

TABLE IV
ANALYSIS OF QUANTUM YIELDS OF HYDROGEN IN THE LIQUID-PHASE PHOTOLYSES OF VARIOUS AROMATIC COMPOUNDS

Source	$\gamma \times 10^4$				
	Mesitylene ^a C ₆ H ₃ (CH ₃) ₃	Toluene ^a C ₆ H ₅ CH ₃	Ethylbenzene ^a C ₆ H ₅ CH ₂ CH ₃	<i>i</i> -Propylbenzene C ₆ H ₅ CH ₂ CH ₂ CH ₃	<i>t</i> -Butylbenzene C ₆ H ₅ C(CH ₃) ₃
Rearrangement (by difference)			2.1	1.2	
β_{C-H}	3.4	1	→ 0.7	→ 0.3	
γ_{C-H}			0.4	← 0.8	← 1.2
Total (H ₂) × 10 ⁴	3.4	1	3.2	2.3	1.2

yields of hydrogen observed in photolyses of these compounds on the basis of these speculations. The

guiding idea is that but a very small fraction of the excited molecules decompose. The amount of the decomposition *via* a particular path (*e. g.*, rupture of a β_{C-H} bond) then depends largely on the number of equivalent paths and the probability of decomposition along one such path. According to the scheme proposed each group makes a characteristic contribution to the total quantum yield (*i. e.* $\sim 1 \times 10^{-4}$ for β_{C-H} and $\sim 0.4 \times 10^{-4}$ for γ_{C-H}). The total quantum yields of hydrogen, $\gamma(H_2)$, were alone determined. The arrows indicate the direction of the speculations. The results are obviously consistent but data on the yields of the styrenes would be required to verify the suggested mechanisms.

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[A CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY OF CONNECTICUT]

The Raman and Infrared Spectra of Nortricyclene

BY ELLIS R. LIPPINCOTT

Spectroscopic data for nortricyclene, tricyclo[2.2.1.0^{2,6}]heptane, C₇H₁₀, are reported. These include the Raman spectrum of the liquid with depolarization factors and the infrared spectrum of the vapor and solid in the region from 3500 to 250 cm.⁻¹. These spectral data, along with those for related molecules, have been considered in terms of postulated models. It is concluded that the best model for nortricyclene is one having a C_{3v} symmetry.

Nortricyclene, tricyclo[2.2.1.0^{2,6}]heptane, C₇H₁₀, has been synthesized by Roberts, Trumbull, Bennett and Armstrong.¹ From its chemical properties and method of preparation, they reasoned that the most probable molecular structure was one where the carbon atoms were connected by single bonds to form three five-membered rings and one three-membered ring, these being such that the molecule possessed a threefold axis of symmetry and three vertical planes of symmetry (see Fig. 1). Such a configuration would belong to a C_{3v} point group. Other structures of lower symmetry such as one containing two five-membered rings and two four-membered rings were not excluded but considered less likely from chemical evidence.

The purpose of this paper is to report the infrared spectrum of solid and gaseous nortricyclene in the region 3 to 40 μ , the Raman spectrum of the liquid with depolarization factors and to form conclusions about its structure from the data presented. These will be drawn from empirical characteristics of the spectra, such as the presence or absence of typical bond frequencies, and also from a comparison of spectral features with those expected from selection rules of the corresponding point groups. Additional data from related compounds has been used to determine the presence or absence of degenerate modes of vibration.

Experimental

Infrared Spectra.—A sample of nortricyclene with b.p. 106° and m.p. 56° was kindly supplied for this work by Professor J. D. Roberts of the Chemistry Department, Massachusetts Institute of Technology. The infrared spectra were obtained on a modified Perkin-Elmer model 12B spectrometer in the Spectroscopy Laboratory at the

(1) Roberts, Trumbull, Bennett and Armstrong, *THIS JOURNAL*, **72**, 3116 (1950).

