise modulation bandwidth of 1000 Hz. For noise-modulated off-resonance proton-decoupled spectra, the ^1H irradiation was centered on Me_4Si and had a noise modulation bandwidth of 300 Hz. For ^{13}C excitation, 90° pulses of 17 μs duration were used, and the frequency was set 13.7 kHz downfield from the ^{13}C resonance of Me_4Si. Time-domain data were accumulated in 8192 addresses, with a spectral width of 14 286 Hz. Fourier transformation was done on 16 384 time-domain addresses,[2] with 2.2-Hz digital broadening. Chemical shifts were measured digitally with respect to peak N26 (Figure 2), which was taken at 108.76 ppm downfield from the ^{13}C resonance of Me_4Si.[3]
(11) K. Dill and A. Allerhand, unpublished work.
(12) R. Deslauriers, A. C. M. Paiva, K. Schaumburg, and I. C. P. Smith, *Biochemistry*, **14**, 878 (1975).
(13) R. Walter, K. U. M. Prasad, R. Deslauriers, and I. C. P. Smith, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 2086 (1973).
(14) R. Deslauriers, G. C. Levy, W. H. McGregor, D. Sarantakis, and I. C. P. Smith, *Biochemistry*, **14**, 4335 (1975).
(15) J. H. Bradbury and R. S. Norton, *Biochim. Biophys. Acta*, **328**, 10 (1973).
(16) A. Allerhand, R. S. Norton, and R. F. Childers, *J. Biol. Chem.*, **252**, 1786 (1977).
(17) R. S. Norton and A. Allerhand, *J. Biol. Chem.*, **251**, 6522 (1976), and references cited therein.
(18) I. D. Campbell, C. M. Dobson, R. J. P. Williams, and A. V. Xavier, *Ann. N.Y. Acad. Sci.*, **222**, 163 (1973); R. A. Dwek, R. E. Richards, K. G. Morallee, E. Nieboer, R. J. P. Williams, and A. V. Xavier, *Eur. J. Biochem.*, **21**, 204 (1971); I. I. Secemski and G. E. Lienhard, J. Biol. Chem., **249**, 2932 (1974); K. Kurachi, L. C. Sieker, and L. H. Jensen, *J. Biol. Chem.*, **250**, 7663 (1975).
(19) I. D. Campbell, C. M. Dobson, and R. J. P. Williams, *Proc. R. Soc. Lond. Ser. B Biol. Sci.*, **189**, 503 (1975).
(20) L. H. Piette and W. A. Anderson, *J. Chem. Phys.*, **30**, 899 (1959).
(21) Here we define the NOE as the ratio of intensities observed with and without proton decoupling.
(22) D. J. Wilbur, R. S. Norton, A. O. Clouse, R. Addleman, and A. Allerhand, *J. Am. Chem. Soc.*, **98**, 8250 (1976), and references cited therein.

Kilian Dill, Adam Allerhand*
Contribution No. 2998, Department of Chemistry
Indiana University, Bloomington, Indiana 47401

Received March 22, 1977

On the Dichotomy between Cycloaddition Transition States Calculated by Semiempirical and ab Initio Techniques

Sir:

The timing of bonding changes in cycloaddition reactions has been the subject of many experimental investigations[1] and heated controversy.[2] The problem may be stated as follows: in a cycloaddition reaction where two new bonds are formed, are both bonds partially formed in the rate-limiting transition state, or is only one partially formed, the formation of the second occurring only after the rate-limiting transition state? Figure 1 shows the problem diagrammatically. All gradations between "bonding-concerted"[3] or "two-bond"[4] synchronous reaction pathways and "bonding-stepwise"[3] or "one-bond"[4] asynchronous pathways are possible. The question of the shape of the energy vs. reaction coordinate profile is, in principle, different, having to do with the absence ("energetically concerted")[3] or presence ("energetically stepwise")[3] of energy minima along the reaction coordinate.

