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

Vibrational Spectra of 1,3,5-Cycloöctatriene, Bicyclo[4.2.0]octa-2,4-diene and their Dichlorides

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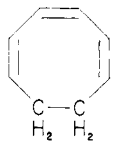
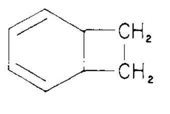
The infrared and Raman spectra of 1,3,5-cycloöctatriene, bicyclo[4.2.0]octa-2,4-diene, 1,6-dichloro-1,3,5-cycloöctatriene and 7,8-dichloro-bicyclo[4.2.0]octa-2,4-diene are reported and discussed. The spectra show clearly that the structures indicated by the names of these compounds are correct, in accordance with previously published chemical evidence.

As part of a spectroscopic investigation of the structures of cycloöctatetraene and closely related compounds,[1–3] the infrared and Raman spectra of 1,3,5-cycloöctatriene (I) and its isomer bicyclo-[4.2.0]octa-2,4-diene (II) have been obtained.

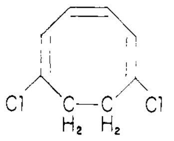


I

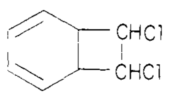


II

Dichlorides of these compounds, 1,6-dichloro-1,3,5-cycloöctatriene (III) and 7,8-dichloro-bicyclo[4.-2.0]octadiene (IV), have been studied.



III



IV

The spectroscopic results and an interpretation of them are presented here because of their pertinence to a parallel investigation of the vibrational spectra and structure of 1,3,5-cycloheptatriene.[4]

It has been shown conclusively by Cope, Haven, Ramp and Trumbull[5] that structures I and II are in mobile equilibrium at 100°. It is possible to prepare each isomer in pure form at room temperature, however, and the present spectroscopic studies were carried out with samples furnished by Professor A. C. Cope. A similar equilibrium presumably should exist between structure III and the analogous bicyclic compound (1,6-dichlorobicyclo[4.2.0]octa-2,4-diene), and also between structure IV and the eight-membered ring compound 7,8-dichloro-1,3,5-cycloöctatetraene. However these interconversions have not yet been reported. IV was first reported by Reppe and coworkers[6] and its preparation and structure further investigated by Cope and Burg.[7] III has been synthesized by Cope and Schmitz.[8]

Experimental

The sample of 1,3,5-cycloöctatriene (I) gave $n^{25}\mathrm{D}$ 1.5249, that of bicyclo[4.2.0]octa-2,4-diene (II), $n^{25}\mathrm{D}$ 1.5035, that of 1,6-dichloro-1,3,5-cycloöctatriene (III), $n^{25}\mathrm{D}$ 1.5651, and that of 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene (IV), $n^{25}\mathrm{D}$ 1.5388. The infrared absorption spectra of I, II and IV have been published by Cope, *et al.*,[5,7] and the data given here were obtained from their original curves. The Raman spectra were photographed with the techniques described previously.[1] The numerical results are listed in Tables I and II. It is estimated that the Raman frequencies are accurate to 2–3 cm.$^{-1}$ except for weak or fuzzy lines. The infrared frequencies are about equally reliable below 1500 cm.$^{-1}$, but at the higher frequencies the error rises gradually to about ±20 cm.$^{-1}$ at 3000 cm.$^{-1}$.

Discussion of Spectra of I and II

The spectra of I and II differ considerably, and it is obvious that two different structures are involved. Both infrared and Raman spectra for both compounds show many frequencies, as is to be expected for non-symmetrical structures. With few exceptions the infrared frequencies coincide within experimental error with those of Raman lines. Each isomer has 48 vibrational degrees of freedom, of which 38 should correspond to frequencies below 1700 cm.$^{-1}$. About 30 of the latter are actually observed in the Raman spectrum of I and about 20 in that of II.

The main features of the infrared and Raman spectra of both compounds are those to be expected from the structures I and II suggested by chemical evidence.[5] In particular the spectra of II bespeak its bicyclic structure. A comparison of the Raman spectrum with that of 1,3-cyclohexadiene[9] shows that the two molecules have many frequencies in common. The most significant of these are the pair at 1579 and 1608 cm.$^{-1}$ in II, which occur at 1576 and 1615 in 1,3-cyclohexadiene. The intensity ratio is about 10:1 in both compounds. The olefinic CH stretching frequencies appear at 3030 and 3057 in II and two of the three frequencies in cyclohexadiene lie at 3041 and 3056. The latter is markedly weaker in both cases. The unusual position of the double-bond frequencies is due both to conjugation and slight ring strain, which also has the effect of raising the CH stretching frequencies.[2]

The infrared and Raman spectra of 1,3,5-cyclo-

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(1) E. R. Lippincott, R. C. Lord and R. S. McDonald, THIS JOURNAL, **73**, 3370 (1951).

