more consistent with a model for diffusion in which there is no potential barrier to displacement than they are to a model in which diffusion involves an activation energy of a few kcal./mole, and the value in hexachlorobutadiene is probably too small to be plausible even if displacements are opposed by no barriers whatsoever. However, the equations used in this argument tacitly assumed that the solvent could be treated as a continuum. Therefore the argument about energy barriers is suspect.

Summary.—If solvent is regarded as a continuum, rather simple mathematical expressions can be derived. These expressions make predictions without disposable parameters that are often in remarkably good agreement with experimental observation but more detailed comparison reveals systematic discrepancies. Any further progress must introduce the discrete molecular nature of the solvent and it should do so in a manner susceptible to quantitative experimental test.

We do not see any tractable conventional mathematical approach to handle this problem of a discrete particulate solvent but we have hopes that the next refinement of theory can be attained by digital computer techniques already developed by Professor B. J. Alder of the University of California.[12]

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[12] B. J. Alder and T. Wainwright, "Proceedings of International Symposium on Transport Processes in Statistical Mechanics," Interscience Publishers, Inc., New York, N. Y., 1958, pp. 97-131.

EUGENE, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND SPECTROSCOPY LABORATORY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Vibrational Spectra and Structure of the Tropilidene Molecule[1]

BY M. V. EVANS[2] AND R. C. LORD

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Study of the Raman spectrum of tropilidene and its infrared spectrum between 300 and 4000 cm.$^{-1}$ shows that the double-bond vibrations of this molecule have surprisingly low frequencies, high intensities in the Raman effect and very weak infrared absorption. Neither of the two structures most often considered for tropilidene—1,3,5-cycloheptatriene and bicyclo-[4.1.0]hepta-2,4-diene—is in complete accord with these and certain other spectroscopic results. An earlier suggestion of the authors that these characteristics indicate a bicyclo[3.2.0]hepta-2,5-diene structure has been disproved by the synthesis and spectroscopic study of this compound. Its spectra and other properties confirm the bicyclic structure but show that it is not tropilidene. The tropilidene structure which best fits the spectroscopic data is a planar quasi-aromatic ring of C_{2v} symmetry, as originally suggested by Doering and Knox, although a structure in which the CH_2 group is displaced slightly out of the molecular plane cannot be excluded. The infrared and Raman data have been interpreted on the C_{2v} basis. The entropy of tropilidene vapor has been calculated to be S^0_{298} = 76.0 cal./mole/deg., as compared with the measured value 75.44 ± 0.25. The discrepancy is probably due to uncertainties in the calculation, although the fact that the calculated value is larger suggests that there may be some residual entropy in crystalline tropilidene at low temperature. Infrared and Raman spectra are also reported for 3,7,7-trimethyltropilidene and 3,4,7,7-tetramethyltropilidene.

Introduction

The discovery of the aromatic nature of the tropylium ion ($C_7H_7^+$) and the growing interest in the related substances tropone, heptafulvene, tropolone and azulene[3] have created new interest in the structure of their parent hydrocarbon tropilidene. Tropilidene was first prepared from the alkaloid tropine by Ladenburg[4] in 1881 and an investigation of the structure of the hydrocarbon was carried out by Willstätter[4] in 1901. Willstätter repeated Ladenburg's synthesis and then prepared tropilidene by several other routes starting from cycloheptene. This set of synthetic methods convinced him that tropilidene had the structure 1,3,5-cycloheptatriene (I), but he also considered the structures bicyclo[4.1.0]hepta-4,6-diene (II), bicyclo-[3.2.0]hepta-2,5-diene (III) and bicyclo[2.21]hepta-2,5-diene (IV) as shown in Fig. 1. Willstätter ruled out structure IV because a hydrocarbon of that structure was known and had different physical and chemical properties. Structure III was rejected by him because he felt that there was no reason to suppose that this type of structure would absorb three moles of hydrogen to give cycloheptane, as was observed for tropilidene and, further, it was difficult for him to explain why such a structure should be formed in any of the reactions leading to tropilidene. Structure II was more acceptable in that an analogous ring system was supposed to be formed in the case of the Buchner acids,[5] but the bicyclo ring system was supposed to be very labile and susceptible to rearrangement to the cycloheptatriene ring-system. This, plus the fact

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[3] (a) A. W. Johnson, *J. Chem. Soc.*, 1331 (1954); (b) T. Nozoe, *Kagaku* (*Science*), **21**, 564 (1951).

[4] (a) A. Ladenburg, *Ber.*, **14**, 2129 (1881); (b) R. Willstätter, *Liebig's Ann.*, **317**, 204 (1901).

[5] E. Buchner, *Ber.*, **31**, 2241 (1898).

that no cyclopropane-1,2-dicarboxylic acid was formed upon permanganate oxidation of tropilidene as might be expected if II were the structure, led Willstätter also to reject II and assign the remaining model I as the structure of tropilidene.

