Chair–Twist Differentiation by Vibrational Spectroscopy

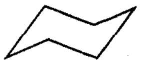
DAVID S. BAILEY AND JOSEPH B. LAMBERT*[1]

Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201

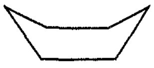
Received June 26, 1972

The infrared and Raman spectra of 1,4-dimethylenecyclohexane (**1**), dispiro[2.2.2.2]decane (**2**), and cyclohexane-1,4-dione-d_8 (**3**-d_8) have been measured in the range 4000–400 cm^{-1}. The centrosymmetric chair form is confirmed for **1** and **2** (liquid phase) and the noncentrosymmetric twist boat for **3**-d_8 by the mutual exclusion rule, by the total number of fundamentals, and by the proportion of polarized Raman bands.

Vibrational spectroscopy offers a rich and, for the most part, untapped source of conformational information in the form of molecular symmetry determinations. This information is obtained from infrared and Raman spectra by application of two rules of group theory.[2] The principle of mutual exclusion states that, for molecules with a center of symmetry, all bands that are symmetry allowed in the infrared are symmetry forbidden in the Raman, and vice versa. As applied to six-membered rings, this rule allows a differentiation to be made between the centrosymmetric chair form A and the noncentrosymmetric boat forms B and C. A chair molecule would be expected to show no coincidences in the infrared and Raman spectra, whereas a boat or twist boat would exhibit only coincident bands. This method has been discussed in a recent application to the structure of cyclobutane photodimers,[3] and has previously been used to make a chair–boat distinction in cyclohexane-1,4-dione.[4,5]


A


B

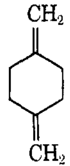

C

The second rule states that bands from totally symmetrical vibrations are polarized in the Raman spectrum. The depolarization ratio ρ is defined as the intensity of scattered light perpendicular to the xy plane ($I_{\perp}$), divided by the intensity of light parallel to the xy plane ($I_{\parallel}$) (eq 1). For totally symmetrical

$$\rho = \frac{I_{\perp}}{I_{\parallel}} \qquad (1)$$

vibrations arising from laser excitation, ρ is less than 0.75, and sometimes nearly zero, whereas, for all other Raman-active vibrations, ρ is close to 0.75. The number of polarized Raman bands depends on the symmetry group of the molecule. More symmetrical molecules have fewer allowed vibrations of the totally symmetrical class, and consequently fewer polarized Raman bands. Thus the symmetrical twist form (D_2) would have fewer polarized bands than the canted twist form (C_2, *vide infra*). The total number of fundamentals is also a predictable function of the symmetry group of the molecule, so that conformational information can be obtained from this source as well.

The compounds to which we have applied these techniques are 1,4-dimethylenecyclohexane (**1**), dispiro[2.2.2.2]decane (**2**), and cyclohexane-1,4-dione (**3**). Our interest in the methylene compound (**1**) arose from an *R*-value analysis that showed the molecule to be extremely flattened, but did not differentiate between the flattened chair and twist boat forms.[6] The spiro compound was of interest because of the formal similarity between the hybridization of cyclopropyl and ethylenic systems. *R*-Value analysis, however, demonstrated that this analogy does not hold up in a conformational sense.[7] The dione was included as a model compound for a twist boat. X-ray studies clearly showed the molecule to be in the unsymmetrical (C_2) twist-boat form in the solid phase,[8] and vibrational experiments[4,5] have confirmed the results in solution. More recent results in the gas phase, however, have cast some doubt on the solution work;[9,10] so we have gathered further vibrational data on the wholly deuterated derivative in order to confirm the previous conformational determination.[11]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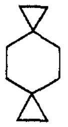
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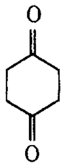
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Results

The infrared and Raman spectra of compounds **1**, **2**, and **3**-d_8 were obtained as described in the Experimental Section. Neat liquids were used for the spectra of **1** and **2**, whereas the spectra of **3**-d_8 were obtained from methylene chloride solutions (infrared and Raman) and from a KBr pellet (infrared only). No data have been reported previously for the methylene and spiro compounds. The one existing vibrational study[5] of **3**-d_8 utilized a method of exchange[12] that would have produced only a mixture of incompletely deuterated materials. The present method ensured complete re-

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(1) This work was supported by the National Science Foundation (Grant GP-22942), the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center, and the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-AC4).

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placement of the hydrogens with deuterium. Tables I–III present the vibrational data in such a way as to emphasize spectral coincidences. Infrared and Raman bands that fall within 5 cm^{-1} of each other are placed on a single line. Noncoincident lines are given separate entries. Polarized Raman lines (ρ <0.75) are labeled "p" and lines exhibiting no polarization are labeled "dp."