(2) R. C. Lord and R. W. Walker, *ibid.*, **76**, 2518 (1954).

(3) In addition to the foregoing, infrared and Raman studies of cycloöctane and cycloöctane-d_{16}, cycloöctene, 1,3- and 1,5-cycloöctadienes, 1,3,6-cycloöctatriene and cycloöctatetraene oxide, chloride and bromide have been carried out and are being prepared for publication.

(4) M. V. Evans and R. C. Lord, Abstracts, 130th Meeting, American Chemical Society, Atlantic City, N. J., Sept., 1956.

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

(6) W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

(7) A. C. Cope and M. Burg, THIS JOURNAL, **74**, 168 (1952).

(8) Private communication from Professor A. C. Cope, who kindly furnished us with a sample of III for Raman study, as well as with its infrared spectrum.

(9) J. W. Murray, *J. Chem. Phys.*, **3**, 59 (1935) and references there cited.

TABLE I

RAMAN AND INFRARED FREQUENCIES IN CM.$^{-1}$ OF COMPOUNDS I AND II[a]

1,3,5-Cycloöctatriene (I)				Bicyclo[4.2.0] octa-2,7-diene (II)			
Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared
140 (4br)			1235 msh	195 (3)		1442 (1)	1440 s
227 (4)		1289 (4)	1285 s	258 (0)			1445 s
260 (4)		1325 (3)	1320 m	295 (0)		1520 (0)	
295 (4)		1360 (1)	1355 m	416 (1)		1579 (10)	1579 s
342 (5)		1385 (0)	1380 w	498 (1)		1608 (1)	
409 (5)		1421 (2)		643 (0)	655 m	1638 (1)	1645 m
531 (3)		1446 (9br)	1440 s	702 (2)	709 s		1710 ms
570 (5)			1455 s		735 m		1900 w
652 (0)	652 m	1520 (0)			777 ms		2170 w
708 (0)	704 s	1558 (1)		811 (2)	813 m		2220 w
740 (2)	740 s	1587 (1)			850 m		2310 w
782 (0)	775 s	1612 (10)	1610 m	920 (4)	992 s		2600 w
818 (5)	813 s	1639 (8)	1638 m	957 (3)	961 s	2855 (0)	
848 (4)	846 s		1680 mw		985 m	2888 (1)	
862 (0)	867 m		1730 w	1050 (3)	1055 s	2928 (1b)	2800
916 (2)	915 m		1780 mw	1100 (1)	1102 s	2951 (1)	to vs
	953 s		1810 w	1154 (1)	1150 m	2968 (1)	
969 (5)	964 m		1870 w	1180 (1)	1170 mw	3030 (5)	3025
987 (4vbr)			1925 mw	1220 (0)	1218 m	3057 (1)	
1024 (1)	1020 w		2320 m		1230 s		
	1036 m		2690 m		1248 m		
1051 (1)	1050 m	2840 (2)		1317 (2)	1316 m		
	1068 s	2910 (5)	2780		1375 s		
1179 (0)	1172 s	2964 (5)	to vs	1414 (2)	1420 s		
1235 (0br)	1223 s	3010 (5)	3010				

[a] Raman intensities, estimated by eye on a scale relative to 10 for the strongest line, are shown in parentheses after the frequencies. Infrared absorption is described qualitatively (s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder) for a liquid sample of 0.025 mm. thickness.

TABLE II

RAMAN AND INFRARED FREQUENCIES IN CM.$^{-1}$ OF COMPOUNDS III AND IV[a]

1,6-Dichloro-1,3,5-cycloöctatriene (III)				7,8-Dichloro-bicyclo[4.2.0]octadiene-2,4 (IV)			
Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared
151 (6)		1082 (6)		136 (5)		1090 (3)	1073 m
168 (4b)				152 (4)			1092 s
251 (8)				189 (4)		1126 (3)	1128 m
289 (9)				273 (3)		1154 (2)	1153 m
323 (3)		1195 (4)	1192 w	313 (5)		1180 (9)	1179 m
354 (6)				378 (5)		1200 (2)	1202 s
403 (6)		1231 (4)	1230 w	418 (5)		1229 (3)	1220 wb
430 (7)		1256 (8)	1250 w			1243 (3)	1245 s
470 (5)		1302 (3)	1300 w			1290 (5)	1286 s
486 (3)		1322 (3)	1330 w			1316 (4)	1316 s
501 (8)				498 (3)		1327 (3)	1329 s
599 (8)		1353 (5)	1352 w	548 (4)			
		1383 (4)	1383 w	576 (5)		1379 (4)	1378 s
652 (5)	625 m	1424 (4)		603 (3)		1416 (6)	1413 s
		1436 (7)	1435 s		650 m		1450 w
692 (4)	689 s			684 (1)			1458 w
	731 w	1582 (4)		717 (3)	705	1588 (>10)	1586 s
784 (7)	752 w	1609 (>10)	1610 m	744 (5)	to vs		
	782 s	1640 (8)	1637 s		760	1646 (3)	
795 (7)	797 s			789 (8)	782 s		1683 m
859 (>10)	856 s			853 (4)	835		1737 m
					to vs		1935 w
881 (6)	880 m				863		2395 w
896 (7)	896 m				890 m		2460 w
912 (2)	917 m	2848 (3)		915 (4)	914 m		2690 w
954 (3)	955 m	2910 (7)	2840 w	954 (5br)	952 mbr	2916 (7)	2900
		2933 (5)	2930 m		975 m		to s
973 (8)	975 m	2964 (5)		1010 (2)	1000 m	2962 (8)	2950
	1008 w	3020 (8)	3010 m		1012 mw		
1058 (5)	1060 vs			1055 (1)	1056 s	3049 (9)	3035 s