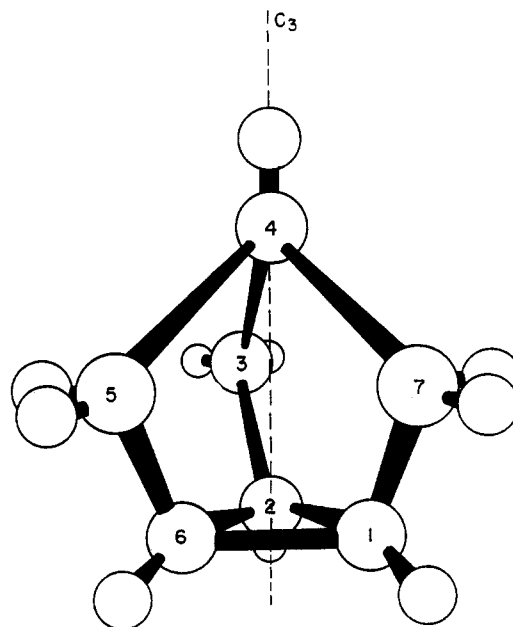


Fig. 1.—C_{3v} model.

Massachusetts Institute of Technology.² Prisms of calcium fluoride, sodium chloride, potassium bromide and thallium bromide-iodide were used in the appropriate regions from 3500 to 250 cm.⁻¹. Spectra of the solid were obtained by using liquid absorption cells of standard design. Liquid nortricyclene was placed in these cells and allowed to solidify. A Beckman IR-2 spectrometer in the Department of Chemistry at the University of Connecticut was used to rerun the spectrum of solid nortricyclene and to obtain spectra of liquid 3-bromonortricyclene in the region from 3500 to 660 cm.⁻¹. A suitable temperature control was not available to keep the sample liquid and consequently no liquid spectra were taken. The vapor spectra were obtained at

(2) Lord, Lynch, Schumb and Slowinski, *ibid.*, **72**, 522 (1950).

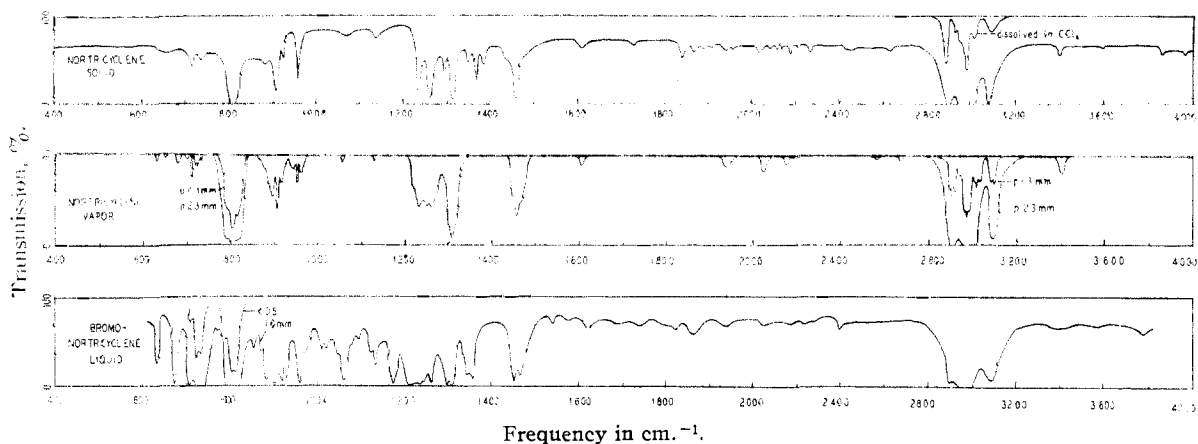


Fig. 2.—Infrared absorption spectra of nortricyclene and bromonortricyclene.

3 mm, pressure using an 80-mm. cell with potassium iodide windows. The thallium bromide-iodide prism was not used to take vapor spectra because no absorption peaks in the solid appeared below 400 cm^{-1} .

