[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

On the Molecular Geometry of *trans*-Cycloöctene

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The dipole moments of the cycloöctenes have been measured, and while that of the *cis* isomer is normal, having a value of 0.4 D., that of the *trans* isomer is unusually large, 0.8 D. The large moment of the strained *trans* isomer is consistent with a significant contribution of *s* character to the π-bond of the olefin, the geometrical implications of which are discussed. Certain aspects of the infrared spectrum are also considered in this connection as well as various other physical and chemical properties.

Introduction

The *cis* and *trans* isomers of cycloöctene were prepared in pure form previously by Cope, Pike and Spencer, and their structures are firmly established.[1] While the *cis* isomer is of little geometrical interest, it is evident that the *trans* isomer must be somewhat unusual since it is geometrically impossible for the latter compound to contain only normal bond lengths and bond angles.

Blomquist, Burge and Sucsy[2] have called attention to the fact that while with the cyclodecenes, the *cis* isomer has the higher density and index of refraction as is typical in acyclic systems, with the cycloöctenes, as first noted by Ziegler and Wilms,[3] the reverse is true. From these refractive indices, by application of van Arkel's dipole rule,[4] the prediction could be made that the *trans*-cycloöctene would have a higher dipole moment than the *cis*.

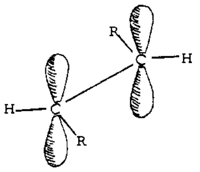
The dipole moments of simple olefins have not been extensively studied, but appear for the most part to be fairly predictable.[5] Thus, the moment of propene is known fairly accurately from measurements in the gas phase, and has the value 0.35 D.[6] Since any unstrained alkyl group must contribute the same moment to a molecule as does a methyl[7] group, the dipole moments of ordinary olefins of the type RCH=CHR must have (as a first approximation ignoring angle deformations and mutual induction) the values 0.60 and 0.0 D for the *cis* and *trans* isomers, respectively. The experimental values available are in general approximately as predicted, and the really anomalous values occasionally reported for unstrained molecules are probably for the most part only a measure of the experimental difficulty of obtaining accurate values for such small moments. The dipole moments of the *cis* and *trans* isomers of cyclodecene were previously determined,[4] and were found to be normal. The conclusion, drawn from the dipole rule, that the *trans*-cycloöctene would have a higher dipole moment than the *cis* represents a situation without analogy. Also, since the dipole moments have a direct bearing on the geometry, the actual measurement of the moments of the cycloöctenes appeared to be in order.

Results and Discussion

In the present work the compounds were obtained by essentially the original procedures and were identical in all respects with those reported earlier. They were each shown to contain less than 3% of the other by a comparison of their infrared spectra.

The dielectric constant measurements were made in *n*-heptane, and the atomic polarizations were ignored in the calculations of the dipole moments. Such a procedure previously was found to yield good results with the homologous cyclodecenes.[4] The values found for the dipole moments of the cycloöctenes were *cis*, 0.43 D.; and *trans*, 0.82 D. These values are in the order predicted by the dipole rule.

Since *trans*-cycloöctene cannot have an unstrained conformation, it will assume that strained conformation (or conformations) which has the minimum free energy content. Because of the relatively large energy required to stretch a bond, this strained conformation must in fact have "bent" bonds. The energy of bond bending is approximately proportional to the square of the angle of bending, and it is therefore energetically more economical for each angle to bend a little than for a smaller number of angles to bend by larger amounts. Hence it can be assumed that each of the carbon–carbon bond angles is distorted somewhat, but the present investigation is concerned mainly with the bending in the vicinity of the double bond.



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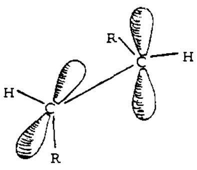

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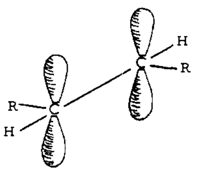

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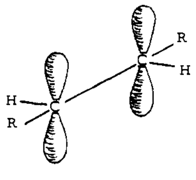

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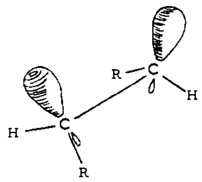

V

The strain on the double bond tends to bring the α-carbons of the R groups in structure I closer together, and this might be accomplished by either (1) twisting (structure II), (2) in-plane bending

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[1] A. C. Cope, R. A. Pike and C. F. Spencer, THIS JOURNAL, **75**, 3212 (1953).

[2] A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *ibid.*, **74**, 3636 (1952).

[3] K. Ziegler and H. Wilms, *Ann.*, **567**, 1 (1950).