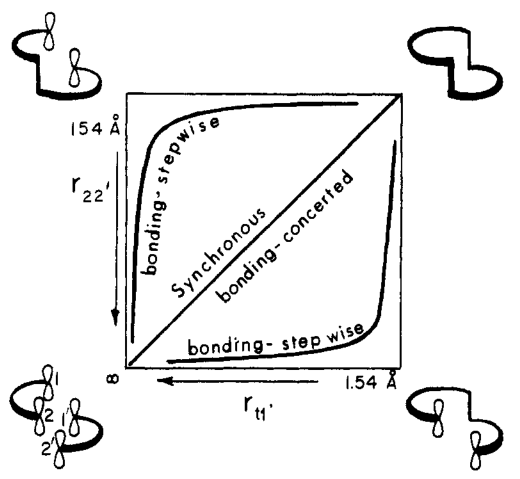
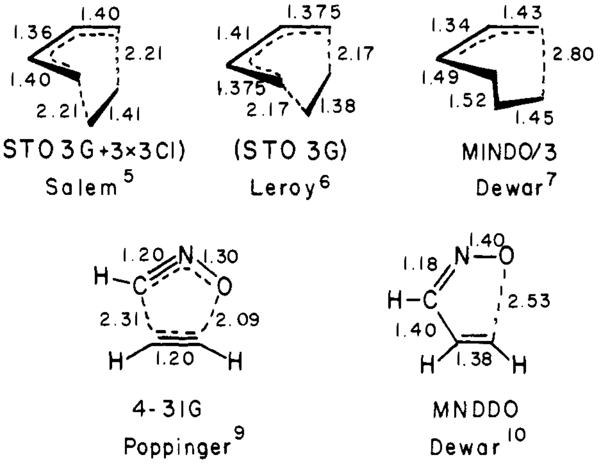


Figure 1. Bonding map for cycloadditions. The extreme pathways are labeled, but all variations are conceivable.



(STO 3G+3×3CI) Salem[5]

(STO 3G) Leroy[6]

MINDO/3 Dewar[7]

4-31G Poppinger[9]

MNDDO Dewar[10]

Figure 2. Cycloaddition transition-state geometries obtained from different calculations.

Recently, detailed quantum mechanical calculations for two "classic" cycloadditions—a Diels–Alder reaction (butadiene + ethylene) and a 1,3-dipolar cycloaddition (fulminic acid + acetylene)—have been performed by several different techniques. These calculations predict distressingly dissimilar transition-state geometries (Figure 2). Two ab initio calculations have been published for the Diels–Alder transition state. The first used the STO-3G basis set with 3 × 3 configuration interaction (CI) to determine the lowest energy pathway, followed by calculations with the 4-31G basis and 3 × 3 CI for important geometries.[5] The second used a STO-3G geometry search, followed by recalculations of energies using a 7s,3p contracted basis set.[6] Although both concur on the synchroneity of σ bond formation in the transition state, the Leroy transition state is slightly "earlier" than the Salem.[6b] More disquieting is the comparison of these with the MINDO/3 transition state,[7] which is extremely unsymmetrical (biradicaloid) in nature. A point of agreement between the ab initio and MINDO/3 transition states is that no intermediates intervene between reactants and product.[8]

The dichotomy between ab initio and semiempirical calculations extends to calculations on the 1,3-dipolar cycloaddition of fulminic acid with acetylene. Figure 2 shows the transition