Fifty years later, Doering and Knox discovered that tropilidene could be prepared by the photochemical addition of diazomethane to benzene. Because photochemical addition of diazomethane to an olefinic double bond results in the formation of a cyclopropane ring, Doering reasoned that it was possible for tropilidene to be structure II and pointed out that the chemical evidence then available did not really distinguish between the isomers I and II. Both chemical evidence[6–8] and nuclear magnetic resonance spectra[9] led to the conclusion that tropilidene could not have structure II, and therefore Doering and Knox[10] proposed that tropilidine is 1,3,5-cycloheptatriene but that the π-orbitals at the ends of the triene chain interact to give some resonance stabilization to the molecule.

Several molecular orbital calculations have been done for such a structure[11] but unfortunately no good method exists for the inclusion of the effects of strain and non-planarity of the molecule, and thus only qualitative statements can be made about this structure. One can conclude that the energy of the π-electron system will be lowered rapidly as the distance between carbons 1 and 6 is decreased and will increase if the ring is puckered. However, these two factors are closely connected with the strain energy of the molecule, since decreasing the distance between carbons 1 and 6 increases the strain at carbon 7 and tends to force carbon 7 away from the plane of the rest of the molecule. This would twist the π-orbitals of carbons 1 through 6 out of parallelism and thereby decrease the resonance energy. Thus there must be a balance of forces between strain and resonance stabilization and the equilibrium structure can be decided only by examining the carbon–carbon distances in the molecule.

Lipscomb and Reed[12] attempted to determine these distances by X-ray diffraction studies of a single crystal of tropilidene, but they found only that the crystal exists in a disordered cubic phase between −80° (melting point) and −120°, at which temperature a phase transition was observed. From the unit-cell dimensions and the density of the crystal, it was calculated that there are eight molecules per unit cell. The reciprocal lattice symmetry is O_h, but because only five reflections were observed, an interpretation of the diffraction pattern sufficiently detailed to yield the structure of the molecule was not obtained. Apparently no other study of the structure of tropilidene has been made by X-ray or electron diffraction.

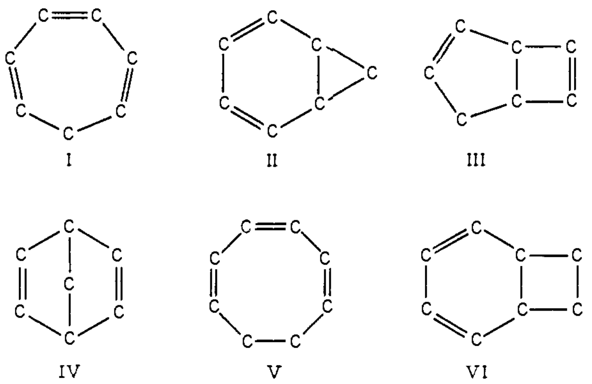

Fig. 1.—Possible structures of tropilidene (I–IV), cyclooctatriene (V) and bicyclooctadiene.

A less direct way to decide on the magnitude of the π-orbital overlap, if any, is to study the heat of combustion and the heat of hydrogenation of tropilidene and compare it with those of other cyclic olefins. This was done by Conn, Kistiakowsky and Smith,[13] and more recently by Turner, *et al.*[14] Their conclusions were that tropilidene has about 9 kcal. per mole of resonance energy compared with 2 kcal. per mole for 1,3,5-cyclooctatriene (V).

The present work was undertaken to see whether any structural conclusions could be drawn from the infrared and Raman spectra of tropilidene.

Spectroscopic Procedures and Results

Infrared spectra in the region 640 to 5000 cm.$^{-1}$ were obtained with a Baird-Atomic Model AB-2 spectrophotometer equipped with NaCl and CaF_2 prisms and in the region from 300 to 700 cm.$^{-1}$ with a Perkin–Elmer Model 112 double-pass monochromator equipped with a CsBr prism.

Raman spectra were obtained with a grating spectrograph equipped with a 60 cm. f/5 Petzval camera, a 100 cm. f/8 paraboloidal collimator and a 1200 groove/mm. Bausch and Lomb transfer grating blazed at 7000 Å. in the first order. Two excitation units were used. With the first, the 4358 Å. line from a pair of Toronto-type low-pressure mercury discharge lamps was isolated by filtering with 1 cm. of saturated sodium nitrate solution and 5 mm. of du Pont Rhodamine GDN Extra. The rhodamine concentration was adjusted so that the solution was 85% transparent at 4360 Å. The second order of the grating was used and the spectrum was photographed on Eastman 103a-J plates. The spectral slit width was 0.85 cm.$^{-1}$/100 μ of slit opening. The second source unit isolated the 5460 Å. line from six General Electric AH-2 mercury lamps by filtering with 1 cm. of 0.1 M Na_2CrO_4, 5 mm. of saturated $Cu(NO_3)_2$ and 5 mm. of saturated $NdCl_3$ solution. The first order of the grating was used and the spectrum was photographed on Eastman 103a-E plates. Polarization ratios were determined by the method of Edsall and Wilson.[15] A Pfund iron arc was used to provide

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[6] K. Alder, K. Kaiser and M. Schumacher, *Liebig's Ann.*, **602**, 80 (1957).

