transition. This remains as future work when computer time becomes available.

Conclusions

A very minimal basis of gaussian lobe functions has been used to analyze the electron populations in aziridine–borane. Simply put, the endo C–H protons on the ring and the amino proton relinquish electron density to the borane protons while the B–N bond is established as clearly covalent between B and N, which remain essentially neutral. The computed dipole moment of 6.294 D is high compared with the experimental value of 4.85 D but comparison with other minimum basis STO work on BH_3NH_3 indicates that the dipole would probably be high in either basis. It is worth noting that the computed dipole for aziridine–borane is less than that of borazane in agreement with experiment.

Acknowledgments. Much credit is due the Director of the Computer Center at Virginia Commonwealth University, Dr. Richard Grove, and his systems programmer, Mr. David Brydon, for making computer time available for this project. Dr. Carl Trindle of the University of Virginia was also helpful in setting up the *ab initio* program. We also thank the referee for making several interesting suggestions which helped interpret our results.

An Electron Diffraction Study of *trans*-Cyclooctene

R. M. Gavin, Jr.,* and Z. F. Wang

Contribution from the Department of Chemistry, Haverford College,
Haverford, Pennsylvania 19041. *Received July 8, 1972*

Abstract: The results of an electron diffraction study of *trans*-cyclooctene in the gas phase strongly imply that the molecule assumes a chair conformation rather than a crossed conformation. Models of both conformations were refined by least-squares analysis of the radial distribution curve. The standard deviation obtained from the chair model, 0.0533, was considerably lower than that for the crossed model, 0.0868. Structural parameters for both models are reported along with a discussion of the limitations intrinsic in the analysis. Bond lengths found are not appreciably different from those of noncyclic unstrained hydrocarbons. The effect of ring strain is apparent in the bond angles and the dihedral angles. Some internal bond angles are distorted 5–7° from comparable parameters found in unstrained molecules and there is a 23° twist about the double bond. The results obtained are compared with previous results reported from X-ray diffraction studies and from theoretical calculations. Difference curves obtained from the single isomer refinements imply that assuming a mixture of the chair and crossed geometries in the sample would not improve the fit of the data.

The molecular structure of *trans*-cyclooctene has been a subject of considerable interest since the highly strained molecule was synthesized in 1953 by Cope, *et al.*[1] Interest has centered on the manner in which ring strain is distributed among the internal coordinates, especially the twist about the carbon–carbon double bond, and whether the optically active molecule assumes a chair configuration, I, or a crossed configuration, II. A sketch of the two configurations is given in Figure 1.

Cope and coworkers[2] separated enantiomers and assigned an absolute configuration to the (−) species using chemical means, but they were not able to distinguish between conformations I and II. Manor, Shoemaker, and Parkes[3] performed an X-ray study of the complex used to separate enantiomers, dichloro[(−)-*trans*-cyclooctene][(+)-α-methylbenzylamine]platinum(II), and confirmed the assignment of Cope.[2] Bowen[4] has reported the structure of a derivative of *trans*-cyclooctene, 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane which also supports the work of Cope. A geometry with the crossed configuration was found in both X-ray studies.

Attempts have been made to use the circular dichroism spectrum of *trans*-cyclooctene to assign electronic transitions in the molecule and to provide supportive evidence for assignments of transitions in the ethylene molecule.[5–8] It has not been possible to come to definite conclusions about the transitions involved, however, because of a lack of accurate structural parameters on which to base calculations of rotational strengths. Most calculations have been made assuming a twist of 10° about the double bond, an angle obtained from measurements of the distortion in Dreiding molecular models.

Predictions of the conformation of the molecule have been made from molecular force-field calculations. Three results have been reported to date,[9–11] all using

---

[1] A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953).

[2] A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *ibid.*, **85**, 3276 (1963); A. C. Cope and A. S. Mehta, *ibid.*, **86**, 5626 (1964).

[3] P. C. Manor, D. P. Shoemaker, and A. Parkes, *ibid.*, **92**, 5260 (1970).

[4] B. J. Bowen, Thesis, University of Texas, Austin, Texas, 1969; *Diss. Abstr. B*, **30** (4), 1617 (1969).