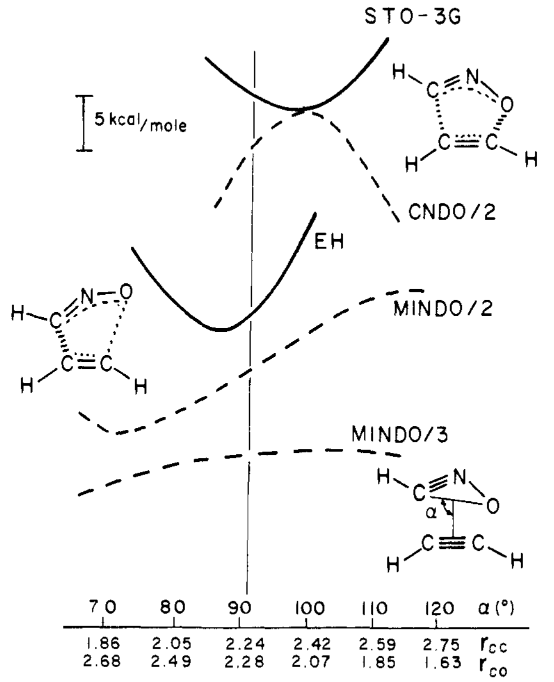


Figure 3. Energies of unsymmetrical "one-bond" and symmetrical "two-bond" "transition-state" geometries for fulminic acid–acetylene by various calculational techniques.

states calculated by ab initio (STO-3G geometry search, followed by 4-31G energy recalculations)[9] and semiempirical (MNDDO)[10] techniques.[11]

One possible source of the difference in transition state structures could reside in the more complete geometry searches carried out in the semiempirical calculations.[12] On the other hand, the divergent geometrical outcomes could reflect inherent differences in calculational techniques. We provide here computational evidence which shows that semiempirical calculations which neglect overlap inherently favor "one-bond" (biradicaloid) transition states for orbital symmetry allowed cycloadditions, whereas ab initio or semiempirical calculations which include overlap favor "two-bond" synchronous transition states.[13] In order to quantitatively compare differing biases for one-bond or two-bond transition states in commonly used calculational methods,[14] slices of the reaction surface perpendicular to the reaction coordinate, $R = r_{11'} + r_{22'}$, were examined.

Figure 3 shows the results for the fulminic acid–acetylene surface. A transition state essentially like that obtained by Poppinger[9] was taken as the synchronous extreme, and the angle, α (see Figure 3), was varied in order to produce geometries corresponding roughly to biradicaloids with the CC bond formed ($\alpha = 60°$), or the CO bond formed ($\alpha = 120°$). Figure 3 shows the striking contrast between the STO-3G and CNDO/2 profiles, which are nearly perfect mirror images. The former has a synchronous minimum corresponding to the CNDO/2 maximum. The profile obtained by EH calculations—which include overlap—is shifted somewhat, but still mimics the shape of the STO-3G curve. The MINDO/2 and MINDO/3 curves are very flat, slightly favoring the CC formed biradicaloid. However, fully optimized MNDDO[10] calculations produce a pronounced maximum at the asynchronous geometry.

Model calculations on the Diels–Alder reaction were somewhat more complex, since the geometries of the biradicaloid and concerted transition states are quite different. A slice of the surface was obtained by MINDO/3, setting the forming CC bond lengths at 2.21 Å + X and 2.21 Å − X, respectively, varying X from 0 to 0.7 Å in 0.1-Å increments; all of the remaining geometrical parameters were then optimized. Ab initio STO-3G, as well as CNDO/2, EHT, and MINDO/2 calculations were then performed using these optimized geometries. A comparison of the results is shown in Figure 4. MINDO/3 and CNDO/2 show definite minima at very unsymmetrical geometries,[15] MINDO/2 gives shallow minima at unsymmetrical geometries, whereas the STO-3G and EHT minima are at the symmetrical geometry.[16] For both the cycloadditions, STO-3G and EHT favor symmetrical (synchronous) transition-state geometries, while CNDO/2, MINDO/2, and MINDO/3 favor unsymmetrical (asynchronous) geometries. Thus, the results summarized in Figure 2 arise from inherent differences in calculational techniques, not from incomplete geometry searches.