[7] A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, THIS JOURNAL, **74**, 4867 (1952).

[8] E. Vogel, *Fortschritte der Chemischen Forschung*, 1955.

[9] E. J. Corey, H. J. Burke and W. A. Remers, THIS JOURNAL, **77**, 4941 (1955).

[10] W. E. Doering and L. M. Knox, *ibid.*, **76**, 3203 (1954).

[11] (a) G. Berthier and B. Pullman, *Trans. Faraday Soc.*, **45**, 484 (1949); (b) J. L. Franklin and F. H. Field, THIS JOURNAL, **75**, 2819 (1953).

[12] T. B. Reed and W. N. Lipscomb, *Acta Cryst.*, **6**, 108 (1953).

[13] J. B. Conn, G. B. Kistiakowsky and E. A. Smith, THIS JOURNAL, **61**, 1868 (1939).

[14] R. B. Turner, W. R. Meader, W. von E. Doering, L. H. Knox, J. R. Mayer and D. W. Wiley, *ibid.*, **79**, 4127 (1957).

[15] J. T. Edsall and E. B. Wilson, *J. Chem. Phys.*, **6**, 124 (1938).

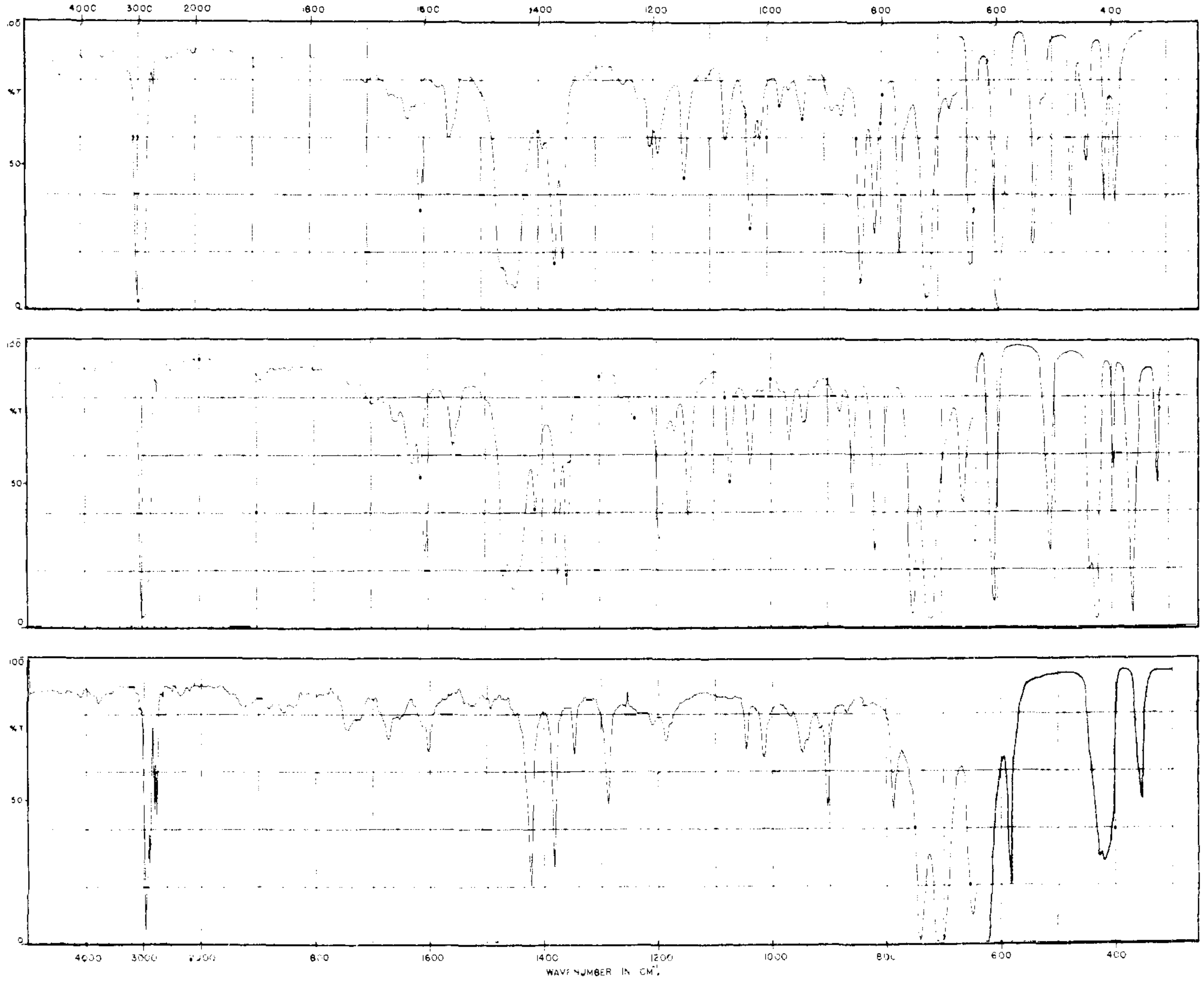

Fig. 2.—Infrared spectra of 3,4,7,7-tetramethyltropilidene (top); 3,7,7-trimethyltropilidene (center); tropilidene (bottom); sample thickness 0.25 mm., 300–640 cm.$^{-1}$; 0.025 mm., 640–5000 cm.$^{-1}$, in all three spectra.

reference spectra for wave length calibration. The Raman frequencies were determined by measuring a 5X enlargement of the plate with a millimeter scale and these measurements converted to wave number shifts in vacuum by the use of the IBM 704 Electronic Data Processing Machine. The program used has been described in a report to the M.I.T. Computation Center as Problem M-208. Photoelectric measurements of relative intensities and polarization ratios for several samples were obtained by the method of Edsall and Wilson with the above spectrometer converted to photo-electric recording as described by Boyd, Lord and Wilmot.[16]

The spectroscopic results for tropilidene, 3,7,7-trimethyltropilidene and 3,4,7,7-tetramethyltropilidene are summarized in Tables I–IV. The infrared spectra are shown in Fig. 2.

