(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 sugges*t* that the force constant for ant*i*symmetric distortion (one new bond lengthening while the other shortens) is slightly positive, in contradistinction to the MINDO results where this force constant is negative.

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(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).

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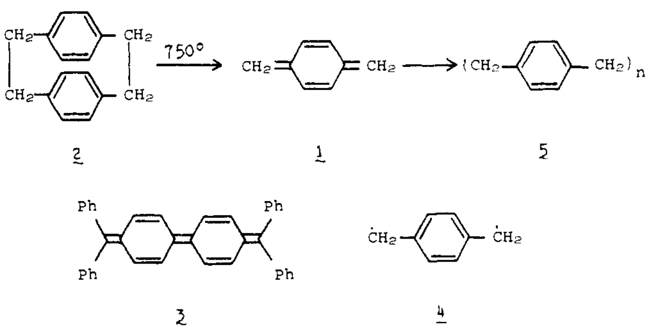
An Electron Diffraction Study of *p*-Xylylene

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.



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 ($37 \le q \le 112$). 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

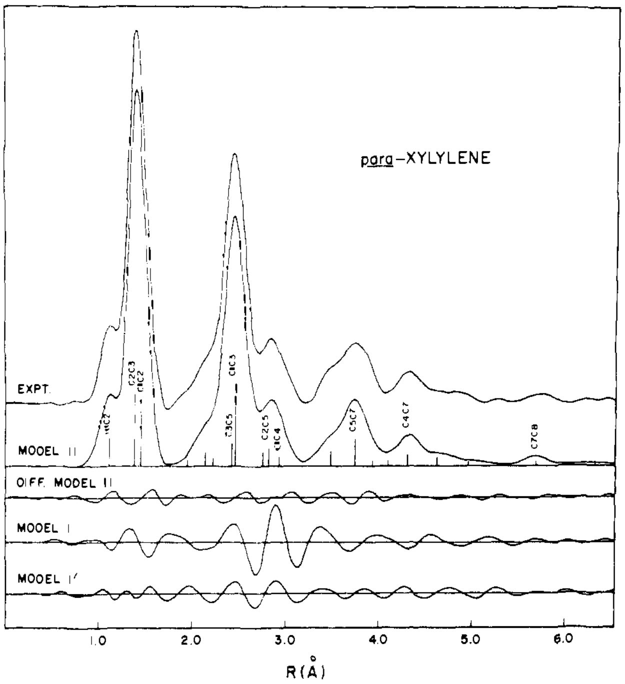


Figure 1. A comparison of the experimental radial distribution curve for *p*-xylylene with theoretical radial distribution curves for models I, I′, and II.

Table I. Structural Parameters for *p*-Xylylene[a]

Parameter[b]	Value[c]	l_{ij},[d] Å	HMO values, Å
C—C	1.451 ± 0.007 Å	0.059	1.45
C=C (av)	1.381 ± 0.008 Å	0.049	1.39 (C_1-C_7), 1.38 (C_2-C_3)
C—H (av)	1.116 ± 0.035 Å	0.078	
∠C_2-C_1-C_6	122.2 ± 3.7°		
∠C_1-C_2-C_3	118.9 ± 1.9°		
∠CCH	120° (assumed)		
∠HCH	120° (assumed)		

[a] The numbering system of the atoms used in defining the parameters is given in the text. [b] Distances are reported as r_g values, while the angles are derived from the r_α structure. [c] Uncertainties are 3σ. [d] Mean-square amplitudes of vibration.

reasonable fit ($R = 0.054$),[12] but the aromatic C-C and C_1-C_7 distances were unrealistically lengthened to 1.413 and 1.553 Å, respectively. It is also noteworthy in regard to model I′ that spectroscopic studies unanimously agree[4-6] that the ground state of *p*-xylylene is best represented by a singlet structure. Moreover, photoelectron spectroscopic evidence[6] suggests that the singlet biradical is the first excited state of *p*-xylylene and lies 4.0 eV above the ground state. This renders it unlikely that either singlet or triplet biradical species are significantly populated under the conditions of the experiment.

The final pair of models yielded lower R factors and were in greater harmony with existing experimental and theoretical evidence concerning the structure of *p*-xylylene. In model II a single average double-bond distance was used for C_2-C_3 and C_1-C_7. Two separate distances were employed for C_2-C_3 and C_1-C_7 in model III. Early in the analysis it became obvious that the C_2-C_3 and C_1-C_7 distances were very closely spaced and highly correlated. In view of the fact that less than perfect data from a single camera distance was being used in the analysis, the final refinements were made on the simpler model II. It is very likely that data of improved quality can be obtained in the future; a meaningful comparison of models II and III may be possible at that time. The least-squares structure ($R = 0.038$) for model II is presented in Table I. The most noteworthy feature of the structural parameters in Table I is that *p*-xylylene is not a simple assemblage of conjugated double and single bonds. The average C-C double-bond length is several hundredths of an Ångström longer than the typical value for a conjugated double bond.[13] Table I also includes several C-C bond lengths estimated[1c,14] from simple HMO theory. The agreement is much better than might reasonably be expected. The extent to which the theoretical and experimental values parallel one another is interesting, however.

Acknowledgment. We wish to thank Professor Richard Hilderbrandt for helpful discussions and significant contributions in the early stages of the design of the nozzle assembly.

Supplementary Material Available: Raw intensity data (Table II), estimated force fields for models I and II (Tables III and IV), comparison of the experimental leveled intensity curve with the least-squares adjusted curve for model II (Figure 2), the correlation matrix for model II, (Table V), the error matrix for model II (Table VI), and the calculated mean-square amplitudes of vibration for model II (Table VII) (7 pages). Ordering information is given on any current masthead page.

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Direct Observation of a Hydroxyphosphorane in Equilibrium with a Phosphate Ester

Sir:

In the hypothesis that transient intermediates with pentacoordinate phosphorus are formed in nucleophilic displacements at tetracoordinate phosphorus, hydroxyphosphoranes are involved when the nucleophile is hydroxide ion in the case of phosphonium salts, and with any protic nucleophile in the case of phosphine oxides, phosphinates, phosphonates, and