[4] N. L. Allinger, THIS JOURNAL, **79**, 3443 (1957).

[5] L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Institute of Technology, Cambridge, Mass., 1948.

[6] K. B. McAlpine and C. P. Smyth, THIS JOURNAL, **55**, 453 (1933).

[7] This point is clearly discussed by L. E. Sutton in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 386.

(structure III), (3) out-of-plane bending (structure V) or by any combination of these three deformations.

If II is regarded as being obtained by twisting one end of the molecule with respect to the other without any change in hybridization, the partial moments of the two halves of the molecule are no longer opposed, and II will have a resultant dipole moment which will increase with increasing angle of twist, becoming a maximum when one end of the molecule has rotated 180° (*cis* isomer).[8] Since the moment found for *trans*-cyclooöctene is in fact greater than that of the *cis* isomer, it is clear that twisting alone is not sufficient to account for the observations, and therefore some bending must occur.

The complete infrared spectra of the *cis*- and *trans*-cyclooöctenes have been published.[1] With respect to distinguishing between the two types of bending, the infrared spectra are quite informative, and the bands of interest are noted in Table I. For comparison the same bands are also listed for a typical pair of olefins, *cis*- and *trans*-4-octene.

TABLE I

INFRARED ABSORPTION MAXIMA,[a] CM.$^{-1}$

Compound	=C—H stretch	C=C stretch	=C—H out-of-plane bending	Reference
cis-4-Octene	3010	1650	709	[b]
trans-4-Octene	(3027)[d]	1670	968	[b]
cis-Cyclooöctene	3010	1664	700	This work
trans-Cyclooöctene	3000	1658[e]	981	This work
Cyclohexene	3020	1650		[b]
Cyclopentene	3065	1612		[b]
Bicyclo[2.2.1]-heptene[b]	3070	1575		[c]

[a] All spectra are with liquid films. [b] N. Sheppard and D. M. Simpson, *Quart. Rev.*, 6, 1 (1952). [c] P. von R. Schleyer and M. M. Donaldson, THIS JOURNAL, **78**, 5702 (1956). [d] Not reported for this particular compound, but homologs have this band at 3025–3029 cm.$^{-1}$. [e] This band is forbidden in the infrared for a simple symmetrical *trans*-olefin, but with *trans*-cyclooöctene the band is appreciably stronger than for the *cis*-isomer (see ref. 1).

The interpretations which follow are derived from the simple, though perhaps not infallible[9] ideas put forth by Walsh,[9a] which assume that a C–H hybrid bond gets progressively stronger as the hybridization of the carbon goes along the series p, sp^3, sp^2, sp. The stronger bonds lead to higher stretching frequencies, but to lower bending frequencies. A similar situation is presumed to hold for carbon–carbon bonds but apparently has not been demonstrated experimentally.

In an ordinary pair of olefins typified by the 4-octenes, it is expected that the *cis* isomer will, for steric reasons, expand the C—C=C bond angles relative to the *trans*. Assuming no change in the π bond, this means that the unsaturated carbon atoms of the *cis* isomer, relative to the *trans*, will have the amount of s character increased in the orbitals of the unsaturated carbons which are directed toward the alkyl groups, but decreased in those directed toward hydrogen. The C–H stretching absorption in the infrared spectrum therefore should be at a higher frequency for the *trans* isomer, as is found. It is found experimentally that the C=C stretching frequency is also greater for the *trans* isomer.

In the present case it is noted that the shift of the =C—H stretching band of the *cis*-cyclooöctene relative to the *trans* is in the opposite direction from that found with ordinary olefins. This fact indicates that if we accept the *cis* as normal, the *trans* isomer has a C–H bond of more than ordinary p character, and the position of the out-of-plane bending absorption of *trans*-cyclooöctene relative to that of *trans*-octene is also consistent with this conclusion.[9] With an ordinary olefin this would probably mean a decreased p character in the C–C single bond, and in terms of geometry the system would tend toward the planar structure IV. Deformation toward such a structure would increase rather than decrease the strain energy in the present case and seems highly unlikely. If both structures II and IV contributed to the actual structure of *trans*-cyclooöctene it might be possible to account for both the dipole moment and the infrared spectrum.

A more reasonable alternative explanation is that the p orbitals which make up the π bond of *trans*-cyclooöctene take on some s character, allowing an approach to the geometry of structure V. The deformation of a simple olefin to this structure is quite analogous to the deformation of a simple acetylene to benzyne.[10] The p character of the bond toward hydrogen is thus increased, and the C–H stretching and bending bands show the appropriate shifts.