Infrared and Raman spectra also were obtained during the course of this work for bicyclo[3.2.0]-hepta-2,5-diene, bicyclo[3.2.0]heptene-2, exo and endo bicyclo[3.2.0]hepta-6-ene-2-ol, bicyclo[3.2.0]-hepta-6-ene-2-one, bicyclo[3.2.0]heptene-2, bicyclo[4.2.0]octene-7, bicyclo[3.3.0]octene-2 and Δ^3-carene. Spectroscopic data on these substances will be presented in a separate publication concerned with the synthesis of the first compound.

The sample of tropilidene (30 g.) was obtained through the courtesy of Dr. D. W. Scott of the Petroleum Experiment Station, U. S. Bureau of Mines, Bartlesville, Oklahoma. The sample was part of a large amount prepared in the laboratory of Dr. W. E. Doering and was subjected at the Petroleum Experiment Station to careful purification procedures in connection with thermodynamic studies on tropilidene.[17] The methyl derivatives of tropilidene were prepared by the methods of Corey, Burke and Remers.[18]

Vibrational Assignment for C$_{2v}$ Structure of Tropilidene

The synthesis of bicyclo[3.2.0]hepta-2,5-diene (III) and the demonstration both by spectroscopic means and by other physical properties that it is a distinctly different substance from tropilidene necessitate the elimination of the bicyclic structure[19]

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(16) D. R. J. Boyd, R. C. Lord and G. Wilmot, to be published.

(17) H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly and G. Waddington, This Journal, **78**, 5469 (1956).

(18) E. J. Corey, H. J. Burke and W. A. Remers, *ibid.*, **78**, 180 (1956).

TABLE I

INFRARED SPECTRUM OF TROPILIDENE

Freq., cm.$^{-1}$ (vac.)	Approx. intens.	Assignment	Freq., cm.$^{-1}$ (vac.)	Approx. intens.	Assignment
353	MS	39	1217	W	9
420	S	13	1245	VW	26
428	S	38	1294	MS	25
590	S	37	1353	M	35 + 36
656	S	36	1394	S	8
705	VVS	35	1432	S	7
740	VS	34	1535	VW	6
793	M	31	1608	W	5, 24
873	VVW	17	1692	W	12 + 31
906	M	12	1757	W	6 + 14
948	W	11	2849	MS	4
968	VVW	30	2890	M	2 × 7
1017	W	10	2967	MS	33
1048	W	29	3026	VVS	1, 2, 3
1192	W	28	3058	M	21