[a] For abbreviations see Table I, footnote *a*.

octatriene are in agreement with structure I. Intense double-bond frequencies appear in the Raman effect at 1612 and 1639 cm.$^{-1}$. The separation of these two frequencies is similar to that found in the spectrum of II but their center of gravity lies some 30 cm.$^{-1}$ higher. This difference is believed to be due to difference in strain between the six- and eight-membered rings. In 1,3,6-cycloöctatriene[3] the unconjugated double bond shows a frequency of 1652, while the conjugated double bonds show frequencies with a center of gravity near 1620. The difference in strain also appears in the olefinic CH stretching frequencies of I, which are found near 3010 cm.$^{-1}$.

Both I and II should have numerous skeletal vibrations of low frequency, but since the bicyclic structure is presumably tighter than the eight-membered ring, the former's skeletal frequencies should be somewhat higher on the average. The Raman spectrum of I has eight frequencies below 600 cm.$^{-1}$ while II has only five, and the lowest frequencies observed for I and II are, respectively, 140 and 195 cm.$^{-1}$.

Finally the relative exposure times required to obtain Raman spectra with equal intensities for corresponding frequencies were about a factor of two longer for II than for I. For the same amount of incident visible light flux, these exposure times depend on the polarizabilities of the respective molecules. Conjugation may be expected to increase the polarizability of a given molecule and in particular a system of three conjugated double bonds may be expected to have a greater polarizability than one of two conjugated double bonds. Therefore the significantly shorter exposure time needed for I is a qualitative indication of a larger number of conjugated double bonds.

Discussion of the Spectra of III and IV

The Raman frequencies and infrared absorption maxima for III and IV appear in Table II. Since III and IV are dichloro derivatives of I and II, their infrared and Raman spectra are expected to resemble closely those of the parent compounds. The chief spectral characteristics of I and II are in fact found in the respective dichloro derivatives and may be used to support the structures assigned to III and IV on chemical grounds.

Compound IV has strong Raman lines at 1588 and 3049 cm.$^{-1}$ (corresponding to the infrared bands at 1586 and 3035), which are frequencies typical of the 1,3-cyclohexadiene ring. No Raman frequencies or strong infrared bands are observed near 1440 cm.$^{-1}$, which is evidence against CH_2 groups in IV, and establishes that the chlorine atoms are in the 7,8-positions. The carbon–chlorine stretching frequency appears at about 740 cm.$^{-1}$, in confirmation of the placement of the chlorines, since a frequency near this value is characteristic of the aliphatic C–Cl bond.

In compound III the double-bond frequencies appear at 1582 (medium), 1609 (very strong) and 1640 (strong) in the Raman effect, in agreement with the values found in I. The C–H stretching frequencies at 3010 cm.$^{-1}$ also fall where one expects them for the eight-membered ring of I. In both infrared and Raman spectra the CH_2 deformation frequency is observed at 1436, in contrast to the spectrum of IV. This frequency taken together with the chemical evidence shows that the chlorine atoms must be attached to one of the olefinic carbons. In further support of the location of the chlorine atoms one can cite the very intense unsaturated C–Cl stretching frequency found at 859 cm.$^{-1}$ in the Raman spectrum.

Finally there is some less definite evidence consistent with the structures III and IV. As was the case with I and II, compound III required much shorter exposure times than IV to obtain satisfactory Raman spectra. This would be expected from the larger number of conjugated double bonds in structure III. In addition more Raman lines are found below 600 cm.$^{-1}$ in the spectrum of III than in that of IV (eleven *vs.* eight). This frequency region is that of the skeletal vibrations, and it is to be expected that the eight-membered ring would exhibit its skeletal frequencies at lower values than those of the tighter bicyclic structure. Thus both the specific values of the group frequencies and these more general features of the spectrum support the structures accepted on chemical grounds.

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