[5] M. Yaris, A. Moscowitz, and R. S. Berry, *J. Chem. Phys.*, **49**, 3150 (1968).

[6] A. I. Scott and A. D. Wrixon, *Chem. Commun.*, 43 (1970).

[7] O. Schnepp, E. F. Pearson, and E. Sharman, *J. Chem. Phys.*, **52**, 6424 (1970).

[8] R. D. Bach, *ibid.*, **52**, 6423 (1970).

[9] N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, in press.

[10] P. C. Manor, Thesis, Massachusetts Institute of Technology, 1968.

[11] G. Buemi, G. Favini, and F. Zuccarello, *J. Mol. Struct.*, **5** 101 (1970).

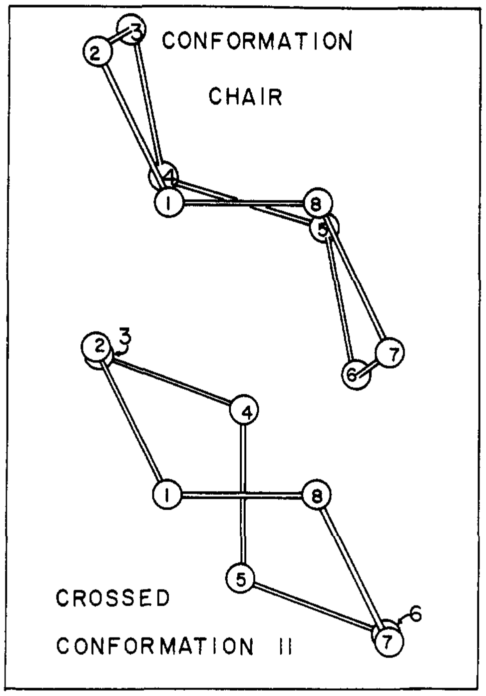

Figure 1. A sketch showing the carbon atom positions for the chair and the crossed conformations of *trans*-cyclooctene.

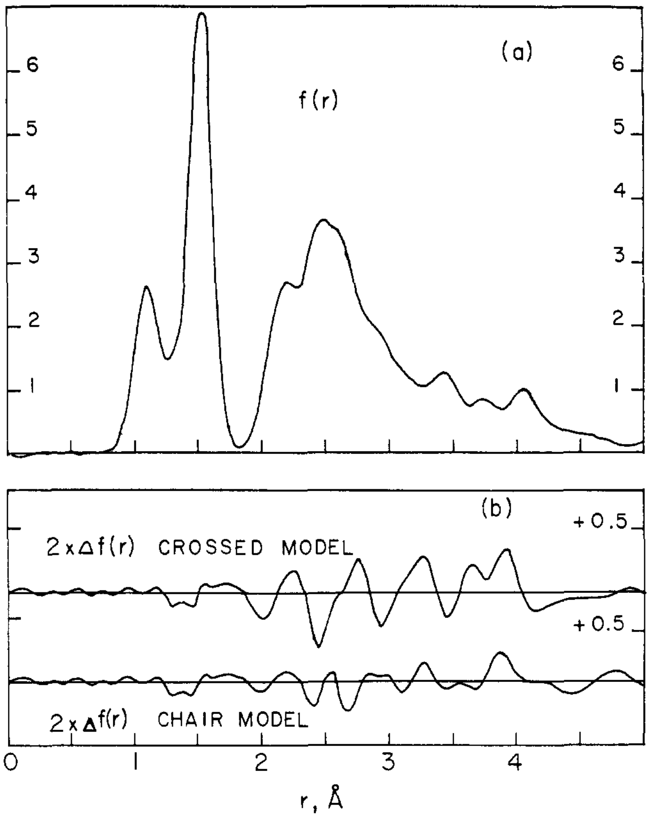

Figure 2. (a) The experimental radial distribution curve, f(r), for *trans*-cyclooctene. (b) Two times the difference between the experimental f(r) and a theoretical f(r) calculated from a crossed and a chair conformation.

slightly different force fields. Two of the calculations[9,10] imply that the crossed conformation is more stable than the chair, but one study[11] favors a chair conformation. In each case the difference in strain energy between conformations is only a few kilocalories per mole.

