The Vibrational Spectra and Structure of 1,4,7-Cyclononatriene and Related Derivatives

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Abstract: The infrared (4000–250 cm^{-1}) and Raman (3100–175 cm^{-1}) spectra of solutions of 1,4,7-cyclononatriene (1,4,7-CNT) have been obtained. The infrared vapor phase spectrum of this material in the 4000–600-cm^{-1} region is measured using a cell of 10-m path length. The infrared spectra of 1,4,7-cyclononatriene-d_2 (4000–660 cm^{-1}), 2,5,8-cyclononatrienol (4000–325 cm^{-1}), and 2,5,8-cyclononatrienone (4000–325 cm^{-1}) have also been obtained. The number of infrared- and Raman-active vibrational modes has been calculated for six different conformations (see Figure 1) of 1,4,7-CNT. The *cis–cis–trans* and conformation I of the *trans–trans–trans* structures have C_1 symmetry while the *cis–cis–cis* (saddle conformation) and *cis–trans–trans* structures belong to the C_s point group. Each of these four structures has 57 Raman- and infrared-active nondegenerate vibrations. Conformation II of the *trans–trans–trans* structure belongs to the C_3 point group and has 38 infrared- and Raman-active modes, while the crown conformation of the *cis–cis–cis* structure belongs to the C_{3v} point group and is expected to have 30 infrared- and Raman-active modes. The observed infrared and Raman spectra agree well with predictions made on the crown conformation for 1,4,7-CNT, both regarding the number of the bands as well as the polarization of the Raman lines. The same structure was also assigned to 1,4,7-cyclononatriene-d_2 and 2,5,8-cyclononatrienol because of the similarity of the spectra of these compounds to that of 1,4,7-CNT. The assignment of the observed bands in the spectra of these three compounds was made on the basis of crown structure. The structure of 2,5,8-cyclononatrienone could not be determined from the infrared spectrum alone because the observed bands could be assigned to group vibrations equally well on the basis of two different structures, *cis,cis,cis*-2,5,8-cyclononatrienone (crown conformation) or *trans,trans,trans*-2,5,8-cyclononatrienone.

The synthesis of 1,4,7-cyclononatriene and the infrared spectrum of a dilute solution of the compound was reported by Radlick and Winstein.[2a] Untch[2b] reported the infrared spectrum of the compound in the vapor phase. Since neither of the reported spectra contained many bands and since the Raman spectrum was not obtained by these workers, a complete structural examination and assignments of the spectral bands could not be made.

In the present work, the infrared spectra of 1,4,7-cyclononatriene in solution and in the vapor phase as well as the Raman spectrum in solution were obtained. The structure of the molecule was determined through the analysis of these spectra. The assignment of the spectral bands of 1,4,7-cyclononatriene to the various vibrational modes of the molecule was aided by a study of the infrared spectra of related compounds.

Experimental Section

A. **Infrared Spectra.** Samples of 1,4,7-cyclononatriene (1,4,7-CNT), 2,5,8-cyclononatrienol (2,5,8-CNT-ol), and 2,5,8-cyclononatrienone (2,5,8-CNT-one) were synthesized, purified, and kindly supplied to us by the members of the research group of Dr. S. Winstein of this department.

The infrared spectra from 4000 to 600 cm^{-1} were obtained by using a Perkin-Elmer Model 421 spectrophotometer. The instrument was calibrated to an accuracy of ±4 cm^{-1} by using water vapor and carbon dioxide gas spectra. The reproducibility of bands in the solutions studied was 5 cm^{-1}.

Infrared spectra in the 910–325-cm^{-1} region were obtained using a Beckman CsBr IR5A spectrophotometer. A reproducibility of 3 cm^{-1} was obtained in recording the sharp absorption bands.

A Beckman spectrophotometer Model IR7 was used to obtain the infrared spectrum of 1,4,7-CNT in the 700–250-cm^{-1} region. A reproducibility of 1 cm^{-1} was observed in the frequency of solvent peaks. Frequencies obtained using this instrument agreed to within 3 cm^{-1} with those obtained using the Beckman CsBr IR5A and to within 4 cm^{-1} with those obtained using the Perkin-Elmer 421.

Infrared spectra of 1,4,7-CNT, 1,4,7-CNT-d_2, 2,5,8-CNT-ol, and 2,5,8-CNT-one (see Tables I–IV, respectively) at several concentrations in carbon disulfide and chloroform solutions were obtained in the 4000–325-cm^{-1} region, and the infrared spectrum of a solution of 1,4,7-CNT in *n*-hexane was obtained in the 700–250-cm^{-1} region. Sodium chloride (0.1-mm path length) and potassium bromide (0.4-mm path length) cells were used in the 4000–325-cm^{-1} region; a cesium iodide absorption cell was used in the 700–250-cm^{-1} region. The infrared spectrum of 1,4,7-CNT-d_2 in carbon tetrachloride solution was recorded on the Perkin-Elmer Model 421. Compensating cells containing the solvent were inserted in the reference beam of the Perkin-Elmer 421 during the recording of the solution of 1,4,7-CNT and 1,4,7-CNT-d_2. Air was present in the reference beam when the spectra of the other compounds were obtained.

The infrared spectrum of 1,4,7-CNT vapor was obtained on the Perkin-Elmer Model 421 using a Perkin-Elmer gas cell with a path length of 10 m. Nitrogen was present in the reference beam. The frequencies and intensities of the important bands appearing in the vapor and solution are compared in Table V.