Absorption peaks obtained are accurate to 2 cm^{-1} or better in the region 250 to 1700 cm^{-1} and 5 cm^{-1} or better from 1700 to 3500 cm^{-1} . The per cent. transmission versus wave number curves for nortricyclene in the solid and vapor states are shown in Fig. 2. The absorption maxima are presented in Table I. The infrared spectrum of liquid 3-bromonortricyclene is also given in Fig. 2.

The Raman spectra were obtained in the Spectroscopy Laboratory at the Massachusetts Institute of Technology using a Zeiss three-prism instrument with a camera lens aperture number 4.5. The plate factor at 4500 \AA . was 30 \AA./mm . Excitation was accomplished using six General Electric Type AH-2 arcs filtered with 10 mm . of saturated sodium nitrite and rhodamine 5DGN extra (0.01 g./l.). The nortricyclene was kept liquid in the Raman tube by passing hot air through the central jacket of the excitation unit.³ All Raman spectra were taken at 90° . Exposure times varied from 40 to 90 minutes. The plates were read with a traveling microscope and the lines converted to wave numbers with a calibration curve made from iron arc readings. The wave number accuracy is good to 2 cm^{-1} for the sharper lines. Semi-quantitative depolarization factors were determined by a single exposure method using a split polaroid to separate the Raman beam, which was excited by radiation from a given direction, into perpendicular and parallel components. A half-wave plate placed after the polaroid was used to rotate the plane of polarization of one component approximately into the plane of the other. In this way unequal polarization of one component over the other by the spectrograph was avoided. The Raman spectrum of nortricyclene with depolarization factors is presented in Table I.

Results and Discussion

Characteristic Bond Frequencies.—Before considering any structure in detail the observed vibrational spectra will be examined for the presence or absence of characteristic bond frequencies consistent with a hydrocarbon-like substance having the molecular formula C_7H_{10} . We will restrict our examination to those spectral regions which might furnish evidence of double and triple bonds, methyl groups and carbon ring systems.

The lack of intense frequencies in the Raman spectrum near 1650 and 2150 cm^{-1} is good evidence that —C=C— and $\text{—C}\equiv\text{C—}$ functional groups are not present. This is consistent with the chemical data.¹ Weak bands at 1600 cm^{-1} in the infrared spectrum of the solid probably are due to combination or overtone frequencies. The presence or ab-

sence of methyl deformation frequencies is more difficult to ascertain because these do not differ much from those of aliphatic $\text{—CH}_2\text{—}$ groups. In general, hydrocarbons which contain —CH_3 groups show absorption maxima in the neighborhood of 1370 cm^{-1} .⁴ However, an absorption peak near this point is not positive evidence of methyl groups, as hydrocarbons which contain no —CH_3 groups sometimes have peaks near 1370 cm^{-1} . Since a weak Raman line is observed at 1374 cm^{-1} and a weak infrared absorption peak at 1373 cm^{-1} in the solid, methyl groups may or may not be present.

The evidence for a strained carbon ring system is good. In cyclopropane the ring system alters the C-H bond force constant significantly. This results in the C-H stretching frequencies appearing as high as 3103 cm^{-1} in the infrared spectrum of the vapor and 3080 cm^{-1} in the Raman spectrum of the liquid, whereas normally these stretching frequencies would appear in the neighborhood of 2960 cm^{-1} .⁵ Nortricyclene has absorption maxima near 3070 cm^{-1} in the infrared spectrum of both the solid and the vapor. The analogous band occurs at 3070 cm^{-1} in the Raman spectrum. Since double bonds are definitely absent, this is conclusive evidence that nortricyclene contains a three-membered ring. From considerations of characteristic bond frequencies little else may be concluded.

Geometrical Considerations.—Two possible geometrical structures will be considered for nortricyclene. The first, designated as I, tricyclo[2.2.1.0^{2,5}]heptane has little symmetry and belongs to the point group C_2 . In structure I the carbon atoms are connected by single bonds into a cage system consisting of two four-membered rings and two five-membered rings (see Fig. 3). A two-fold axis passes through carbon atom 7 and the middle of the connecting carbon atoms 2 and 5. In addition to I, there are several other structures of low symmetry possible, but I is the only one very likely from the chemical evidence, and will serve to indicate how all structures of low symmetry are elim-

(4) See, for example, N. B. Colthup, *J. Optical Soc. Am.*, **40**, 397 (1950).