The present electron diffraction study was undertaken to establish the molecular geometry in the gas phase and to compare it with that found in crystal studies. It was hoped also that the study could provide data of value for interpreting spectroscopic properties of the molecule and for evaluating the reliability of the molecular force-field calculations. This paper reports the best geometries obtained for the chair and the crossed conformations. The chair conformation I provided the best fit of the electron diffraction data. This result is in contrast to the results obtained in X-ray crystal studies.[3,4] The structural parameters obtained from the electron diffraction data are provided along with a comparison of these results with those of previous experiments and calculations.

Experimental Section

Procedure. The sample of *trans*-cyclooctene used in this study was provided by Dr. A. C. Cope. It was stored at −20° in a light-tight, sealed ampoule for a short time prior to its use. Care was taken to avoid heating the sample above room temperature and to avoid prolonged exposure to light while the experiment was in progress. Electron diffraction patterns were recorded on Kodak 4 × 5 in. process plates using the University of Michigan apparatus.[12] Camera distances of 21 and 11 cm were used with an r^3 sector of radius 4.8 cm. The sample temperature was maintained at 22° during exposure which ranged from 6 to 10 sec. Five diffraction patterns from each camera distance were averaged to provide intensity data over the range of scattering variable $10 < q = (40/\lambda) \sin (\varphi/2) < 120$. The University of Michigan microphotometer was used to obtain absorbance values for each plate and relative intensities were calculated from absorbance, A, according to

$$I_{\rm rel}(q) = A(q)(1 + 0.05A(q))$$

Averaging of relative intensities for the plates and corrections for atomic background scattering were made in the manner described previously.[13] Complete tables of intensity and background data are included in Appendix A of the microfilm edition.[14]

Data Analysis. The electron diffraction data were analyzed using the radial distribution curve method[15] employing a Degard damping factor of 0.0018. A computer program similar to that of Boates[16] was written to perform least-squares refinements of structures incorporating geometric constraints. The program permits symmetry constraints on the molecule and ensures that carbon atom positions maintain a closed ring during the least-squares refinement. Shrinkage corrections were not made on the nonbonded distances.

The experimental radial distribution curve, f(r), is shown in Figure 2. Background intensity values were refined using the usual criterion of nonnegativity of the f(r) until the maximum noise in the radial distribution curve was 0.57%. The region of the f(r) for 3 Å $< r <$ 5 Å is somewhat sensitive to the geometry assumed when generating data for the experimentally inaccessible range $0 < q < 10$ Å^{-1}. The relative heights of the peaks at 3.45, 3.75, and 4.05 Å change somewhat with different theoretical models, but the positions of the maxima do not vary. Radial distribution curves generated from the more refined molecular models and background functions, however, show no dependence on the conformation assumed.

---

(12) L. S. Bartell in "Physical Methods in Chemistry," A. Weissberger and B. W. Rossiter, Ed., 4th ed, Interscience, New York, N. Y., 1972.

(13) R. M. Gavin, Jr., and L. S. Bartell, *J. Chem. Phys.*, **48**, 2460 (1968).

(14) Appendix A and Appendix B will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-1425. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(15) I. J. Karle and J. Karle, *J. Chem. Phys.* **17**, 1052 (1949).

(16) T. L. Boates, Thesis, Iowa State University, 1966.

The parameters to which the electron diffraction data are most sensitive are the coordinates of the eight carbon atoms. Since there are only about ten distinct features in the radial distribution curve, it is reasonable to make some symmetry assumptions when performing the least-squares analysis of the 24 coordinates required to locate these atoms. The assumptions made were that the molecule possesses overall C_2 symmetry and that all carbon–carbon single bond lengths are equal. Under these two assumptions the positions of the eight carbon atoms are determined by seven parameters, as listed in Table I. A number of refinements were attempted in the later stages of analysis in which the overall C_2 symmetry and equal bond length assumptions were relaxed. The results obtained from these unconstrained refinements were no better than those obtained with symmetry restrictions. Bond lengths, bond angles, and dihedral angles for the best fits were within three times the standard errors estimated for these parameters in the constrained calculations.