TABLE II

RAMAN SPECTRUM OF TROPILIDENE

Freq. cm.$^{-1}$ (vac.)	Relat. intens.	Depol. factor	Assignment	Freq., cm.$^{-1}$ (vac.)	Relat. intens.	Depol factor	Assignment
223	25	0.52	14	1218	25	0.45	9
291	17	.86	20	1235	1	..	26
355	17	.86	39	1298	0.1	..	25
405	(15)	.86	19	1393	6	.30	8
421	53	.49	13	1433	15	.90	7
588	12	.9	37	1441	15	.90	7
657	1	..	36	1517	5	.15	C^{13}?
712	0.3	..	35	1535	100	.10	6
743	0.3	..	34	1609	34	.93	5, 24
792	2	.86	31	1623	3	..	....
876	0	..	17	2772	0.1	..	....
908	66	.08	12	2838	10	.28	4
920	3	.9	16	2880	11	.38	2 × 7
952	27	.32	11	2944	13	.8	....
973	10	1.0	30	2966	14	.8	33
994	0.1	..	15	2993	1	..	....
1019	1	0.8	10	3026	65	.24	1, 2, 3
1049	3	.8	29	3039	(5)	.8	22
1192	24	.86	28	3066	10	.8	21

TABLE III

RAMAN SPECTRUM OF 3,7,7-TRIMETHYLCYCLOHEPTATRIENE

Freq., cm.$^{-1}$ (vac.)	Approx. intens.	Esti. polar.	Freq., cm.$^{-1}$ (vac.)	Approx. intens.	Estim. polar.
109	7	dp	964	2	p
192	7	dp	1071	2	p
238	4	dp?	1143	3	dp
295	6	dp	1168	1	p
308	5	p	1195	2	p
323	5	dp	1242	4	p
365	5	p	1262	1	dp
398	0	p	1339	3	p
430	1	dp?	1376	3	p
440	2	dp?	1406	2	dp
514	5	p	1416	5	p
610	3	dp	1452	6	p
670	8	p	1460	5	dp
695	2	p	1496	0	p
723	2	p	1553	10	p
750	1	p	1611	8	p
818	1	p	2865	4	
881	2	p	2902	5	
924	0	p	2915	7	
936	5	p	2937	6	
941	5	p	2962	7	
958	5	dp	3009	9	

TABLE IV

RAMAN SPECTRUM OF 3,4,7,7-TETRAMETHYLCYCLOHEPTATRIENE

Freq., cm.$^{-1}$ (vac.)	Approx. intens.	Estim. polar.	Freq., cm.$^{-1}$ (vac.)	Approx. intens.	Estim. polar.
105	9	dp	1027	1	dp?
156	5	dp	1072	2	dp
197	8	dp	1109	2	dp
249	2	dp	1144	3	dp
296	0	dp?	1189	1	dp
325	8	p	1206	2	dp
350	4	p	1230	2	p
390	3	p	1257	2	dp
412	3	dp	1309	3	p
442	3	dp	1373	3	
467	5	dp	1382	4	p
553	7	p	1396	5	p
592	7	p	1408	3	dp
643	6	p	1441	3	dp
685	4	p	1464	5	dp
721	3	p	1551	10	p
813	2	dp	1575	3	p
838	2	p	1613	8	p
873	4	dp?	2865	6	p
919	0	dp?	2914		p
938	2	dp?	2926	10	p
945	7	p	2943		p
961	2	dp?	2961		dp?
975	3	p	3011	8	p

as a basis for interpretation of the spectra of tropilidene. The bicyclo[4.1.0]heptadiene structure (II) also appears incompatible with certain prominent features of the vibrational spectra. The most important of these is the presence of CH stretching frequencies in both the infrared and Raman spectra below 3000 cm.$^{-1}$. Since all of the CH bonds in the bicyclo[4.1.0] structure should be either olefinic or cyclopropyl bonds, it would be expected that no CH stretching fundamentals should fall lower than about 2970 cm.$^{-1}$ at the very least. The existence of both polarized and depolarized Raman lines of moderate intensity in the frequency range 2830–2970 cm.$^{-1}$ is an indication that another kind of aliphatic CH is present. In addition, the upper component of the usual doublet structure for cyclopropyl CH stretching at about 3010 and 3080 cm.$^{-1}$ is not observed in either the infrared or Raman effect.

In the C=C region of the spectrum the cyclohexadiene-1,3 ring usually exhibits double bond frequencies near 1580 and 1610 cm.$^{-1}$, whereas the lowest C=C fundamental in tropilidene lies at

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(19) M. V. Evans and R. C. Lord, Abstracts of Papers, 130th Meeting, American Chemical Society, Atlantic City, N. J., September 16, 1956, p. 41-R.

1535. To be sure, it is conceivable that fusion of a cyclopropyl to a cyclohexadienyl ring would affect one and not the other of these frequencies. In bicyclo[4.2.0]octa-2,4-diene, however, where a cyclobutyl ring is thus fused, the double-bond frequencies appear close to the same positions as in cyclohexadiene-1,3.[20] It is therefore concluded that the bicyclo[4.1.0]structure is not the correct one for tropilidene.