(5) For a summary of the Raman and infrared data on cyclopropane see, G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, N. Y., 1945, p. 352.

(3) Lord and Nielsen, *J. Optical Soc. Am.*, **40**, in press. (1950).

TABLE I

Raman spectrum of liquid nortricyclene			Infrared spectrum of solid nortricyclene		Infrared spectrum of vapor nortricyclene		Infrared spectrum of liquid 3-bromonortricyclene		
Frequency in cm. ⁻¹	Relative intensity	ρ	Frequency in cm. ⁻¹	Relative intensity	Frequency in cm. ⁻¹	Relative intensity	Frequency in cm. ⁻¹	Relative intensity	
429 b	2	6/7			642	w	631	s	
639	3	6/7	640 b?	w	653	w			
					678	w	673	s	
					700-P	}			
			709	m	711-Q		m	707	s
					719-R				
			729	w	722	w	725, 735	vs	
783	5	<1/7			791-P	}	788	m	
802	8	6/7	802	vs	803-Q		vs	800, 812	vs
					815-R				
846	2	<6/7					851	m	
			872	w	895-Q-P	}	868	m	
895	6	<6/7	898	s	902-Q		s	878	s
					911-R			900	vs
913 sh	2		915	m	918	m	915	s	
					939-P	}	927	s	
951	10	<4/7	951	s	951-Q		m	956	s
					960-R				
980	3	6/7					977	m	
							1008	m	
							1016	m	
1060	9	6/7	1052	w	1058	w	1043 m, 1057	s	
1098	3						1090	m	
1129	6	6/7	1129	w	1126	w	1125, 1132	m	
1179 b	4	6/7					1170	s	
1224 b	3	6/7	1224	s	1231	s	1212, 1228	vs	
					1247	s	1240	s	
1252	5	<3/7	1252	s	1258 or 1266	s	1258	s	
1291 sh	2		1278	m	1297-P	}			
1303	7	6/7	1303	s	1305-Q		vs	1293, 1305	vs
					1315-R				
1337	2		1336	m			1339	s	
1355	4	<6/7	1354	m			1350	s	
			1373	m					
					1445-P	}			
1447	7	6/7	1446	s	1452-Q		s	1448, 1462	s
					1459-R				
			1602	w	1602	w	1602, 1617	w	
			1778	w					
			1824	w			1812	w	
							1850	m	
			1912	w			1930	w	
			2008	w			2030	w	
			2090	w					
			2145	w					
			2235	w					
2810	2	<4/7			2881-P	}			
2870	9		2871	s	2982-Q		s	2875	s
					2899-R				
			2905	m					
2912	8	<4/7	2925	s	2921	m			
2945	8	6/7	2950	vs	2948-P	}	2940	vs	
					2958-Q		vs		
					2987-R				
					2992-P	}			
2988	6	<4/7	2995	s	3002-Q		s		
3056 sh	3				3012-R				
3070	8	<4/7	3072	s	3067	s	3060	s	
					3080	s			

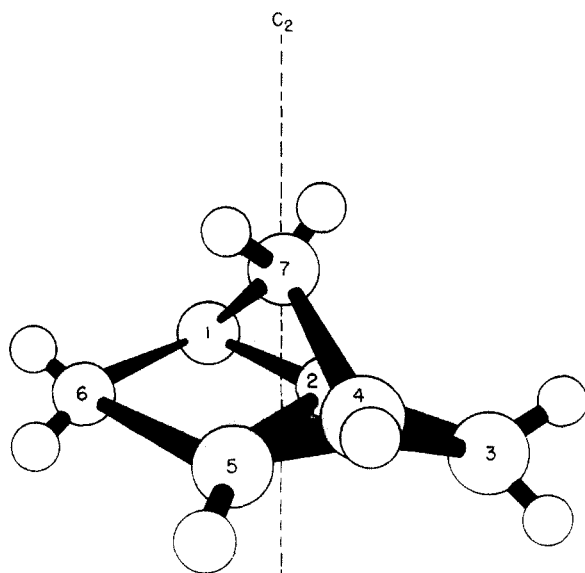
TABLE II
 PREDICTED AND OBSERVED INFRARED AND RAMAN ACTIVE FUNDAMENTAL VIBRATIONS FOR A C_2 MODEL