Table I. Symmetry Assumptions and Independent Parameters Adopted for the Least-Squares Analyses

Assumptions
(1) C_2 molecular symmetry
(2) Equal carbon–carbon single bond lengths
(3) Equal carbon–hydrogen bond lengths
(4) Local C_{2v} symmetry for CH_2 groups
(5) Equal hydrogen–carbon–hydrogen bond angles
Parameters
(1) r_g(C=C) carbon–carbon double bond distance
(2) r_g(C—C) carbon–carbon single bond distance
(3) r_g(C—H) carbon–hydrogen bond distance
(4) θ_1 $C_8C_1C_2$ bond angle
(5) θ_2 $C_1C_2C_3$ bond angle
(6) θ_3 $C_2C_3C_4$ bond angle
(7) θ_4 $C_3C_4C_5$ bond angle
(8) θ_5 HCH bond angle for CH_2 groups
(9) ω_{23} dihedral angle about bond C_2–C_3

Table II. Bond Distances, r_g, Amplitudes of Vibration, l_α, Bond Angles, θ, and Dihedral Angles, ω, for *trans*-Cyclooctene

Both Conformations			
r_g(C—C)	1.538 ± 0.003 Å	l_α(C—C)	0.055 ± 0.003 Å
r_g(C=C)	1.363 ± 0.008 Å	l_α(C=C)	0.045 Å[a]
r_g(C—H)	1.107 ± 0.002 Å	l_α(C—H)	0.081 ± 0.002 Å
l_α(C···C, <3.45 Å)	0.130 ± 0.010 Å	l_α(C···H, 2.2 Å)	0.093 ± 0.008 Å
l_α(C···C, 3.45 Å)	0.120 ± 0.010 Å	l_α(C···H, >2.2 Å)	0.120 ± 0.010 Å
l_α(C···C, >3.45 Å)	0.090 ± 0.015 Å	l_α(H···H)	0.150[b] Å

	Conformation I Chair	Conformation II Crossed
Std dev	0.0533	0.0868
θ_1	115.3 ± 2.1°	114.9 ± 3.6°
θ_2	101.8 ± 1.6°	101.3 ± 2.0°
θ_3	110.9 ± 2.0°	115.9 ± 2.5°
θ_4	115.3 ± 2.4°	107.7 ± 3.0°
θ_5	114 ± 2°	114 ± 2°
ω_{23}	22.3 ± 4.0°	45.4 ± 6.5°

[a] Assumed to be 0.010 Å less than l_α(C—C). [b] Not varied in least-squares analyses.

The radial distribution curve for *trans*-cyclooctene is not very sensitive to the exact location of the hydrogen atoms. The only peaks due to carbon–hydrogen distances which appear are at 1.1 Å, the carbon–hydrogen bonded distances, and at about 2.1 Å, the shortest carbon–hydrogen nonbonded distances. In light of this fact, only two parameters were used to locate these atoms. Each CH_2 group was assumed to have C_{2v} symmetry. The hydrogen atom in CH groups was assumed to lie in the plane formed by the carbon atom to which it is attached and by the two carbon atoms contiguous to that carbon. The carbon–hydrogen bond is placed on the bisector of the carbon–carbon–carbon bond angle. If all carbon–hydrogen bond lengths are assumed to be equal, the hydrogen atoms can be located relative to the carbon atom skeleton using two parameters: a mean carbon–hydrogen bond distance and a mean hydrogen–carbon–hydrogen bond angle.

A complete list of the nine parameters necessary to locate all 22 atoms under the assumptions made is given in Table I.

Results

The structural parameters obtained from the least-squares refinements of the chair and crossed conformations are listed in Table II along with the total standard deviations and the standard deviations of the parameters. Also listed are the amplitudes of vibration for both bonded and nonbonded distances.

Atomic coordinates are provided in Appendix B of the microfilm edition.[14] Difference curves $\Delta f(r)$, $f(r)_{\text{theor}} - f(r)_{\text{exp}}$, for both conformations are shown at the bottom of Figure 2. Sketches of the two structures viewed along the twofold symmetry axis are given in Figure 1.