All of the bands that were observed in the spectrum of the vapor also appeared in the solution spectra. Since some bands of lesser intensity were observed in the solution spectra but were not observed in the vapor spectrum, the solution spectra are considered in the discussion that follows.

The bands observed in the infrared spectrum of 1,4,7-cyclononatriene are listed in Table I. Those above 650 cm^{-1} were obtained from the Perkin-Elmer 421 data while those below 650 cm^{-1} were obtained from the Perkin-Elmer 421 data while those below 650 cm^{-1} were obtained from the Beckman IR7 data. The frequencies reported here above 650 cm^{-1} are those for which the solvent correction was least. All frequencies are given in air because the correction to vacuum is so small compared with the estimated error.

Bands are designated as very strong (vs), strong (s), medium (m), weak (w), or very weak (vw), depending upon their relative absorbance. Peaks that are shoulders (sh) to stronger peaks are noted.

B. **Raman Spectra.** A Cary Instrument Model 81 Raman spectrophotometer was used to obtain the Raman spectrum of 1,4,7-cyclononatriene in CS_2 from 3100 to 175 cm^{-1}. A wavenum-

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[1] (a) This work is in partial fulfillment of the M.Sc. requirement at UCLA. (b) Alfred P. Sloan Fellow.

[2] (a) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963); (b) K. Untch, *ibid.*, **85**, 345 (1963).

Table I. The Infrared Spectrum[a] of 1,4,7-CNT Solution

Wavenumber, cm^{-1}	Intensity	Assignment[b]
3318	vw	3010 + 304 = 3314
3265	vw	2958 + 304 = 3262 1637 × 2 = 3274
3239 sh	vw	3010 + 228 = 3238 2856 + 384 = 3240
3176	vw	2958 + 228 = 3186
3045	m	20
3010	vs	1, 21
2958	s	2
2924	s	22
2906	s	3
2889	vw	1637 + 1250 = 2887
2856	s	23
2819	vw	1637 + 1175 = 2812 1438 + 1383 = 2821
2770	w	1383 × 2 = 2766
2752	w	
2710	vw	1468 + 1250 = 2718 1438 + 1274 = 2712
2568	vw	1669 + 904 = 2573 1637 + 932 = 2569 1383 + 1175 = 2558
1721	vw	960 + 757 = 1717
1669	m	24
1650	vw	1274 + 383 = 1657 932 + 727 = 1659 932 + 714 = 1646
1637	s	4
1473	s	5
1463	ss	
1438	m	25
1398	vw	727 + 666 = 1393
1383	m	26
1304	vw	714 + 594 = 1308
1274	m	27
1250	m	28
1175	w	6
1045	w	
1030	w	14
1018	w	
960	s	29
932	s	7
904	vw	15
875	vs	30
830 sh	vw	594 + 228 = 822
792	w	567 + 228 = 795
757		31
727	vs	8
714	vs	32, 33 (?)
666		9
594	m	10
567	w	34
545		35
503	m	36
383	w	11
304	s	37
228		38

[a] Thirteen weak bands also appeared in the spectrum between 1735 and 2527 cm^{-1} which could be assigned as combination bands. These bands are not included in this table for space restriction. [b] See also Table III.

ber accuracy of ±2 cm^{-1} was obtained by using the carbon disulfide band at 796.0 cm^{-1}, and the reproducibility of the instrument was estimated to be 6 cm^{-1}. Solvent emission lines obscured the 825–775- and 700–610-cm^{-1} spectral regions. Bands were said to be depolarized (dp) if the depolarization ratio was greater than or equal to $^6/_7$ (0.86) and to be polarized (p) if it was less than $^6/_7$. Bands of uncertain polarization are indicated in Table I. Polarization data were used to discriminate between vibrations of symmetry a_1 (polarized) and the others (depolarized).[3]

Table II. Frequencies and Assignments of Infrared Bands of 1,4,7-CNT-d_2 in Solution

Wave-number,[a] cm^{-1}	Intensity	Assignment
3590	vw	2125 + 1460 = 3585
3256	w	2962 + (304) = 3266 1633 × 2 = 3266
3180	vw	2962 + (228) = 3190
3051	m	20
3018[b]	vs	1
2962	s	2
2955sh	s	
2930	s	22
2908	m	3
2864	m	23
2770	w	1387 × 2 = 2774
2755	w	2215 + (545) = 2760 1659 + 1089 = 2748
2268	vw	1437 + 822 = 2259 1089 + 1175 = 2264
2226	w	C–D asymmetric stretching (split into triplet by Fermi resonance with 1387 + 822 = 2209 1250 + 963 = 2213)
2215	m	
2192	w	
2166 sh	vw	1460 + 701 = 2161
2125	m	C–D symmetric stretching (split by Fermi resonance with 1387 + 723 = 2110)
2103	m	
2070	vw	1250 + 822 = 2072
1926 sh	vw	1387 + (545) = 1932 963 × 2 = 1926
1911	vw	1089 + 822 = 1911
1872	w	1272 + (594) = 1866 963 + 907 = 1870
1787	w	1089 + 701 = 1790 963 + 822 = 1785
1659	m	24
1633	m	4
1460	s	5
1437	vw	25
1424	vw	822 + (594) = 1416 723 + 701 = 1424
1387	m	26
1367	vw	822 + (545) = 1367 701 + 664 = 1365
1348	vw	963 + (383) = 1346 (?)
1306	vw	710 + (594) = 1304
1272	w	27
1250	w	28 (split by Fermi resonance with 701 + (545) = 1246)
1238	w	
1175	w	6
1089	m	CD_2 bending
963	m	29
923 sh	w	7
907	s	CH_2 wagging
881	m	30
856	w	(304) + (545) = 850
822	s	CD_2 twisting
723[b]	s	8
710[b]	vs	32,33
701[b]	s	CD_2 wagging
664[b]	w	9

[a] In CCl_4. [b] Indicates bands obtained from spectrum of 1,4,7-CNT-d_2 isolated after 16 min.