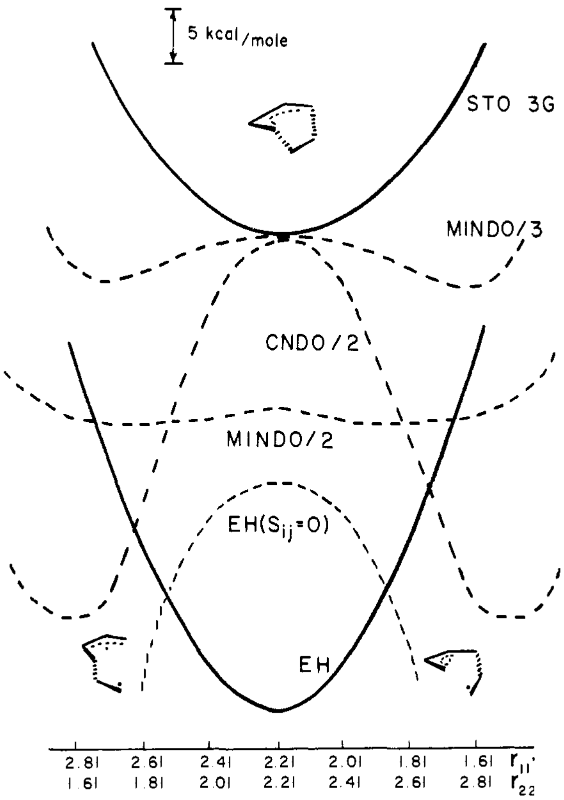


Figure 4. Energies of unsymmetrical "one-bond" and symmetrical "two-bond" Diels–Alder "transition-state" geometries by various calculational techniques.

What is the origin of these differences? Calculations including overlap favor two-bond synchronous transition states, while calculations neglecting overlap favor one-bond (biradicaloid) geometries. Thus, the closed-shell (exchange) interactions appear to be the differentiating factor. This "closed-shell" or "exchange" repulsion takes into account the interaction of two filled orbitals which results in greater destabilization of the antibonding combination than stabilization of the bonding combination.[17] Its energetic consequences are expressed numerically as

$$\Delta E = \frac{4(\epsilon_{av} S_{ij}^2 - H_{ij} S_{ij})}{1 - S_{ij}^2} \approx 4S_{ij}^2(\epsilon_{av} - k)$$

where ϵ_{av} is the average energy of the interacting orbitals, and the approximate expression arises from the assumption that $S_{ij}^2 \ll 1$ and that $H_{ij} \approx kS_{ij}$ (the Mulliken approximation).[18] When diatomic overlap is neglected (CNDO/2, INDO, MINDO, MNDDO), this repulsion is also neglected. In CNDO/2 computations, the tendencies for bimolecular reactions to be far too exothermic, and to occur without activation,[19] may be attributable to this effect.

However, MINDO/2 and MINDO/3 calculations over-

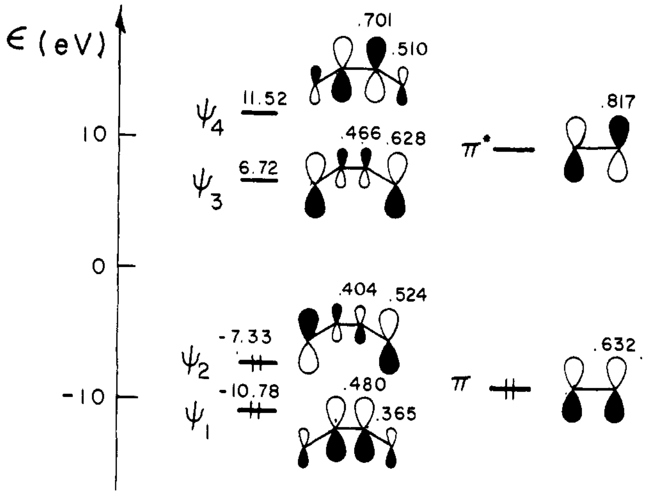


Figure 5. MOs of butadiene and ethylene used for calculations of closed-shell repulsion.