Symmetry type	Infrared active vibrations	Raman active vibrations	Infrared active vibrations below 1500 cm.^{-1}		Raman active vibrations below 1500 cm.^{-1}	
			Predicted	Obsd. in vapor	Predicted	Obsd.
A	23	23 ($\rho < 6/7$)	35	12 to 14	18 ($\rho < 6/7$)	7 ($\rho < 6/7$)
B	22	22			17	13

 TABLE III
 PREDICTED AND OBSERVED INFRARED AND RAMAN ACTIVE FUNDAMENTAL VIBRATIONS FOR A C_{3v} MODEL

Symmetry type	Infrared active vibrations	Raman active vibrations	Infrared active vibrations below 1500 cm.^{-1}		Raman active vibrations below 1500 cm.^{-1}	
			Predicted	Obsd. in vapor	Predicted	Obsd.
A_1	10	10 ($\rho < 6/7$)	7	12 to 14	7 ($\rho < 6/7$)	6 ($\rho < 6/7$)
A_2	0		0		0	?
E	15	15	12		12	13

inated by a consideration of the infrared and Raman data.


 Fig. 3.— C_2 model.

The second structure, II, has considerable symmetry and belongs to the point group C_{3v} . The carbon atoms of II are connected by single bonds to form a cage system consisting of three five-membered rings and one three-membered ring (see Fig. 1). A threefold axis of symmetry passes through carbon atoms 4 and the middle of the cyclopropane ring formed by carbon atoms 1, 2 and 6. All carbon atoms lie in planes of symmetry passing through the threefold axis. Structure II is in best agreement with the chemical data. We shall show that it is the only structure with enough symmetry to be consistent with the observed spectral data.

The selection rules for structure I along with the predicted and observed numbers of frequencies are shown in Table II. Every vibrational degree of freedom is active both in the infrared and Raman spectrum. So far as proof or disproof of structure I is concerned we attach little significance to the lack of agreement between predicted and observed numbers of frequencies. The relatively small number of frequencies observed both in the infrared and Raman spectrum may be due to the small change of dipole moment and of polarizability for certain modes of vibration of the hydrocarbon molecule. Furthermore, the small number of Raman lines be-

low 1500 cm.^{-1} with depolarization factors less than $6/7$ may be deceiving because our method of determination was semi-quantitative and a depolarization factor of $5/7$ could barely be distinguished from one of $6/7$. Consequently a quantitative determination of ρ might show a greater number of polarized lines.

A comparison of the infrared spectra of nortricyclene with those of 3-bromonortricyclene shows that the latter has a much richer spectrum. This would be expected to some extent, for the bromo group should cause an increase of intensity of the absorption peaks as compared to the corresponding ones in nortricyclene. However, a comparison shows an additional splitting effect for a number of bands. For example the strong band at 802 cm.^{-1} which is single in nortricyclene splits into two bands separated by 12 cm.^{-1} . A consideration of structure II shows that this splitting effect may be explained better on the basis of a structure of higher symmetry.

The strongest piece of evidence against structure I is the appearance of strong infrared and Raman frequencies near 3070 cm.^{-1} . As mentioned above this is a positive evidence for a cyclopropane ring which contradicts the postulated structure in that I contains no three-membered ring.