All of the bands that appeared in the Raman spectrum of 1,4,7-CNT also appeared in the infrared spectra of solutions of this material. The maximum difference between corresponding bands in the two spectra was 9 cm^{-1}, which was within the experimental error. The frequencies of the observed Raman lines, their polari-

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(3) G. R. Harrison, R. C. Lord, and J. R. Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1948, p 520.

Table III. Frequencies and Assignments of Infrared Bands of 2,5,8-CNT-ol in Solution

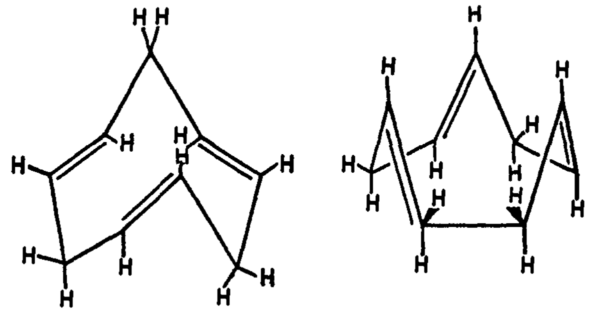
Wavenumber, cm^{-1}			
In CS$_2$	In CHCl$_3$	Intensity	Assignment
3602	3602	s	O–H stretching
3124		w	1670 + 1462 = 3132 (?)
3048		w	20
3011		vs	1
2960	2967	s	2
2951		s	
2926	2931	s	22
2903	2907	s	3
2862	2868 sh	m	23
	2185	w	1462 + 722 = 2184 (?)
1670		m	24
1639	1639	s	4
	1462	s	5
	1387	w	
1374 sh	1375	w	26
1330		w	757 + (567) = 1324
1287		m	27
1269		w	
1248		m	28
1230 sh		w	
1209		m	C–O–H deformation (ip) split by Fermi resonance with (666) + 546 = 1212
1200 sh		w	
1184		w	6
1032		vs	C–O stretching split by Fermi resonance with 722 + (304) = 1026
1022 sh		vs	
976	975 sh	w	29
962	965	s	
948	946	w	
921		s	7
879	881	s	30
757		vs	31 (CH$_2$ rocking) C–O–H deformation (op)
722		vs	8
715		vs	32, 33
592	594	w	10
546	547	vw	35
504		vw	36
	432	w	Crown point rocking

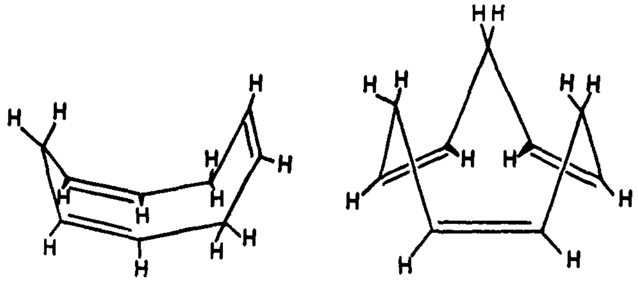
zation, as well as their relative intensities for 1,4,7-CNT in CS$_2$ are given in Table VI.

Interpretation of the Spectra

A. Possible Structures. Radlick and Winstein[2a] concluded that the structure of the molecule was *cis,cis,cis*-1,4,7-CNT (crown conformation) from study of proton magnetic resonance, ultraviolet, and infrared spectra.

In the present work the number of infrared- and Raman-active vibrational modes was calculated for all four possible structures (six conformations) (see Figure 1) and listed in Table VII. *cis,cis,trans*-1,4,7-CNT and *trans,trans,trans*-1,4,7-CNT (conformation I) belong to symmetry point group C$_1$, while *cis,cis,cis*-1,4,7-CNT (saddle conformation) and *cis,trans,trans*-1,4,7-CNT belong to symmetry point group C$_s$. These four structures of low symmetry have 57 Raman- and infrared-active vibrational modes and no inherent degeneracies. *trans,trans,trans*-1,4,7-CNT (conformation II) belongs to symmetry point group C$_3$ and has 38 infrared- and Raman-active vibrational modes. The most symmetrical structure is *cis,cis,cis*-1,4,7-CNT (crown conformation), which belongs to symmetry point group C$_{3v}$ and has 30 infrared- and Raman-active vibrational modes.


trans,trans,trans-1,4,7-CNT
conformation I — conformation II


cis,cis,cis-1,4,7-CNT
saddle conformation — crown conformation

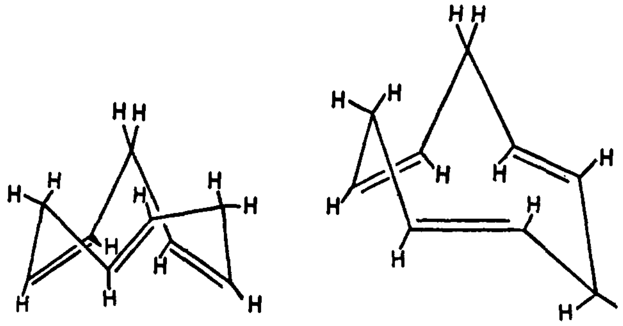

cis,cis,trans-1,4,7-CNT — *cis,trans,trans*-1,4,7-CNT

Figure 1. Different possible structures for 1,4,7-cyclononatriene.