come this problem to some extent, presumably by an artificial increase in repulsive forces which are retained in the calculations—namely, electron-electron and nuclear-nuclear repulsions. While it may be possible to successfully parameterize MINDO for ground-state geometries, there is no guarantee that the functional form used for repulsive forces which are included will exactly compensate for those which are neglected at distances such as those involved in transition states.[20]

Furthermore, there is an orbital symmetry restriction on closed-shell repulsion just as there is on attraction arising from interactions of filled and vacant orbitals. That is, for orbital-symmetry-allowed cycloadditions, the HOMOs of the two molecules will always be of opposite symmetry, so that there will be no net overlap in a symmetrical transition state, and no closed-shell repulsion will arise from HOMO-HOMO interactions. In the absence of symmetry, such as in the HCNO-acetylene reaction, the synchronous transition state will still have very small overlap between the HOMOs of the two molecules. On the other hand, in a highly asynchronous transition state, all filled orbitals of the two molecules will mix, leading to higher closed-shell repulsion than in the synchronous transition state. Since this factor favors symmetrical (or synchronous) transition states, and is left out of overlap-neglected calculations, and since the more crowded symmetrical (or synchronous) transition state may have greater electron-electron and nuclear-nuclear repulsive interactions, which may be overestimated in semiempirical schemes, the differences between ab initio and some semiempirical transition states arises, at least in part, from an inherent defect in the latter techniques resulting from neglect of overlap.

Figure 5 shows the STO-3G MOs for butadiene and ethylene. Using these to compute closed-shell repulsions for the symmetrical and unsymmetrical transition states gives repulsive energies of 4.4 and 8.8 kcal/mol, respectively, using $k = -20$ eV, or 13.7 and 25.3 kcal/mol, respectively, using $k = -39.9$ kcal/mol.[21] All of the closed-shell repulsion in the symmetrical transition state arises from ψ_1-π interaction, while 66% of the closed-shell repulsion arises from ψ_2-π interaction in the unsymmetrical transition state.[22]

In order to verify that neglect of overlap is responsible for the energy maximum at symmetrical transition state geometries, calculations on the Diels-Alder surface were repeated using the extended Hückel method with neglect of overlaps involving orbitals on different centers. That is, in the Hamiltonian matrix, $|H_{ij} - \epsilon S_{ij}|$, all values of S_{ij} were set equal to zero for $i \neq j$. The pronounced maximum in the resulting curve at the symmetrical geometry (Figure 4) indicates that overlap must be included to find an energy minimum at a symmetrical geometry.

Although a systematic discrepancy between the calculations with and without overlap has been identified in the transition states of allowed cycloadditions, this information regrettably does not lead to a definitive answer as to the true structures of cycloaddition transition states. That is, ab initio calculations are nonempirical, but, even with a very extended basis set and inclusion of limited configuration interaction, a large part of the correlation energy is omitted. Whether or not calculations including correlation energy will favor one-bond or two-bond transition states and, thus, support ab initio or MINDO/3 conclusions is, as yet, untested. However, the use of 3 × 3 CI in Salem's Diels-Alder calculations should overestimate the stability of the one-bond (biradicaloid) geometry as compared to the two-bond (synchronous) geometry.[23] The parallelism between STO-3G and 4-31G + 3 × 3 CI calculations suggest that the actual transition state for allowed cycloadditions will be a synchronous one.[24]

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully acknowledged. We wish to thank Robert W. Strozier for programming assistance.

References and Notes

(1) For recent examples of Diels–Alder Studies, see L. M. Stephenson, R. V. Gemmer, and S. Current, *J. Am. Chem. Soc.*, **97**, 5909 (1975); J. A. Berson and R. Malherbe, *ibid.*, **97**, 5910 (1975).

(2) For an example from the area of 1,3-dipolar cycloadditions, see the continuing dialogue between R. Huisgen and R. A. Firestone, *J. Org. Chem.*, **37**, 2181 (1972), and references therein; R. Huisgen, *J. Org. Chem.*, **41**, 403 (1976), and references therein.