The selection rules for structure II along with the predicted and observed numbers of frequencies are shown in Table III. Five fundamental vibrations of symmetry type A_2 should not be active in the infrared or Raman spectrum. Since structure II must also have degenerate fundamentals of symmetry type E, this predicts a simplified vibrational spectrum. The observed spectra agree reasonably well with such a prediction. Seven Raman lines with depolarization factors less than $6/7$ are predicted below 1500 cm.^{-1} and at least six are observed in this region. Twelve depolarized Raman lines are expected in this same region and fourteen are observed. Nineteen infrared bands should persist in the vapor below 1500 cm.^{-1} , whereas twelve to fourteen are counted. This low number is probably due to the small change of dipole moment associated with a number of vibrational modes. Part of this discrepancy might be removed if the vapor spectrum was run at higher pressures or longer path lengths.

The selection rules for structure II enable one to interpret qualitatively the spectra of the substituted nortricyclenes, particularly the bromo compound.

The substitution of a bromine atom for a hydrogen atom will alter the force system as well as the geometry. The alteration of the force system will be greatest near the carbon atom to which the bromine atom is attached. To a first approximation, it may be assumed that the force system has the property that the vibrations associated with large displacements of the bromine atom are not coupled with vibrations of the rest of the molecule. We would then expect a large number of modes to be nortricyclene-like in nature and to appear in the same region as the corresponding vibrations of nortricyclene. Since the substituted group is polar an increased change of dipole moment occurs during most vibrations with a resulting increase of intensity of most absorption bands.

Because of the C_{3v} symmetry two additional effects should occur. First the modes of vibration which had symmetry type A_2 are now active and should appear as additional absorption peaks. It is hard to distinguish these from weak absorption peaks of nortricyclene which pick up intensity in the substituted compound. Secondly, the degenerate modes of vibration in nortricyclene, symmetry type E, should appear split. This splitting is the result of both a change of symmetry and of force system and should only be associated with infrared bands corresponding to Raman lines with depolarization factors equal to 6/7 in nortricyclene. Infrared bands corresponding to polarized Raman lines should not appear split.

An examination of the infrared spectra shown in Fig. 2 and presented in Table I shows several cases of infrared peaks in 3-bromonortricyclene appearing split by 8 to 13 cm^{-1} , whereas, the corresponding peaks in nortricyclene are definitely single. The most prominent examples are the doublets at 1448-1462, 1293-1305 and 800-812 cm^{-1} . Other less clear-cut examples of split peaks, because of band overlapping or low absorption intensity, are at 1212-1228, 1125-1132, 915-927 and 725-735 cm^{-1} . The Raman lines of nortricyclene which probably correspond to these peaks are observed at 1447, 1303, 802, 1224 and 1129 cm^{-1} , respectively, and have depolarization factors equal to 6/7 within the experimental error. No Raman line is observed near 735 cm^{-1} while one at 913 cm^{-1} was too weak to have its depolarization factor measured. Raman lines with depolarization factors less than 6/7 are found at 783, 846, 895, 951, 1252 and 1355 cm^{-1} , respectively. An examination of the infrared spectrum of 3-bromonortricyclene near these regions shows no clear-cut evidence that the peaks are split. The very intense doublet near 805 cm^{-1} obscures a comparison with the 783 cm^{-1} Raman line. However, the 805 cm^{-1} doublet, in addition to being double, shows a shoulder which may correspond to the 783 cm^{-1} Raman line. The peaks at 851, 1258 and 956 cm^{-1} , respectively, in the bromo compound definitely are not split. The latter peak probably corresponds to the totally symmetric carbon cage frequency which occurs at 951 cm^{-1} in nortricyclene. The peak at 1355 cm^{-1} appears close to another at 1337 cm^{-1} and could perhaps be considered double. However, the infrared spectrum of solid nortricyclene as well as the Raman

spectrum show peaks near 1356 and 1337 cm^{-1} and suggest that the former two do not arise from the splitting of a doubly degenerate frequency. In liquid infrared spectra taken of 3-carboxynortricyclene and 3-hydroxynortricyclene the 802 cm^{-1} frequency again appears as a doublet separated by about 10 cm^{-1} . This frequency probably corresponds to a doubly-degenerate cage-breathing frequency.