B. Assignment of Fundamentals. The 22 bands that appeared in the Raman spectrum of 1,4,7-CNT are assigned to fundamental vibrational modes. An overtone or combination band in the Raman spectrum usually has an intensity of less than $^1/_{100}$th of a fundamental,[4] and only a tenfold variation in intensity was observed for the bands in the Raman spectrum.

Of the 21 fundamental bands that appeared in both the infrared and Raman spectrum in the 4000–325-cm^{-1} region, 19 were designated as very strong, strong, or medium on the intensity scale adopted for infrared bands in solution. It was assumed that the four bands with comparable intensities in the infrared spectrum, which did not appear in the Raman spectrum, were also due to fundamental vibrations.

Twelve bands in Table I are listed as weak. Two of these bands were classed as fundamentals because they also appeared in the Raman spectrum. Two other weak bands, which were not observed in the Raman spectrum, were assigned to fundamental vibrational modes because they appeared with approximately the same frequency in the spectra of the related compounds as in that of 1,4,7-CNT. The other bands with the

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(4) Reference 3, p 523.

Table IV. Frequencies and Assignments of Infrared Bands of 2,5,8-CNT-one in Solution

Wavenumber, cm^{-1}			Assignment	
In CS_2	In $CHCl_3$	Intensity	*cis,cis,cis*-2,5,8-CNT-one (crown conformation assumed)	Assuming *trans,trans,-trans*-2,5,8-CNT-one (conformation II)
3275	3275	w	1637 × 2 = 3274	1637 × 2 = 3274
3246		w	1639 + 1614 = 3253	1639 + 1614 = 3253
3225		w	1614 × 2 = 3228	1614 × 2 = 3228
3042		m	20	C—H stretching
3019		s	1	C—H stretching
2956	2969	m	2	CH_2 asymmetric stretching
2916	2925	s	3	CH_2 symmetric stretching
2848		m	23	CH_2 symmetric stretching
1950		w	1614 + 338 = 1952	1614 + 338 = 1952
1808	1814	w	1033 + 785 = 1818 1227 + 581 = 1808 830 + 977 = 1807	1033 + 785 = 1818 1227 + 581 = 1808 830 + 977 = 1807
1639	1637	vs	C=O stretching	C=O stretching
			24	C=C stretching
1614	1609	s	4	C=C stretching
	1440 1436 sh	s	25 (split by Fermi resonance with 977 + 462 = 1439	CH_2 bending
1395	1400	s	C—H deformation (ip) α_2 symmetry type in 1,4,7-CNT	C—H deformation (ip)
1377	1383	m	26 (e symmetry type in 1,4,7-CNT)	C—H deformation (ip)
	1379	m		
	1361	w	1021 + 338 = 1359 830 + 523 = 1353 830 + 535 = 1365 786 + 581 = 1366	1021 + 338 = 1359 830 + 523 = 1353 830 + 535 = 1365 786 + 581 = 1366
1292	1294	m	27 (e symmetry type in 1,4,7-CNT)	C—H deformation (ip)
1274	1279	s		
1247		m	28 (e symmetry type in 1,4,7-CNT)	CH_2 twisting
1227		s		
1162	1166	m	6	C—H deformation (ip)
1033		m	CH_2 twisting	CH_2 twisting
1021		w	(a_2 symmetry type in 1,4,7-CNT)	C—H deformation (op)
993	997	s	Ring stretching	C—H deformation (op)
977	981	m	29	CH_2 wagging
939		m	7	CH_2 wagging
922		s		CH_2 rocking
830	835	vs	30	Ring stretching
785		m	C—H deformation (op)	Ring stretching
754		s	C—H deformation (op)	CH_2 rocking
673		s	9	Ring stretching
581	576	m	10	Ring stretching
535 sh		m	35 (C—C—C ∠ bending)	C—C—C ∠ bending
523		m	36	C—C—C ∠ bending
462		m	Crown point rocking	Crown point rocking
338		m	37 or 38	Ring deformation or ring puckering

intensity designations of weak or very weak were assigned to overtones or combinations of fundamental vibrational modes or to fundamental vibrational modes that, although forbidden by symmetry, may appear weakly due to perturbation effects.

The four structures for which the symmetry permits 57 nondegenerate Raman- and infrared-active normal modes of vibration can be eliminated on the basis of the Raman spectrum alone. Some bands that theoretically could appear may be too weak to be seen in the Raman spectrum. Accidental degeneracy may occur in some cases, but *it is unreasonable to assume that only 22 bands would appear in the Raman spectrum of a molecule having 57 Raman-active vibrational modes* with no inherent degeneracies due to its symmetry.

Twenty-eight bands have been assigned to fundamental vibrations. This assignment suggests that the structure is *cis,cis,cis*-1,4,7-CNT (crown conformation) for which 30 infrared and Raman bands are expected rather than *trans,trans,trans*-1,4,7-CNT (conformation II) for which the 38 infrared- and Raman-active vibrational modes are expected.

The crown structure is also supported by the observed polarizations of the bands in the Raman spectrum. For the structure with C_{3v} symmetry, 11 polarized and 19 depolarized bands are expected, while 19 of each are expected for the structure with C_3 symmetry. Of the 22 bands observed in the Raman spectrum, only eight are polarized, while 11 are depolarized. It was impossible to obtain a polarization ratio for three of the bands.