Ordinarily an olefin is planar, since the p orbital overlap is then at a maximum. In this case it would appear that the strain energy of the planar form is so large that the minimum energy is obtained by the introduction of an appreciable out-of-the plane bending, which localizes the π electrons on one side of the double bond to some extent. Such an unsymmetrical electron distribution as is indicated in V would be expected to lead to a substantial dipole moment in a manner analogous to that previously proposed for the non-bonding electron pair in the ammonia molecule.[11] Since the atomic dipole resulting from a single unshared electron in an sp^3 orbital on carbon is close to 2D.,[12] it is clear that an olefin, if it were correctly represented by structure V with two electrons contributing, would have a dipole moment very much larger than that observed for *trans*-cyclooöctene. It would therefore appear that in this case V contributes only a relatively small amount to the actual structure.

It is also likely that the bonds are "bent" to some

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(8) The effects of bond twisting on dipole moments as well as on other physical properties have been discussed recently in considerable detail by L. L. Ingraham in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 479. Also see M. Szwarc and F. Leavitt, THIS JOURNAL, **78**, 3590 (1956).

(9) (a) A. D. Walsh, *Disc. Faraday Soc.*, **2**, 18 (1947); (b) T. L. Cottrell and R. E. Richards, *ibid.*, **2**, 63 (1947); (c) A. D. Walsh, *ibid.*, **2**, 65 (1947).

(10) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, THIS JOURNAL, **78**, 601 (1956).

(11) For a good discussion of this problem, see C. A. Coulson, "Valence," Oxford Press, 1952, p. 210.

(12) Reference 11, p. 207.

extent, in other words the angles between the atoms may be deformed by a greater amount than the angles between the orbitals joining them. These "bent" bonds are known to occur, for example, in cyclopropane.[13]

One other striking difference in the infrared spectrum of the cycloöctenes may be pointed out. In an acyclic polymethylene chain, $-CH_2-$ deformation leads to a band at 1465 cm.$^{-1}$, while if the methylene groups are in a six-membered saturated ring[14] the frequency is lowered to 1450 cm.$^{-1}$. *cis*-Cycloöctene, as well as *cis*-cyclodecene and cyclodecane, show both of these bands, but in *trans*-cycloöctene and *trans*-cyclodecene, only the 1450 cm.$^{-1}$ band is observed.

The chemical consequences of having a significant contribution from structure V to an olefin also may be considered. The result would be to raise the energy content of the olefin relative to the transition state through which it would go in becoming a tetrahedral product (I strain[15]) by *cis* addition.

Phenyl azide has been used as a test for "strained" olefins.[16] It adds very slowly, if at all, to ordinary isolated double bonds; for example, it is without effect on *cis*-cycloöctene, *cis*-cyclodecene or *trans*-cyclodecene.[2] It reacts vigorously, however, with *trans*-cycloöctene.[1,3] The best known substances which are reactive toward phenyl azide are the bicyclo[2.2.1]heptenes. These are also "strained," but their deformation about the double bond is quite different from that of the *trans*-cycloöctene. This difference is clear from simple geometry and is supported by the infrared spectra. Thus, while cyclohexene has its olefinic C–H stretching band at 3020 cm.$^{-1}$, bicyclo[2.2.1]-heptene has the corresponding band at 3070 cm.$^{-1}$ (Table I). This shift is consistent with the bicycloheptene having more *s* character in the bond directed to hydrogen. The bond to the carbon substituent then would be expected to have more *p* character, which would yield a smaller C—C=C angle, as the molecule must have. Thus, although bicycloheptene and *trans*-cycloöctene are both strained molecules and although both show this strain in their chemical reactions, the actual deformations involved are quite different, and this difference is shown by a comparison of the infrared spectra. With respect to the C–H stretching band, it has been said[17] that ring strain causes an increase in the frequency. It is clear from the present case that this idea must be applied with discretion.

Acknowledgment.—The author wishes to thank Professor Max T. Rogers of Michigan State University for making available his apparatus for the dipole moment measurements reported herein.