(3) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Fortsch.*, **15**, 281 (1970).

(4) K. N. Houk and L. L. Munchausen, *J. Am. Chem. Soc.*, **98**, 937 (1976).

(5) R. E. Townsend, G. Ramunni, G. Segal, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **98**, 2190 (1976).

(6) (a) L. A. Burke, G. Leroy, and M. Sana, *Theoret. Chim. Acta*, **40**, 313 (1975). (b) Professor Leroy has informed us that the geometry shown in Figure 2 is obtained by a more complete optimization than was carried out for the geometry reported in ref 6a.

(7) M. J. S. Dewar, A. C. Griffin, and S. Kirschner, *J. Am. Chem. Soc.*, **98**, 6225 (1974).

(8) The calculated activation energies are unfortunately of no assistance in evaluating the relative accuracy of different calculations; the calculated activation energies by the three techniques are 42.6,[5] 20.8,[6] and 28.2 kcal/mol,[7] which were compared by the authors of these calculations to experimental values of 34.3 (M. Uchiyama, T. Tomioka, and A. Amano, *J. Phys. Chem.*, **88**, 1878 (1964); W. Tsang, *Int. J. Chem. Kinet.*, **2**, 311 (1970)), 25.1 (D. Rowley and H. Steiner, *Discuss. Faraday Soc.*, **10**, 198 (1951)), and 27.5 kcal/mol (same reference), respectively.

(9) D. Poppinger, *J. Am. Chem. Soc.*, **98**, 7486 (1975); *Aust. J. Chem.*, **29**, 465 (1976).

(10) M. J. S. Dewar, Chemistry Departmental Seminar, Louisiana State University, Baton Rouge, La., Feb. 17, 1976. These calculations involve a parameterized version of the neglect of diatomic differential overlap approximation developed by Pople and coworkers.

(11) Here the calculated activation energies are quite different (30.4 kcal/mol (ab initio)[9] and 7 kcal/mol (MNDDO)),[10] but the experimental activation energy has not been determined.

(12) This results both from the greater economy of the semiempirical calculations and the efficient gradient optimization routines available in semiempirical programs.

(13) A number of differences between ab initio and MINDO calculations on equilibrium geometries and energies have been pointed out in the literature: J. A. Pople, *J. Am. Chem. Soc.*, **97**, 5306 (1975); W. J. Hehre, *ibid.*, **97**, 5308 (1975); W. N. Lipscomb, *Science*, **190**, 591 (1975); M. J. S. Dewar, *J. Am. Chem. Soc.*, **97**, 6591 (1975); *Science*, **190**, 591 (1975). These differences do not seem to follow a systematic pattern of the type we point out here for transition-state geometries.

(14) EHT calculations used Quantum Chemistry Program Exchange Program No. 64, by E. B. Moore, W. C. Cook, and A. R. M. Rom. The EH technique is described in R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); CNDO/2 calculations used CNINDO, QCPE No. 141, by Paul A. Dobosh, described in J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970; MINDO/2 calculations used OPTMO, QCPE No. 217, by A. Komornicki and J. McIver. MINDO/2 is described by M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970); STO-3G calculations used Gaussian 70, QCPE No. 236, by W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, and the STO-3G basis set described by W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969); MINDO/3 calculations used MINDO/3, QCPE No. 279, by M. J. S. Dewar, H. Metiu, P. J. Student, A. Brown, R. C. Bingham, D. H. Lo, C. A. Ramsden, H. Kollmar, P. Weiner, and R. K. Bischof. MINDO/3 is described in R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302, 1307 (1975).

(15) For comparison, Dewar et al.[7] state that the optimized C_s symmetrical transition state (with 2 × 2 Cl) lies 40 kcal/mol above the unsymmetrical.