The symmetry of structure II demands that the molecule possess two equal moments of inertia. Consequently the vibration-rotation band envelopes in the infrared spectrum of the vapor should be typical of a symmetric top molecule. Gerhard and Dennison have related the form of parallel and perpendicular bands of symmetric top molecules to the parameter ($\beta = I_A/I_C - 1$), where I_A and I_C are the respective moments of inertia of the molecule.⁶ For a cage molecule such as nortricyclene β might be zero or nearly zero which would correspond to an accidental spherical top, and excluding other factors, parallel bands would be the same as perpendicular bands. However, the rotational energy levels in a vibrational state of a symmetric top molecule in which one degenerate vibration is excited will be split by Coriolis coupling, and even though the molecule approximates a spherical top the perpendicular bands should be distinguishable from the parallel bands where weak Coriolis coupling occurs.⁷ We have calculated a value of 0.11 for β using 238×10^{-40} and 215×10^{-40} g. cm^2 for I_A and I_C , respectively. The following values for interatomic distance and angles were assumed in the calculation of I_A and I_C : C-C, 1.54 Å., C-H, 1.08 Å., $C_1-C_2-C_3$ angle, 100° , $C_2-C_3-C_4$ angle, 100° , $C_3-C_4-C_5$ angle, 105° , and C_4-C_3-H angle, 112° (see Fig. 1). The bond angles used represent values which approximate minimum strain for the equilibrium configuration of the molecule. It is difficult to predict the band contour in detail but as a general rule parallel bands have a strong Q branch which is resolved from the envelopes of the P and R branches. Perpendicular bands usually show less clearly resolved P , Q and R envelopes because of their more complicated structure.

The vapor spectrum shows two types of bands with envelopes of the form described above. Absorption peaks at 950, 902 and 711 cm^{-1} resemble parallel bands, while the remaining strong peaks below 1500 cm^{-1} correspond to perpendicular bands. For a C_{3v} model the former must coincide with polarized Raman lines. Actually the Raman lines at 951 and 895 cm^{-1} are polarized. No Raman line has been observed near 711 cm^{-1} . A comparison of the remaining polarized lines shows that none coincide with a band in the vapor infrared spectrum which has perpendicular-like contours. In connection with this the selection rules for structure II demand that the perpendicular bands be degenerate and thus split in 3-bromonortricyclene. Actually the intense bands near 804, 1304 and 1452 cm^{-1} all are double in this compound.

(6) Gerhard and Dennison, *Phys. Rev.*, **43**, 197 (1933).

(7) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, N. Y., 1945, p. 403.

Using the formula given by Gerhard and Dennison⁶ and our calculated values of I_A and I_C , we have evaluated for parallel bands the separation in cm.^{-1} of the maximum of a P branch from that of a R branch at 27° as 20 cm.^{-1} . The observed value of this separation for the parallel band with its center at 951 cm.^{-1} is 21 cm.^{-1} . This agreement between observed and calculated separations indicates that the moments of inertia of nortricyclene do not differ greatly from those calculated and that its actual shape does not differ much from that of structure II.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

An X-Ray Diffraction Study of Calcium Stearate Monohydrate-Cetane Systems^{1,2}

BY ROBERT D. VOLD AND THOMAS D. SMITH³

This paper describes a study by X-ray diffraction methods of the system calcium stearate monohydrate-cetane as conditioned by variations in composition and thermal history. These systems are particularly interesting, as it is known that the addition of water to anhydrous calcium stearate-cetane systems results in a considerable increase in stability,^{4,5} and it is important to attempt to discriminate between phase state and colloidal structure as the primary cause of this effect. A similar study of the anhydrous system has already appeared.⁶

The X-ray experiments were carried out at room temperature on quenched systems subjected to different temperatures of initial heating, and on systems subjected to controlled slow cooling. It is possible to derive information on the possible phase state of the system both at room temperature and at elevated temperatures from the resultant patterns, although this process is complicated by the question of degree of reversibility at transitions on cooling through a succession of phases.