According to the criterion usually employed in electron diffraction analyses, that is, the standard deviation between experimental and theoretical curves, the best structure for *trans*-cyclooctene in the gas phase is a chair-type conformation. It is important to note, however, that the chair is considerably distorted. The four carbon atoms C_1, C_4, C_5, and C_8 do not lie in the same plane and a model in which these atoms are constrained to lie in the same plane provides a poor fit to the data. Earlier analyses were made with a planar constraint applied to the chair model and led to the conclusion that under this constraint the crossed model provides a better fit of the experimental data. If the seat of the chair is allowed to distort as shown in Figure 1, on the other hand, the chair conformation I is clearly superior in fit to the crossed configuration II.

Two major factors contribute to the larger standard deviation for the crossed model. First, it was not possible to obtain a distribution of carbon–carbon nonbonded distances which produced peaks in the radial distribution curve at 3.45, 3.75, and 4.05 Å while still fitting the large peak between 2.4 and 2.9 Å. Second, the contribution to the radial distribution curve from carbon–hydrogen nonbonded distances longer than 2.2 Å for conformation II is significantly different from that for conformation I. The chair model has a large number of carbon–hydrogen distances between 2.4 and 2.7 Å whereas these distances are shifted to between 2.6 and 2.9 Å in the crossed conformation. The carbon–hydrogen distances for both models contribute a very broad featureless hump to the radial distribution curve between 2.4 and 2.9 Å. Because the hump is

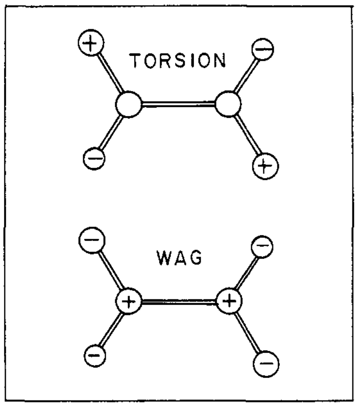

Figure 3. Two different displacements about the carbon–carbon double bond which reduce the dihedral angle. The + signs indicate atoms displaced above the plane of the paper whereas the − signs indicate atoms displaced below the plane. A torsional displacement was assumed in the least-squares analyses.

shifted to slightly longer distances in the crossed model the total f(r) is generally too high between 2.7 and 3.5 Å and two low between 2.2 and 2.7 Å. The combined effect of the two factors is that the lowest standard deviation crossed model produces a theoretical radial distribution curve which is almost featureless beyond 2.5 Å. This is apparent in the difference curve Δf(r) shown in Figure 2.

Discussion

The average carbon–carbon single bond distance of 1.538 Å is close to the average of 1.534 Å found for normal paraffins[17] and for cyclic hydrocarbons.[18] The amplitude of vibration of 0.055 Å is also close to that found for other hydrocarbons,[17,18] but it is hard to infer much from its magnitude since it was obtained assuming that all carbon–carbon single bond lengths are equal. Because the amplitude is not significantly larger than that found for unstrained molecules, however, it does seem to provide some evidence to indicate that the differences in bond lengths in the molecule are not large and that the assumption of equal bond lengths is not an unreasonable one to adopt for the analyses. The average carbon–hydrogen bond distance, 1.107 Å, and the associated amplitude of vibration, 0.081 Å, are in good agreement with parameters reported previously.[17,18] The carbon–carbon double bond length, 1.363 Å, is somewhat longer than that found for ethylene,[19] 1.333 Å, and for isobutylene,[20] 1.330 Å, but it is very close to the 1.35 Å reported for the double bond by Manor, *et al.*[3]

The possibility that the sample was highly contaminated or that it contained significant amounts of *cis*-cyclooctene was considered. The excellent fit of the data in the region of the bonded distances, the reasonable bond lengths and amplitudes of vibration obtained and the index of resolution, 1.01 ± 0.01, indicate that the sample is quite likely a hydrocarbon of the formula C_8H_{14} and that significant contamination with molecules other than ones with the same chemical formula is unlikely. Attempts were made to fit the experimental radial distribution curve with a theoretical curve generated using a cis configuration about the double bond. Boat, chair, and twist configurations were investigated. Models which provided a reasonable fit in the region 2.4 Å $< r <$ 2.9 Å did not fit well for $r >$ 3 Å, whereas, those which had a better fit for $r >$ 3 Å had a poor fit in the shorter distance region. None of the models fit the data well in the region about 4 Å and none refined on least-squares analysis to a standard deviation less than four times that found for conformation I.