It has been proposed by Doering and Knox[10] that the π-electrons of tropilidene form a closed aromatic system analogous to those of the cyclopentadienyl anion, $C_5H_5^-$, benzene, C_6H_6, and the tropylium cation, $C_7H_7^+$. The chief difference between these three and tropilidene is that none of the former has a CH_2 group to interrupt the ring system housing the six delocalized electrons. Doering and Knox therefore proposed that in tropilidene these electrons form a ring encompassing six carbon atoms and bypassing the seventh (the CH_2 group).

Such a structure might well have fairly uniform C–C distances (apart from the bonds to the CH_2 group), in contrast to the situation that presumably exists in 1,3,5-cycloöctatriene. It would be expected to have quasi-aromatic character, as Doering and Knox point out, and to be planar (possibly apart from the CH_2 group). Moreover the C–C bond force system should be more like that in benzene or tropylium ion[21a] than that in cycloöctatriene and thus the discordance with the spectrum of the latter could be understood.[21b]

The vibrational spectra have therefore been interpreted in terms of a planar ring system of C_{2v} symmetry. It has been assumed that all seven carbons are in the same plane. This assumption has permitted a straightforward understanding of the infrared and Raman data, although the data might fit almost as well a structure in which the methylene carbon atom is displaced somewhat out of the ring plane. It is certainly possible that the latter structure is the correct one but the sensitivity of the selection rules to a slight departure from the planar-ring structure is too small to make such a departure apparent.

The distribution of vibrations among the four symmetry species of the C_{2v} structure is given in Table V, and a summary of the assignment of the observed frequencies is presented in Table VI. The latter table also indicates the spectroscopic behavior of each species of vibration (column 1) and a rough description of each vibration (column 3). The assignment of frequencies to the individual modes of vibration was made as shown in Table V.

TABLE V

DISTRIBUTION OF VIBRATIONAL DEGREES OF FREEDOM AMONG VIBRATIONAL SPECIES FOR C_{2v} STRUCTURE OF TROPILIDENE

Species[a]	No. of C vibrat.	No. of H vibrat.	Total
A_1	6	8	14
A_2	2	4	6
B_1	5	7	12
B_2	2	5	7

[a] "A" means the vibrations of the species are symmetric to the two-fold axis, "B," antisymmetric; subscript 1, symmetric to the plane of the carbon ring, subscript 2, antisymmetric.

TABLE VI

ASSIGNMENT OF VIBRATIONAL FREQUENCIES IN TROPILIDENE (C_{2v} STRUCTURE)

Frequencies enclosed in ( ) are estimated.

Species of vibrat.	Vibrat. no.	Approx. descrip. of vibrat.	Assigned frequency Raman	Assigned frequency Infrared
A_1	1	CH stretching	3026	3026
Polarized in	2	CH stretching	(3026)	(3026)
Raman;	3	CH stretching	(3026)	(3026)
infrared-	4	CH_2 stretching (sym.)	2838	2849
active	5	C=C out-of-phase stretching	1609	1608
	6	C=C in-phase stretching	1535	1535
	7	CH_2 deformation	1433	1432
	8	CH bending (in-plane)	1393	1394
	9	CH bending (in-plane)	1218	1217
	10	CH bending (in-plane)	1020	1017
	11	Ring stretching I	952	948
	12	Ring stretching II	908	906
	13	Ring deformation I	421	420
	14	Ring deformation II	223	. .
A_2	15	CH_2 twisting	904	. .
Depolarized	16	CH bending (out-of-plane)	920	. .
in Raman;	17	CH bending (out-of-plane)	876	873
infrared-	18	CH bending (out-of-plane)	(650)	. .
forbidden	19	Ring puckering I	405	. .
	20	Ring puckering II	291	. .
	21	CH stretching	3066	3058
	22	CH stretching	3039	. .
	23	CH stretching	3026	3026
B_1	24	C=C out-of-phase stretching	1600	1608
Depolarized in Raman;	25	CH_2 wagging	1298	1294
infrared-	26	CH bending (in plane)	1235	1245
active	27	CH bending (in plane)	(1218)	(1217)
	28	CH bending (in plane)	1192	1192
	29	Ring stretching I	1049	1048
	30	Ring stretching II	973	968
	31	Ring bending I	792	793
	32	Ring bending II	. .	. .
B_2	33	CH_2 stretching (anti)	2966	2967
Depolarized	34	CH bending (out-of-plane)	743	740
in Raman;	35	CH bending (out-of-plane)	712	705
infrared;	36	CH bending (out-of-plane)	657	656
active	37	CH_2 rocking	588	590
	38	Ring puckering I	. .	428
	39	Ring puckering II	355	353

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(20) E. R. Lippincott and R. C. Lord, THIS JOURNAL, **79**, 567 (1957).