A comparison of the behavior of anhydrous and hydrous systems was made, and the role of water and cetane in the system is discussed. The conditions of decomposition and formation of the hydrate were examined and are discussed in relation to the degree of dehydration at elevated temperatures. The occurrence of a hitherto unreported modification⁷ of calcium stearate in systems containing both cetane and water is also

reported. This modification appears to differ from the usual form of calcium stearate VI-H only in the degree of randomness of its crystal structure. Consequently the possibility must be considered that *different types of disorder* of the crystal structure of a single phase as well as *different sorts of orderly arrangement* (different phases) can contribute to the number of realizable, discrete, solid modifications.

Experimental Methods

Materials.—Calcium stearate monohydrate (laboratory no. 5R3AH) was made from stearic acid by metathesis with calcium chloride in aqueous methanol.⁸ The acid had been purified from Armour Neofat 1-65 by two recrystallizations from acetonitrile and had the following characteristics: iodine value (Wijs), 0.34; equiv. wt., 286.5. The hydrate contained 2.97% water, determined by drying to constant weight at 110° (calcd. 2.88%), and was in a crystal form which, on dehydration, gave the anhydrous soap in the VIA crystal form.^{8,9}

The cetane was obtained from the du Pont Co., freed from dissolved air by sweeping with nitrogen, and dried over calcium chloride.

Procedure.—Calcium stearate monohydrate, taken directly from the stock bottle, and cetane, were weighed into dry, Pyrex glass tubes, mixed thoroughly and sealed. For systems which were to be cooled from temperatures greater than 130° , the tubes were maintained at the desired temperature for 2 hours before being quenched in a Dry Ice-acetone freezing mixture, or before being cooled slowly at 0.5° per minute. If the systems were to be heated at lower

(8) M. J. Vold, G. S. Hattiangdi and R. D. Vold, *J. Colloid Sci.*, **4**, 93 (1949).

(9) X-Ray diffraction patterns of the polymorphic forms of anhydrous calcium stearate designated as VI-A, VI-H and VI-N are presented in reference 8. The long spacing given by the present preparation of calcium stearate is slightly shorter than the previously reported value,¹⁰ possibly because of impurities,¹¹ and there are indications of some slight tendency toward a VI-H rather than a VI-A pattern, such as the abnormal weakness of the usual peak at 3.70 \AA .^{8,10,12} although in general the remainder of the pattern is similar.

The diffraction pattern of the anhydrous VI-H form is indistinguishable from that of calcium stearate monohydrate. However, in the present work calcium stearate crystallized dominantly in the VI-A form which has a pattern easily distinguishable from that of the hydrate, thus permitting recognition of changes in the extent of hydration of the system.

(10) R. D. Vold, J. D. Grandine, 2nd., and M. J. Vold, *J. Colloid Sci.*, **3**, 339 (1948).

(11) R. D. Vold and G. S. Hattiangdi, *Ind. Eng. Chem.*, **41**, 2311 (1949).

(12) M. J. Vold and R. D. Vold, *J. Am. Oil Chem. Soc.*, **26**, 520 (1949).

(1) Presented in part before the Division of Colloid Chemistry at the 115th Meeting of the American Chemical Society, San Francisco, Calif., March, 1949.

(2) This work is part of a project "Phase Studies of Greases" supported by the Office of Naval Research, Contract No. N6-onr-238-TO-2; NRO57057.

(3) Department of Colloid Science, Cambridge University, England.

(4) D. H. Birdsall and B. B. Farrington, *J. Phys. Colloid Chem.*, **52**, 1415 (1948).

(5) R. J. Coswell, "A Study of the Pressure Stability of Calcium Stearate-Cetane Systems Containing Additives," M.S. Thesis, University of Southern California, 1949.

(6) R. D. Vold and M. J. Vold, *J. Phys. Colloid Chem.*, **52**, 1424 (1948).

(7) The term "modification" is here used in a sense similar to that of K. J. Mysels and J. W. McBain [*ibid.*, **52**, 1471 (1948)] to denote a material having clearly different properties but without commitment as to its phase nature.