In view of the good agreement between the number and Raman polarization of observed fundamentals with the number and Raman polarization of fundamentals expected for *cis,cis,cis*-1,4,7-cyclononatriene (crown conformation), and the poor explanation of the data which would be offered by the structures of lower symmetry, the *cis–cis–cis* structure (crown conformation) was assumed to be correct and the assignment of bands to specific vibrations and symmetry types proceeded on this basis.

Table V. Comparison of the Solution and Vapor Infrared Spectra of 1,4,7-CNT

Solution			Vapor	
Wavenumber, cm^{-1}	Intensity	Solvent	Wavenumber, cm^{-1}	Intensity
3045	m	CS_2	3066	m
			3060	
3010	vs	CS_2	3030	vs
			3027	
2958	s	CS_2	2975	s
			2970 sh	. . .
2924	s	CS_2	2940	s
2906	s	CS_2	2929	s
			2918 sh	. . .
2856	s	CS_2	2878	s
			1651 ?	m
1635	s	$CHCl_3$	1646 ?	m
			1635 ?	m
			1480	s
1473	s	$CHCl_3$	1474	s
1463	s	$CHCl_3$	1470	s
1250	s	CS_2	1250*	w
971 sh	m	$CHCl_3$	963 sh*	w
964	s	$CHCl_3$	957*	w
932	s	CS_2	933*	w
			888	m
879	vs	$CHCl_3$	881	vs
			872 sh	s
			737 sh	s
727	vs	CS_2	730	vs
			722	vs
714	vs	CS_2	719 (min)	vs
			716 sh	vs
			714 sh	
			713 sh	
666	m	CS_2	666*	m

Table VI. Raman Bands of 1,4,7-CNT in CS_2 Solution

Wavenumber, cm^{-1}	Intensity	Depolarization ratio	Polarization
3054	2	1.2	dp
3015	10	0.64	p
2962	5	0.82	p?
2942	4	. . .	. . .
2938	4	0.95	dp
2913	5	0.72	p
2860	2	0.89	dp?
1640	10	0.53	p
1471	1	. . .	. . .
1465	1	. . .	. . .
1443	1	. . .	. . .
1435	1	. . .	. . .
1386	0	. . .	. . .
1278	2	1.0	dp
1252	5	1.0	dp
970 sh	1	. . .	. . .
964	2	1.0	dp
933	4	0.61	p
877	1	0.90	dp?
728	4	0.58	p
594	1	0.75	p?
562	1	1.0	dp?
556	1	1.0	dp?
501	1	1.0	dp
381	1	0.63	p?
303	1	1.0	dp?
228	3	1.0	dp

Table VII. The Different Possible Structures of 1,4,7-CNT and the Corresponding Number and Symmetry Type of Their Normal Modes of Vibration

Structure	Point group	No. and symmetry type of vibration modes
cis, cis, cis-1,4,7-CNT		
Crown conformation	C_{3v}	$11a_1 + 8a_2 + 19e$
Saddle conformation	C_s	$33a' + 24a''$
cis,cis,trans-1,4,7-CNT	C_1	57a
cis,trans,trans-1,4,7-CNT	C_s	$30a' + 27a''$
trans,trans,trans-1,4,7-CNT		
Conformation I	C_1	57a
Conformation II	C_3	19a + 19e

C. Infrared Spectra and Structure of 1,4,7-CNT-*d*$_2$ and 2,5,8-CNT-ol. Except for the addition of bands due primarily to vibrations of the CD_2 group in 1,4,7-CNT-*d*$_2$ and those associated with the C–O–H group in 2,5,8-CNT-ol, the spectra of these compounds resembled that of 1,4,7-CNT very closely.

Bands in the infrared spectrum of 1,4,7-CNT-*d*$_2$ and 2,5,8-CNT-ol, which were within 11 cm^{-1} of bands in the infrared spectrum of 1,4,7-CNT, were assigned to the same fundamental vibrational mode in all three compounds. The experimental error in the measurements is less than 11 cm^{-1}, but slight differences in the frequency of the same vibrational mode would be expected for slightly different compounds. A 1:1 correspondence between most of the bands in the three spectra was obtained using this criterion.

The only fundamental band in the spectrum of 1,4,7-CNT that was absent from the spectrum of 1,4,7-CNT-*d*$_2$ in the 4000–650-cm^{-1} region was the band at 757 cm^{-1}. Four fundamental bands appearing in the infrared spectrum of 1,4,7-CNT in the 4000–325-cm^{-1} region were missing from the infrared spectrum of 2,5,8-CNT-ol. Two of these bands (1438 and 666 cm^{-1}) were obscured by solvent absorption in the same region. The other two bands (567 and 383 cm^{-1}) appeared only in the spectrum of 1,4,7-CNT recorded on the Beckman IR7 and not in that obtained by using the CsBr IR5A. Therefore, the bands would not necessarily be expected to appear in the spectrum of 2,5,8-CNT-ol recorded on the less sensitive CsBr IR5A.

Because of the striking similarity between the spectra of 1,4,7-CNT, 1,4,7-CNT-*d*$_2$, and 2,5,8-CNT-ol, it was concluded that the three compounds have the same structure. Since the spectrum of 1,4,7-CNT can be completely explained on the basis of the *cis,cis,cis*-1,4,7-CNT (crown conformation) structure, this structure was also proposed for 1,4,7-CNT-*d*$_2$ and 2,5,8-CNT-ol.

The infrared spectrum of 2,5,8-CNT-one did not closely resemble those of the other three compounds. It was possible to explain the spectrum of the ketone on the basis of two structures, *cis,cis,cis*-2,5,8-CNT-one (crown conformation) or *trans,trans,trans*-2,5,8-CNT-one (conformation II). Because it could not be determined from the infrared spectrum that the conformation of the ketone was the same as that of the hydrocarbon, the infrared spectrum of the ketone was not used in the interpretation of the spectrum of 1,4,7-CNT and will not be considered further.