The dihedral angle about the double bond is 157.0° for conformation I and 148.3° for conformation II. These angles are considerably different from the 136° angle found by Manor, *et al.*,[3] but close to those predicted from theoretical calculations.[9–11] If the hydrogen atoms of the CH groups are in the plane formed by the carbon atom and the two contiguous atoms, as assumed in the least-squares analyses, then the twists about the double bonds are torsional deformations of 23.0 and 31.7° for I and II, respectively. It is quite likely, however, that this assumption about the hydrogen atoms is not valid. A decrease in the dihedral angle can result both from a torsional displacement about the double bond and from an out-of-plane wag-like displacement as shown in Figure 3. During the wag displacement the hydrogen atoms are not in the planes assumed and the decrease in dihedral angle results from a bending along the double-bond axis rather than the twisting motion of a torsion. Since vibrational frequencies for both the out-of-plane wag and the torsion are approximately 1000 cm^{-1},[21] the energy change associated with either type of distortion should be about the same. In light of this, it is plausible that the distortion along the double bond is actually a combination of torsional and wag-like displacements. The electron diffraction data are not sensitive enough to allow a definitive test of this hypothesis.

Crossed geometries proposed from theoretical calculations[9–11] and X-ray diffraction[3] were tested by least-squares analysis. When unmodified these geometries provide a poor fit of the experimental data and extensive least-squares refinement is necessary to obtain the crossed geometry listed in Table II. On the other hand, the proposed chair geometries[9–11] provide a relatively good initial fit of the experimental data and converge rapidly to the structure of Table II. Bond angles and dihedral angles predicted for the chair conformation are in Table III with the experimental results. Unfortunately the exact positions of hydrogen atoms are of crucial importance in the model force-field calculations but are not sensitive parameters in the electron diffraction radial distribution curve. Because of this, it is not possible to make a meaningful judgment about the *relative* merits of the force fields adopted in ref 9, 10, and 11, but it can be said that the calculated geometries are very similar to the electron diffraction result. Also, the structures obtained from these calculations do not provide a better fit of the experimental data than that of the models given in Table II.

There is no obvious reason for the chair conformation to be favored in the gas phase and for the crossed conformation to be favored in dichloro[(−)*trans*-cyclo-

---

[17] R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Amer. Chem. Soc.*, **81**, 4765 (1959).

[18] A. Almenningen, G. G. Jacobsen, and H. M. Seip, *Acta Chem. Scand.*, **23**, 1495 (1969); A. Almenningen, O. Bastiasen, and H. Jensen, *ibid.*, **20**, 2680 (1966).

[19] L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **31**, 400 (1959).

[20] L. S. Bartell and R. A. Bonham, *ibid.*, **32**, 824 (1960).

[21] B. N. Cyvin and S. J. Cyvin, *Acta Chem. Scand.*, **17**, 1831 (1963).

Table III. Bond Angles and Dihedral Angles for Experimental and Theoretical Chair Conformations

Parameter	Electron diffraction, deg	Angles, deg Ref 9	Ref 10	Ref 11
θ_1	115.3	119.3	119	117.5
θ_2	101.8	104.4	103	98.0
θ_3	110.9	117.2	114	108.8
θ_4	115.3	120.6	118	114.5
ω_{81}	−157.0	−151.7	−153	−163.0
ω_{12}	−70.9	−65.5	−70	−64.0
ω_{23}	22.1	28.5	23	32.7
ω_{34}	−90.3	−82.8	−86	−96.4
ω_{45}	120.8	95.3	110	115.2

octene][(+)-α-methylbenzylamine]platinum(II)[3] or in 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane.[4] The bond lengths reported by Manor, *et al.*,[3] for carbon–carbon single bonds in *trans*-cyclooctene molecules which are complexed to platinum range from 1.30 to 1.76 Å. In fact, the average structure for all *trans*-cyclooctene molecules in the unit cell has adjacent single bonds with distances of 1.36 and 1.61 Å. Variations of this magnitude are not compatible with the electron diffraction data and would be extremely unusual in a hydrocarbon molecule, regardless of the strain involved. Since the authors report considerable difficulty with obtaining untwinned crystals and with decomposition of the crystals, it is possible that a reinvestigation of the platinum complex would lead to a different conformation for the *trans*-cyclooctene molecules.