(16) McIver has suggested that transition states of cycloadditions (and many other reactions, as well) may generally be nonsymmetric, the symmetric (C_s, for example, for the Diels-Alder reaction) transition state representing a stationary point with *two* negative force constants (J. W. McIver, Jr., *J. Am. Chem. Soc.*, **94**, 4782 (1972); *Acc. Chem. Res.*, **7**, 73 (1974)). While this has been proven to be the case in MINDO/2 and MINDO/3 calculations on the Diels-Alder transition state, the results reported here and those of Salem and coworkers suggest that the force constant for antisymmetric distortion (one new bond lengthening while the other shortens) is slightly positive, in contradistinction to the MINDO results where this force constant is negative.

(17) R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950); K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970).

(18) R. S. Mulliken, *J. Phys. Chem.*, **56**, 295 (1952).

(19) O. Kikuchi, *Tetrahedron*, **27**, 2791 (1971), and references therein; K. B. Wiberg, *J. Am. Chem. Soc.*, **90**, 59 (1968).

(20) Because of the number of parameters involved in these techniques it is difficult to prove which interactions are treated unrealistically. M. V. Basilevsky, *Adv. Chem. Phys.*, **33**, 345 (1975), has commented on possible underestimation of repulsive forces at transition-state distances by MINDO/2. On the other hand, Gordon and workers found that MINDO/3 grossly underestimates long-range interactions of the type which result in the phenomenon of "spiroconjugation": M. D. Gordon, T. Fukunaga, and H. E. Simmons, *J. Am. Chem. Soc.*, **98**, 8401 (1976). Thus, one short-range interaction such as that present in the asynchronous transition states may well be overestimated relative to the two long-range interactions present on the synchronous transition states. We thank Dr. Gordon for a preprint of these results.

(21) Epiotis and Yates have shown that "aromatic" molecules have less closed-shell repulsion than "nonaromatic" (and by extension, antiaromatic molecules will have the most): N. D. Epiotis and R. L. Yates, *J. Am. Chem. Soc.*, **98**, 461 (1976). Our treatment of transition states is similar—"aromatic" (synchronous allowed) transition states having less closed-shell repulsion than "nonaromatic" (nonsynchronous).

(22) MINDO/3 gives a symmetrical transition state for the ethylene-singlet oxygen reaction: M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **97**, 3978 (1975), but this transition state lacks significant closed-shell repulsions. For orbital-symmetry-forbidden reactions such as $[_\pi 2_s + {}_\pi 2_s]$ reaction, this type of reasoning leads to the expectation that MINDO, or other overlap-neglected, calculations will tend to give more symmetrical transition states than overlap-included calculations. A. R. Gregory and M. N. Paddon-Row have recently shown that CNDO/2 and INDO calculations predict stability for molecules which we feel should experience serious closed-shell repulsions: *J. Am. Chem. Soc.*, **98**, 7521 (1976).

(23) We thank Professor Lionel Salem for a helpful discussion of this and related points.

(24) After submission of this work, Basilevsky and coworkers reported a deficiency in ZDO methods in accounting for exchange effects in regions of weak interactions: M. V. Basilevsky, A. G. Shamov, and V. A. Tikhomirov, *J. Am. Chem. Soc.*, **99**, 1369 (1977).

(25) (a) NATO Fellow, 1975-1976. (b) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1972-1977; Alfred P. Sloan Foundation Fellow, 1975-1977.