D. Assignment of Fundamental Bands to Group Vibrations. *cis,cis,cis*-1,4,7-Cyclononatriene-*d*$_2$ (crown conformation) belongs to symmetry point group C_s.

The symmetry of *cis,cis,cis*-2,5,8-cyclononatrienol is C_s if the oxygen and hydrogen atoms of the hydroxyl group are in the plane perpendicular to the opposing carbon–carbon double bond and passing through the carbon atom to which the hydroxyl group is attached. The symmetry is C_1 if both oxygen and hydrogen atoms are not in this plane. For molecules with C_s or C_1 symmetry, no vibrational modes are forbidden by symmetry in either the infrared or the Raman spectrum, and there are no inherent degeneracies.

The substitution of two deuterium atoms for the hydrogen atoms on one methylene carbon atom in 1,4,7-cyclononatriene-d_2 can be considered as a perturbation on the structure of 1,4,7-cyclononatriene. The replacement of one methylene hydrogen atom by a hydroxyl group in 2,5,8-cyclononatrienol is a similar perturbation. In both cases the C_{3v} symmetry of the skeleton and the ethylenic hydrogen atoms present in 1,4,7-cyclononatriene is preserved. The substitutions, therefore, would not be expected to greatly perturb the normal modes of vibrations due primarily to the ethylenic hydrogen atoms (C–H) or skeleton motions in 1,4,7-cyclononatriene. Bands that correspond to degenerate (e) vibrations of the skeleton or C–H groups in 1,4,7-cyclononatriene will probably be accidently degenerate in the spectra of 1,4,7-cyclononatriene-d_2 and 2,5,8-cyclononatrienol. Fundamental skeleton and C–H vibrations of a_2 symmetry type, which are inactive in the infrared spectrum of 1,4,7-cyclononatriene, would not be expected to appear with appreciable intensity in the spectra of 1,4,7-cyclononatriene-d_2 and 2,5,8-cyclononatrienol even though they are not forbidden by symmetry.

Normal modes of vibration that are due primarily to motions of the three CH_2 groups in 1,4,7-cyclononatriene would most likely be perturbed by the substitutions occurring in 1,4,7-cyclononatriene-d_2 and 2,5,8-cyclononatrienol. Bands due to degenerate (e) vibrations of the CH_2 groups in 1,4,7-cyclononatriene can be split in the spectra of the less symmetrical compounds. The fundamental CH_2 twisting and wagging vibrations of a_2 symmetry, which are forbidden in the infrared spectrum of 1,4,7-cyclononatriene, may appear in the spectra of 1,4,7-cyclononatriene-d_2 and 2,5,8-cyclononatrienol.

These differences appearing on substitution of two deuterium atoms or an =O for the hydrogen atoms on one methylene group were used to distinguish vibrations of the $-CH_2$ groups of 1,4,7-CNT from carbon skeleton or ethylenic hydrogen vibrations.

E. Assignment of Bands to Group Vibrations in 1,4,7-CNT. The assignment of the bands in the vibrational spectra of 1,4,7-CNT to group vibrations and symmetry species is given in Table VIII.

Table VIII. Assignment of Fundamental Bands in the Spectrum of 1,4,7-CNT

Symmetry species	Vibration no.	Approx mode of vibration	Assignment
a_1	1	–C–H stretching	3010
	2	$-CH_2$ antisymm stretching	2958
	3	$-CH_2$ symmetric stretching	2906
	4	C=C stretching	1635
	5	CH_2 bending	1468 (center of doublet)
	6	C–H deformation (ip)	1175
	7	CH_2 rocking	932
	8	C–H deformation (op)	727
	9	Ring stretching	666
	10	Crown point rocking	594
	11	C–C–C angle bending	383
a_2	12	–C–H stretching	3060–3010^a
	13	–C–H deformation (ip)	1405–1035^a
	14	CH_2 twisting	1030
	15	CH_2 wagging	904
	16	C–H deformation (op)	728–675^a
	17	C–C antisymm stretching	1405–698^a
	18	Ring puckering	887–194^a
	19	Ring deformation	887–194^a
e	20	C–H stretching	3045
	21	C–H stretching	3045,^{b} 3010^b
	22	CH_2 antisymm stretching	2924
	23	CH_2 symmetric stretching	2858
	24	C=C stretching	1669
	25	CH_2 bending	1438
	26	C–H deformation (ip)	1387
	27	C–H deformation (ip)	1274
	28	CH_2 twisting	1250
	29	CH_2 wagging	960
	30	Ring stretching	875
	31	CH_2 rocking	757
	32	C–H deformation (op)	714
	33	C–H deformation (op)	714^b
	34	Crown point rocking or C–C–C angle bending	567
	35	Crown point rocking or C–C–C angle bending	545
	36	C–C antisymm stretching	503
	37	Ring puckering or ring deformation	304
	38	Ring puckering or ring deformation	228

[a] These values were estimated from the literature sources cited in part E. [b] These peaks were assigned to more than one vibration.

The assignment of the bands above 1600 cm^{-1} was made on the basis of the observed frequencies and polarizations. One of the nine bands above 1600 cm^{-1} that was expected for the structure with C_{3v} symmetry was not observed. This band is due to the C–H stretching mode of e symmetry type and occurs in the 3060–3010-cm^{-1} region. If the vibration is accidently degenerate with another vibration, interaction that will split the band is expected to occur,[5] possibly giving rise to one strong and one weak band. This interaction may explain the observed intensity of the band at 3010 cm^{-1}, which was the second strongest band in both the infrared and Raman spectra.