(21) (a) W. G. Fateley, B. Curnutte and E. R. Lippincott, *J. Chem. Phys.*, **26**, 1471 (1957); (b) it would appear that the mean C=C—C bond angles in cycloöctatriene (non-planar) and cycloheptatriene (planar) should not differ much (~3°), which should affect the mean C=C frequency by 10 cm.$^{-1}$ or less. The difference in the mean C=C frequency will be mainly due to difference in the C=C potential constants. The mean C=C force constant in cycloheptatriene should be smaller because of the greater delocalization of the π-electrons implied by the quasi-aromatic system. The respective mean values of the two observed C=C frequencies in each of the two molecules are 1625 and 1572, implying a difference in the mean force constants of about 6% (the percentage difference in diatomic constants is twice that in frequency for small differences). If the C=C force constant is about equally composed of contributions from the σ- and π-electrons, it would appear that the π-bonding in the C=C bonds is about 12% less in cycloheptatriene than in cycloöctatriene. This larger amount of delocalization is consistent with the greater resonance energy reported for cycloheptatriene.[14]

Species A_1: The frequencies of the totally-symmetrical A_1 species are readily recognized by the polarized nature of their Raman lines. By standard methods it can be shown (as stated in Table V) that six are due to vibrations mainly of the carbon ring and eight to those of the hydrogen atoms. With the help of symmetry reasoning and analogy to other molecules, particularly benzene, these fourteen vibrations can be given the appropriate descriptions in Table VI.

Eleven polarized lines were found in the Raman spectrum and ten of these can be placed in A_1, as shown in Table VI. The one omitted is the line at 2880, which must arise from the CH_2 group in some fashion, and there is another frequency (2830) which fits the A_1 CH_2-stretching vibration equally well. It is assumed that the 2880 line is an overtone which has picked up intensity and a low depolarization factor by interaction with the fundamental at 2830.

The remaining four places in A_1 are readily filled. There must be a frequency at or near 1450 which is due to the A_1 CH_2 deformation (scissors-like) vibration.[22] The doublet 1433–1441, presumably double because of Fermi interaction with an over-tone or combination-tone, is indicated as the correct assignment despite the fact that these lines are depolarized. The other three frequencies are those of CH stretching vibrations and it is assumed that the strong polarized line at 3026 is a superposition of the three.

Thus the assignment of the A_1 species is made without difficulty. The only surprising result is the very low value (223 cm.$^{-1}$) of the lowest bending frequency. This is perhaps attributable to the low bending force constants associated with the part of the ring adjacent to the CH_2 group. In benzene and tropylium ion[23] the lowest observed ring deformation frequencies are 606 and 433 cm.$^{-1}$, respectively. It might be, of course, that the 223 frequency is due to an out-of-plane vibration which is totally symmetrical because the molecule is not planar, but the ease with which the polarized lines can be assigned on the basis of a C_{2v} structure is evidence against such an explanation.

Species B_1: The twelve vibrations of this species are analogous to those of the A_1 species except for the absence of one CH_2 stretching vibration and one high ring frequency and the replacement of CH_2 deformation by CH_2 wagging. Therefore, one tries to find moderately intense depolarized Raman lines of frequencies comparable to the polarized ones. For frequencies expected to lie above 800 cm.$^{-1}$, there is not much difficulty in doing this. However, the two ring-bending vibrations are expected to fall below 800 cm.$^{-1}$ and there is ambiguity about the assignment of the available low frequencies to species B_1 and B_2, the latter also having a good many low frequencies. The assignment of the B_1 vibrations No. 31 and 32 is therefore deferred until the completion of the B_2 assignment.

Species B_2: This species contains the infrared-active out-of-plane vibrations. By analogy with benzene and tropylium ion, the three B_2 hydrogen vibrations are expected to be intense in infrared absorption and weak in the Raman effect. This enables the assignment of the three very strong infrared bands at 657, 712 and 743 cm.$^{-1}$ to these vibrations. The CH_2 frequencies at 588 and 2966 are straightforward assignments, leaving only the ring puckering vibrations. One of these must be assigned as the Raman line at 355, which is low in frequency and is also observed as moderately strong in the infrared. No Raman line which can be attributed readily to the other ring-puckering vibration was found but an infrared band is observed in the reasonable position of 428. The corresponding Raman line could easily be hidden by the intense polarized line at 421 cm.$^{-1}$. This completes assignment of all infrared bands below 800 cm.$^{-1}$ except that at 793 cm.$^{-1}$. There is therefore only one candidate for B_1 vibrations 31 and 32, the 973 band being assigned to the former, and no assignment made for the latter, although its frequency would be expected in the range 400–600 cm.$^{-1}$.