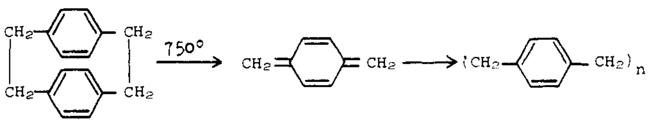
Pierluigi Caramella*[25a]
Istituto de Chimica Organica
Viale Taramelli 10, 27100 Pavia, Italy

K. N. Houk,*[25b] **L. N. Domelsmith**
Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803
Received September 11, 1976

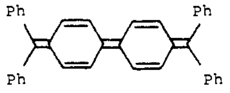
An Electron Diffraction Study of *p*-Xylylene

Sir:

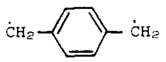
We wish to report a preliminary electron diffraction study of the molecular structure of *p*-xylylene (**1**) or *p*-quinodimethane (3,6-bis(methylene)-1,4-cyclohexadiene), which was generated by the pyrolysis of [2.2]paracyclophane (**2**) at 750 °C. *p*-Xylylene has been of theoretical interest for over 30 years,[1] because of its fundamental structural relationship to Chichibabin's hydrocarbon (**3**) and the possibility that it possessed a biradical ground state (**4**). Szwarc provided the first experimental evidence for the existence of *p*-xylylene and showed that it polymerized rapidly at room temperature in the condensed phase to poly-*p*-xylylene (**5**).[2] Since then, the basic chemistry of *p*-xylylene has been outlined and its polymer chemistry explored extensively.[3] A number of spectroscopic studies of *p*-xylylene have been reported,[4-6] including IR and UV measurements in the solid phase at 77 K[5] and a recent photoelectron spectroscopy study.[6] Our reasons for undertaking the present investigation were twofold. First, of course, was the longstanding interest in *p*-xylylene. Second, the [2.2]paracyclophane-*p*-xylylene pyrolysis reaction was uniquely suited for developing a high temperature nozzle assembly. Gorham[3c] has shown that [2.2]paracyclophane can be cleaved quantitatively to *p*-xylylene at elevated temperatures.



2 1 5



3



4

The *p*-xylylene was generated in the sample nozzle immediately prior to encountering the electron beam. The [2.2]paracyclophane was vaporized in an adjoining reservoir (~290 °C). A thermocouple at the tip of the nozzle measured the experimental temperature. Details of the entire nozzle assembly will be presented elsewhere. Numerous diffraction patterns were recorded at a single camera distance[7] (12 cm) at 750 °C on 4 × 5 in. Kodak Electron Image plates using the Indiana University electron diffraction unit (40-keV accelerating potential, 0.3-μA beam current, maximum chamber pressure 6×10^{-6} Torr). The plates were processed[8a] and microphotometered.[8b] Preliminary examination of the diffraction data and chemical analyses of the thermolysis products which collected on the liquid nitrogen trap opposite the nozzle indicated that the cleavage was complete at 750 °C. Two plates, which were somewhat lighter (0.2-0.5 o.d.) than the optimum optical density range,[9] were selected for final processing. The general method of data reduction has been outlined previously.[10] Fourth-order polynomials were employed as background functions. The data were interpolated to integral q intervals and averaged for the least-squares analysis ($37 \leq q \leq 112$). Calculated mean-square amplitudes of vibration were used exclusively. The force fields which were used are provided in the supplementary material. Since it was conceivable that the vibrational temperature of the *p*-xylylene entering the diffraction chamber was less than the experimental temperature at the nozzle tip,[11] the entire data reduction procedure was repeated assuming that the vibrational temperature was only 550 °C. The structural parameters changed very little and were well within the quoted error limits for 750 °C.

In the following discussion, the ring carbons of *p*-xylylene are numbered starting at one of the methylene groups; C_7 and C_8 are attached to C_1 and C_4, respectively. Three models were considered, which differed principally in terms of the number of parameters needed to specify the carbon skeleton. All were planar. The first used two C-C-bonded distances, one for the ring and one for the external (C_1-C_7) bonds. This was the simplest of the three structural alternatives and also served as a prototype for biradical **4**. It is instructive to consider the theoretical radial distribution curve of the trial structure for this model (Figure 1, model I difference curve). Although reasonable values (1.397, 1.48 Å) were assigned to the two C-C-bonded distances, the fit in this portion of the curve was poor. The agreement in the 2-3-Å region was even worse. Least-squares refinement of model I (model I′) produced a