The doublet at 1473–1463 cm^{-1} was probably split by Fermi resonance with one of the following combinations.

$$960\ cm^{-1} + 503\ cm^{-1} = 1463\ cm^{-1}$$

$$875\ cm^{-1} + 594\ cm^{-1} = 1469\ cm^{-1}$$

$$757\ cm^{-1} + 714\ cm^{-1} = 1471\ cm^{-1}$$

The center of the doublet (1468 cm^{-1}) was chosen as the frequency of this vibration because the intensities of the peaks were about equal.

The 1468-cm^{-1} band, which was more intense than the one at 1438 cm^{-1}, was assigned to the CH_2 bending vibration of a_1 symmetry type while the band at 1438 cm^{-1} was assigned to the CH_2 bending vibration of e symmetry type.

The assignment of the weak 1438-cm^{-1} band to the e CH_2 bend is substantiated by the very weak intensity of the band at 1437 cm^{-1} in the spectrum of 1,4,7-CNT-

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(5) M. A. El-Sayed, *J. Chem. Phys.*, 37, 680 (1962).

d_2 and the absence of this band from the spectrum of the alcohol. Only two CH_2 groups are present in these molecules, and in the vibration corresponding to the e vibration in 1,4,7-CNT the two CH_2 groups vibrate out-of-phase. The dipole moment change due to the motion of one group practically cancels that due to the motion of the other group, and the intensity of the band in the infrared spectrum would be expected to be very weak.

The assignment of the bands in the 1400–600-cm^{-1} region was complicated by the fact that vibrations due to the CH_2 groups, the C–H groups, and the carbon skeleton may all occur in this region. Furthermore, the corresponding modes, being so close in energy, are expected to interact with one another.

Bands that appeared as single bands in the spectrum of 1,4,7-CNT but that were split in the spectra of 1,4,7-CNT-d_2, 2,5,8-CNT-ol, or both were assigned to vibrations of e symmetry type. In some cases this assignment was substantiated by the observed polarization of the Raman bands.

Four bands are observed in the 1405–1035-cm^{-1} region where three bands due to C–H deformation (ip) are expected. Only one of these bands (1250 cm^{-1}) was split in the spectrum of 1,4,7-CNT-d_2; this band was assigned to a vibration of the CH_2 group because the other CH_2 groups are perturbed more than the C–H groups by the substitution of one CD_2 group for a CH_2 group.

The bands at 1387, 1274, and 1175 cm^{-1} were then assigned to the C–H deformation (ip) by elimination. The band at 1274 cm^{-1} was assigned to one of the e vibrational modes on the basis of its observed polarization while that at 1387 cm^{-1} was assigned to the other e mode because it appeared as a doublet in the spectrum of 2,5,8-CNT-ol. The band at 1175 cm^{-1} was assigned to the a_1 mode because it appeared as a single band in the spectra of 1,4,7-CNT, 2,5,8-CNT-ol, and 1,4,7-CNT-d_2.

The intensity of the bands at 960 and 932 cm^{-1} was considerably enhanced in the solution spectrum as opposed to the vapor phase spectrum. The solvent would be expected to affect vibrations involving hydrogen atoms more than those involving the carbon skeleton. No vibrations due to the C–H group are expected at these frequencies, so the bands were assigned to vibrations of the CH_2 group rather than to skeletal vibrations. This assignment for the band at 960 cm^{-1} was substantiated by the splitting of the corresponding band in the spectrum of 2,5,8-CNT-ol.

The band at 757 cm^{-1} was also assigned to a vibration of the CH_2 group. The intensity of this band varied greatly in the spectra of 1,4,7-CNT, 1,4,7-CNT-d_2, and 2,5,8-CNT-ol, suggesting that the vibration is due to CH_2 groups, the number of which is different in the three molecules, rather than to the skeleton, which is relatively unchanged.

The four bands assigned to CH_2 vibrational modes were assigned to the particular CH_2 vibrations on the basis of their frequencies. The band at 1250 cm^{-1} was assigned to CH_2 twisting,[6–13] while that at 960 cm^{-1} was assigned to CH_2 wagging[6–13] by analogy with other cyclic hydrocarbons in which bands assigned to CH_2 twisting occurred at higher frequencies than those assigned to CH_2 wagging.

The frequency of the band assigned to CH_2 wagging was below that expected for a large ring hydrocarbon.[6–11,14] However, the band assigned to CD_2 wagging was observed at 701 cm^{-1} which is lower in frequency than the bands in the spectrum of 1,4-cyclohexadiene-d_8[10] assigned to CD_2 wagging, so that the CH_2 wagging vibration would also occur at a lower frequency.

The band at 932 cm^{-1} was assigned to the CH_2 rocking mode of a_1 symmetry type on the basis of both its frequency and its polarization since only one of the four CH_2 vibrations expected in the 1000–600-cm^{-1} would give rise to a polarized Raman band.

The band at 757 cm^{-1} was assigned to the CH_2 rocking mode on the basis of its frequency and to an e mode by elimination since the a_1 mode was already assigned.