The structure reported by Bowen[4] has no unusual bond lengths and, except for the C_1C_8 bond length, is not very different from the models shown in Table II. When a structure close to that of Bowen is tested on the least-squares program, it refines to configuration II of Table II. It is possible, but not likely, that the twist configuration is favored in the cyclopropane derivative but the chair configuration is favored in *trans*-cyclooctene itself. Even if this is the case, however, it is hard to imagine a mechanism by which this conformational change could take place with retention of configuration as reported. A more plausible explanation might be that the synthesis of *trans*-cyclooctene does not produce molecules in the thermodynamically most stable conformation. A large fraction of the sample could be in conformation I even though conformation II is favored thermodynamically if I is formed in the synthesis and if there is a large barrier preventing conversion to the more favorable conformation II. Energy sufficient to bring about thermodynamic equilibrium might be available during the reaction in which the bicyclononane derivative is formed. Under these conditions an electron diffraction study of the pure *trans*-cyclooctene would yield a chair structure whereas an X-ray study of a reaction product might imply a crossed structure. Clearly, further X-ray studies of *trans*-cyclooctene compounds would help to resolve the apparent contradictions between the gas-phase results and the crystal results.

All refinements were carried out assuming only one isomer. It can be seen from the difference curves of Figure 2 that a mixture of isomers with the geometries obtained from the single isomer calculations would not improve the fit of the radial distribution curve.

Acknowledgments. We thank Professor L. S. Bartell for his numerous helpful suggestions. This work was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society. We gratefully acknowledge this support. We also acknowledge support for Z. F. W. from the National Science Foundation Undergraduate Research Participation Program.

Vacuum Ultraviolet Absorption Spectra of Methyl-Substituted Allenes

John D. Scott and B. R. Russell*

Contribution from the Molecular Structure Group, Department of Chemistry, North Texas State University, Denton, Texas 76203. *Received May 30, 1972*

Abstract: The vacuum ultraviolet absorption spectra of two methyl-substituted allenes, 2,4-dimethyl-2,3-pentadiene and 2-methyl-2,3-butadiene, are reported in the spectral region 2200–1200 Å and compared with those of allene and 3-methylpropene. The assignments of $\pi^* \leftarrow \pi$ transitions and tentative assignments of molecular Rydberg transitions are made. The energies of the $\pi^* \leftarrow \pi$ transitions are discussed relative to that of allene in terms of both molecular orbital theory and independent systems theory. The apparent success of the independent systems treatment suggests the possibility that substituted allenes are good models for the study of interacting electronic transitions.

The vacuum ultraviolet (vuv) absorption spectrum of allene[1-3] has appeared several times in the literature; however, there appears to be a lack of experimental and theoretical data concerning the electronic states of two of the methyl-substituted allenes, 3-methyl-1,2-butadiene or 1,1-dimethylallene (DMA) and 2,4-dimethyl-2,3-pentadiene or tetramethylallene (TMA). Streitwieser[4] has reported a theoretical ionization potential (IP) of 9.02 eV for DMA, but no other

---

(1) L. H. Sutcliffe and A. D. Walsh, *J. Chem. Soc.*, 899 (1952).

(2) A. A. Iverson and B. R. Russell, *Spectrochim. Acta, Part A*, **28**, 447 (1972).

(3) J. W. Rabalais, J. M. McDonald, V. Scherr, and S. P. McGlynn, *Chem. Rev.*, **71**, 74 (1971).

(4) A. Streitwieser, *J. Amer. Chem. Soc.*, **82**, 4123 (1960).