Species A_2: The A_2 vibrations are expected to be weak in the Raman effect and missing from the infrared. Since the infrared spectrum was not studied in the vapor phase, the latter expectation may not be fulfilled. Actually only three Raman frequencies have been found in the range 300–1300 cm.$^{-1}$ without infrared counterparts. These are at 405, 920 and 994 cm.$^{-1}$ and are assigned to species A_2 as shown in Table VI. In addition, the very weak line at 876 is assigned to vibration 17, despite the occurrence of a feeble infrared band at this point and the Raman line at 291 to vibration 20. The infrared study did not extend low enough to determine whether there is a band at 291. Finally an estimate of 650 cm.$^{-1}$ is made for the missing A_2 out-of-plane bending vibration 18 by analogy with B_2 vibration 36. The failure to observe the A_2 lines more definitely is perhaps not surprising in view of the fact that the B_2 CH_2-bending vibrations, which are similar to the A_2 ones, give rise to extremely weak Raman lines. The frequencies assigned to the A_2 vibrations are therefore rather uncertain.

Although the assignment of fundamentals in Table VI is incomplete, we feel that most of the fundamental frequencies have been established. To make a more secure allocation of frequencies to the various species, further work needs to be done, particularly on the spectra of isotopic derivatives of tropilidene.

Entropy of Tropilidene Vapor

A check on the identification of the low frequencies in tropilidene can be made by a comparison of the spectroscopic and thermodynamic values of the entropy of the vapor. A careful study of the low-temperature heat capacity and of the various heats of transition of tropilidene has been made by Finke, Scott, Gross, Messerly and Waddington.[17] For present purposes the most useful result of their study is the value of the standard entropy of tropilidene at 298.16°K., $S^0_{298.16}$ =

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[22] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen & Co., London, 1958, pp. 20–25.

[23] R. D. Nelson, W. G. Fateley and E. R. Lippincott, THIS JOURNAL, **78**, 4870 (1956).

75.44 cal./mole deg. Using the vibrational assignment of Table VI, setting the missing frequency 32 at 600 cm.$^{-1}$ and making an approximate estimate of the moments of inertia of the C_{2v} structure,[24] one calculates for the same quantity by the standard methods of statistical mechanics the value $S^0_{298.16} = 76.0$.

The discrepancy of 0.67 unit is somewhat larger than the estimated experimental error of 0.25. Part of this undoubtedly is due to the roughness of our estimate of the moments of inertia but an error of 10% in each of these would make no more than 0.3 unit error in the rotational entropy. Also it is hardly to be expected that the vibrational assignment is completely reliable. However, nearly all the frequencies below 1000 cm.$^{-1}$ are distinct, definite fundamentals as observed in the infrared and/or Raman spectra (apart from ν_{32}). Since no question of vibrational degeneracy exists, it is immaterial whether the assignment of Table VI is correct so long as the fundamental frequencies have been located correctly.

Moreover, the effect of an incorrect inference about molecular symmetry would be to increase the present discrepancy if the actual symmetry is C_s rather than C_{2v}. In consequence, we feel that some of the discrepancy may be due to residual entropy in the crystal at 0°K.

Conclusions

1. Since the bicyclo[3.2.0]hepta-2,5-diene structure proposed by us earlier for tropilidene has been shown to be incorrect by the synthesis of that bicyclic diene and since the infrared and Raman spectra are incompatible with the bicyclo[4.1.0]hepta-2,4-diene structure, it is concluded that tropilidene has a monocyclic seven-membered-ring structure.

2. Unusual values for the intensities and frequencies of the double-bond vibrations of tropilidene in the Raman and infrared spectra indicate that the conventional name 1,3,5-cycloheptatriene does not adequately describe the electronic structure of tropilidene. It is inferred from these data that the structure of tropilidene is more satisfactorily described, as first suggested by Doering and Knox, in terms of a molecule of C_{2v} symmetry in which the six π-electrons form a quasi-aromatic set like those in benzene, cyclopentadienyl anion and tropylium cation.

3. The infrared and Raman spectra of tropilidene have been interpreted without difficulty on the basis of a C_{2v} structure, although a structure departing slightly from C_{2v} cannot be excluded. All but two of the thirty-nine fundamentals have been assigned frequency values from the observed spectra, and estimates of these two frequencies have been made.

4. A calculation of the entropy of tropilidene vapor using the frequency assignment and estimated values for the moments of inertia yielded the value $S^0_{298} = 76.0$ cal./mole deg. The measured entropy (75.44 ± 0.25) is in fair agreement with the calculated one but it seems possible that part of the discrepancy may be due to residual entropy in the crystal at 0°K.

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[24] The moments of inertia of tropilidene were estimated by assuming a regular heptagonal structure with a mean C–C distance of 1.43 Å., a C–H distance of 1.09 Å. and a mass of 2 for one of the hydrogens. The product $I_xI_yI_z$ so calculated was 2.765×10^{-113} g.^{3} cm.^{6}.