Three bands due to C–H deformation (op) are expected in the 728–675-cm^{-1} region.[10,13,15] Only two bands are observed. The band at 727 cm^{-1} is polarized and was assigned to the C–H deformation (op) vibration of a_1 symmetry type. The band at 714 cm^{-1} did not appear in the Raman spectrum but was the strongest band in the infrared spectrum. Two bands due to C–H deformation (op) vibrations (e type) are expected to appear in this region; and each one would be expected to be less intense in the infrared spectrum than that due to the a_1 mode, in which all six hydrogen atoms move in phase. However, the band at 714 cm^{-1} is more intense than that at 727 cm^{-1}, suggesting that the interaction of two accidently degenerate C–H deformation (op) modes might have resulted in the increase in intensity of the band at 714 cm^{-1}.[4]

The bands at 875 and 666 cm^{-1} were assigned to vibrations of the carbon skeleton.[6–10,12,13] Both bands appeared as single peaks when they were observed in the spectra of 1,4,7-CNT, 1,4,7-CNT-d_2, and 2,5,8-CNT-ol. (The band at 666 cm^{-1} was obscured by solvent in the spectrum of 2,5,8-CNT-ol.) The intensities of corresponding bands in the various spectra were comparable.

The seven bands below 600 cm^{-1} were assigned to skeletal vibrations on the basis of their frequencies. Two of these bands were polarized. Three polarized bands due to skeletal vibrations are expected below 1600 cm^{-1}; so the band at 666 cm^{-1}, which was obscured by solvent absorption in the Raman spectrum, was also assumed to be due to a vibrational mode of a_1 symmetry type.

A definite assignment of the skeletal vibrations below 600 cm^{-1} could not be made. The C=C—C angle bending vibration (crown point rocking) of a_1 symmetry type was assigned to a band with higher frequency than the C–C–C angle bending vibration because the inter-

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action of the methylene groups in the former vibration would increase the potential energy of the vibration.

The band at 503 cm^{-1} [6–10,12,13] was assigned to C–C antisymmetric stretching, in which one of the bonds to the methylene carbon atom is stretched while the other is condensed. This assignment was made because the band was the strongest of those below 600 cm^{-1}; the bands at 875 and 666 cm^{-1}, which were also assigned to C–C stretching, were also stronger than the other bands assigned to skeletal vibrations.

Conclusions

The infrared and Raman spectra of 1,4,7-cyclononatriene can be completely explained on the basis of the C_{3v} *cis,cis,cis*-1,4,7-cyclononatriene crown structure. The similarity of the spectra of 2,5,8-cyclononatrienol and 1,4,7-cyclononatriene-d_2 to that of 1,4,7-cyclononatriene indicate that the former also possess a crown conformation.

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The Crystal Structures of the Isomers *trans*- and *cis*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane

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Abstract: *trans*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane crystallizes in space group P2$_1$/c with $Z = 4$ and cell parameters $a = 7.16$, $b = 13.18$, $c = 12.07$ A, and $\beta = 105° 11'$. *cis*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane crystallizes in space group P2$_1$/n with $Z = 4$ and cell parameters $a = 6.21$, $b = 11.21$, $c = 15.64$ A, and $\beta = 95° 55'$. The *trans* molecule possesses an approximate twofold axis while the *cis* molecule is completely asymmetric. In each isomer the cyclobutane ring is puckered with a dihedral angle near 150°.

In some cyclobutane derivatives, such as C_4Cl_8[1] and anemonin,[2] the four-membered ring is puckered whereas in other derivatives, such as 1,2,3,4-tetraphenylcyclobutane[3] and the dimer of cyclopentanone,[4] the four-membered ring is planar. The structure investigation of *trans*- and *cis*-1,2-dibromo-1,2-dicarbomethoxycyclobutane was undertaken in order to collect more information about the conformation of cyclobutane rings and to correlate the structural results with those from nuclear magnetic resonance studies on these molecules.[5]

Experimental Section

Crystals of both materials were prepared by Drs. E. Lustig and E. T. Ragelis of the Food and Drug Administration. They were in the form of colorless, elongated prisms. The *trans* and *cis* compounds had melting points of 86–87 and 40–40.5°, respectively. Each of the materials was somewhat volatile although it was possible to collect the diffraction data without the use of sealed capillaries. Cell dimensions were obtained from precession photographs, whereas intensity data were collected from multiple film, equi-inclination Weissenberg photographs with copper radiation and a nickel filter. The crystal of the *trans* compound was mounted parallel to the *c* axis while the crystal of the *cis* compound was mounted parallel to the *a* axis. The intensities were estimated visually by comparison with a calibrated film strip. They were corrected for Lorentz and polarization factors and spot size. The data were placed on an absolute scale by means of a K curve.[6] Space groups were determined unambiguously from the systematic absences. The cell parameters, space groups, and number of observed reflections are shown in Table I.

Table I. Experimental Data for the Isomers of 1,2-Dibromo-1,2-dicarbomethoxycyclobutane

	trans	*cis*
a, A	7.16 ± 0.02	6.21 ± 0.02
b, A	13.18 ± 0.02	11.21 ± 0.02
c, A	12.07 ± 0.02	15.64 ± 0.03
β	105° 11′ ± 15′	95° 55′ ± 15′
$\rho_{\text{X-ray}}$, g cm^{-3}	1.995	2.024
Space group	P2$_1$/c	P2$_1$/n
Total obsd refl	1714	1695
No. of refl obsd >0	1567	1430

Structure Analysis

The symbolic addition procedure for determining phases directly from the structure factor magnitudes[7] was used for both crystals. In each case the most probable set of signs proved to be the correct set. For equal atom problems, 10–12 reflections per atom in the asymmetric unit are sufficient to compute a well-resolved *E* map.[8] In the present investigations, with two Br atoms and twelve light atoms in each asymmetric

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