Experimental[18]

***cis*- and *trans*-Cycloöctene.**—Cycloöctanone was prepared by a one-step ring expansion of cyclohexanone with diazomethane, following a procedure similar to that described for the preparation of cycloheptanone.[19] The product was fractionally distilled through a 2-foot column of the Podbielniak type; yield 25%, b.p. 73–75° (12 mm.). The ketone was converted to the oxime, which after distillation at reduced pressure was carefully recrystallized from ether-pentane at −20°, m.p. 36–37°, reported[20] m.p. 36–37°. The oxime was reduced to the amine with sodium and alcohol, and the amine was converted to the trimethylammonium hydroxide.[1] Pyrolysis of the latter gave the mixed olefins, which were separated by taking advantage of the solubility of the *trans* isomer in aqueous silver nitrate solution.[1] The olefins were then separately distilled at reduced pressure, and the refractive indices found were *cis*, n^{25}D 1.4681; *trans*, n^{25}D 1.4744; reported[1] *cis*, n^{25}D 1.4684, *trans*, n^{25}D 1.4741. From 10.6 g. of the oxime a total of 1.6 g. (19%) of the *cis*- and 3.0 g. (36%) of the *trans*-olefin was obtained.

The infrared spectra were obtained employing a Baird double beam infrared spectrophotometer, AB model with sodium chloride prism, and were indistinguishable from the published[1] spectra. It was found that the reproducibility of the spectra was about ±10 cm.$^{-1}$ in the 3000 cm.$^{-1}$ region, and ±5 cm.$^{-1}$ in the 1600 cm.$^{-1}$ region. The difference in band positions between the isomeric cycloöctenes was far more reproducible when samples were run one immediately after the other on the same paper. Under these circumstances the separation of the olefinic C–H stretching bands was 10 ± 5 cm.$^{-1}$ while the C=C stretching bands were separated by 6 ± 3 cm.$^{-1}$, the *cis* being at the higher frequency in both cases.

Dipole Moments.—The apparatus used for the dielectric constant measurements has been described.[21] The solvent used was *n*-heptane, which was purified by passing through a column of silica gel, and then distilling from phosphorus pentoxide. The measurements were made at 25°; the density of the solution and its dielectric constant were measured at various mole fractions as indicated in Table II. The densities of the pure olefins reported[1] are *cis*, 0.8448; and *trans*, 0.8456. The calculations were made following the general procedure of Halverstadt and Kumler[22] as described earlier.[4] The values calculated for the molar refractivity from the refractive indices observed in the present work and the densities reported[1] are *cis*, 36.27 cc., *trans* 36.65 cc., and by addition of atomic refractivities[23] 36.94 cc. The experimental rather than the theoretical values of *R* were used, although use of the latter instead does not significantly affect the results.

TABLE II

DIELECTRIC CONSTANTS OF CYCLOÖCTENE SOLUTIONS IN *n*-HEPTANE AT 25°

cis			*trans*		
N_2	d	ϵ	N_2	d	ϵ
0.0290946	0.682981	1.9224	0.0512233	0.685968	1.9476
.0190642	.681503	1.9181	.0374698	.683937	1.9378
.0108697	.680302	1.9157	.0230511	.681843	1.9279
.0063999	.679509	1.9143	.0133763	.680432	1.9213
.0037021	.679127	1.9134	.0082940	.679787	1.9183
.0000000	.678512	1.9120	.0000000	.678512	1.9121
$\alpha = 0.3472$, $\beta = 0.15354$, $P_{2\infty} = 40.12$ cc., $\epsilon_1 = 1.9120$, $d_1 = 0.67855$			$\alpha = 0.68765$, $\beta = 0.14492$, $P_{2\infty} = 50.41$ cc., $\epsilon_1 = 1.9122$, $d_1 = 0.67852$		

The *cis* isomer was found to have $\mu_{cis} = 0.43 \pm 0.06$ D. which may be compared with the value found for *cis*-cyclodecene of 0.44 D.[4] The *trans* isomer was found to have a dipole moment of 0.82 ± 0.03 D., compared with the value zero found for *trans*-cyclodecene.[4]

DETROIT 2, MICHIGAN

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[13] C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

[14] R. N. Jones and A. R. H. Cole, THIS JOURNAL, **74**, 5648 (1952).

[15] H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

[16] K. Alder and G. Stein, *Ann.*, **485**, 211 (1931); see J. H. Boyer and F. C. Canter, *Chem. Revs.*, **54**, 1 (1954).

[17] A. R. H. Cole and D. W. Thornton, *J. Chem. Soc.*, 1332 (1957).

[18] Infrared spectra by Mrs. Dolores Phillips.

[19] T. J. de Boer and H. J. Backer, *Org. Syntheses*, **34**, 24 (1954).

[20] L. Ruzicka, M. Kobelt, O. Häfliger and V. Prelog, *Helv. Chim. Acta*, **32**, 544 (1949).

[21] M. T. Rogers, THIS JOURNAL, **77**, 3681 (1955).

[22] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

[23] J. A. Leermakers and A. Weissberger, in H. Gilman's "Organic Chemistry," Vol. II, second edition, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 1751.