TABLE I

INFRARED AND RAMAN SPECTRAL FREQUENCIES (CM^{-1}) AND INTENSITIES FOR 1,4-DIMETHYLENECYCLOHEXANE (1)

Infrared		Raman	
Frequency	Intensity	Frequency	Intensity
		182	20 (dp)
402	80	401	50 (p)
		442	16 (dp)
		552	40 (p)
695	90		
		703	2
		757	100[a] (p)
789	50	790	4 (dp)
893	100[a]	894	12 (p)
945	10		
983	40		
		996	31 (p)
1015	10		
		1061	10 (p)
1067	10		
		1134	8 (dp)
1167	50		
1188	40		
		1216	20 (p)
		1261	2
1313	50	1311	50 (p)
		1389	16 (p)
1406	50		
		1420	16 (p)
		1436	2 (dp)
1442	90		
1455	50 (sh)		
		1467	1
1524	10		
1540	10		
		1589	2
1595	20 (sh)		
1628	20 (sh)		
		1651	84 (p)
1659	100[a]		
		1671	15 (p)
1680	30 (sh)		
1721	20		
1735	10		
		1772	1
1791	40		
(2410)[b]	10		
		(2433)[b]	1
		(2473)	1
		(2557)	1 (p)
		(2587)	1 (p)
		(2601)	3 (p)
(2618)	10		
		(2635)	1 (p)
(2656)	10		
(2711)	10		
		(2722)	1
		(2778)	1
		2843	32 (p)
2851	40		
		2888	16 (p)
2913	40		
2942	80	2944	30 (p)
2989	40	2986	35 (p)
3079	40	3075	8 (dp)
		(3287)	1 (p)

[a] Base peak. [b] Numbers in parentheses are assumed not to be fundamentals; see text.

TABLE II

INFRARED AND RAMAN SPECTRAL FREQUENCIES (CM^{-1}) AND INTENSITIES FOR DISPIRO[2.2.2.2]DECANE (2)

Infrared		Raman	
Frequency	Intensity	Frequency	Intensity
		184	6 (p)
		302	4 (dp)
		352	19 (p)
		469	16 (p)
583	40		
691	80	688	69 (p)
779	12	783	4 (dp)
		802	3 (dp)
		854	25 (dp)
870	12		
894	95		
934	100	933	60 (p)
		948	4 (dp)
997	70		
1010	100[a]	1011	12 (p)
1041	47	1039	4 (p)
		1091	55 (p)
		1144	3 (dp)
1153	12		
		1169	7 (dp)
1174	30		
		1193	22 (p)
		1278	4 (p)
1291	80		
		1332	3 (p)
1339	17		
		1353	60 (p)
1383	55		
1426	85	1428	29 (dp)
1441	85	1437	25 (dp)
		1457	23 (p)
		1458	20 (p)
1465	53		
(2041)[b]	17		
(2077)	8		
2847	90	2849	27 (p)
		2874	10 (p)
2888	72	2891	42 (p)
2910	70		
2922	100		
		2931	65 (p)
2995	86	2994	100[a] (p)
3065	83	3060	27 (dp)
		3071	(sh) (dp)

[a] Base peak. [b] Numbers in parentheses are assumed not to be fundamentals; see text.

Discussion

In applying the rule of mutual exclusion, it has been customary to make comparisons only below 2000 cm^{-1}.[3] Above this value, overtones and combination bands are too common to make meaningful comparisons. The lower limit of infrared observations was 400 cm^{-1}; so our full range of comparisons is 2000–400 cm^{-1}.

Examination of the vibrational spectra of dimethylenecyclohexane (1) reveals 4 coincident bands out of a total of 21 possibilities. The limiting figure in this case is the number of bands (21) observed (2000–400 cm^{-1})

TABLE III

INFRARED AND RAMAN SPECTRAL FREQUENCIES (CM^{-1}) FOR CYCLOHEXANE-1,4-DIONE-d_8 (**3**-d_8)

Infrared[a]	Raman[b]	Infrared[a]	Raman[b]
	395 (p)	1043 (m)	1047
417 (vs)		1065 (w)	
429 (m)	434 (dp)	1074 (m)	1074
450 (vs)		1089 (w)	1089
	468 (dp)	1125 (w)	
541 (m)	541 (p)	1143 (m)	
655 (s)		1188 (s)	
675 (m)	673 (vs, p)	1226 (s)	1225
686 (w)	687[c] (s)	1263 (m)	
706 (m)		1297 (w)	
759 (vs)		1712 (s)	1712 (m, p)
779 (vs)	776 (p)		1728 (s, p)
	786 (p)		2060
818 (w)	814[c]	2068 (w)	
839[d]	842		2078
859[d]		2106 (w)	
	890	2123 (w)	2123 (m, p)
929 (m)	926 (m)	2130 (m)	
938[d]	937 (m)	2146[d] (w)	2144 (vs, p)
975 (m)		2165 (m)	
1008 (m)		2186[d] (w)	
1031 (m)			2220 (s, p)
1037 (m)		2228 (w)	2233 (s, dp)
			2245 (s, p)
			2266 (m, p)

[a] KBr pellet unless otherwise noted. [b] CH_2Cl_2 solution unless otherwise noted; because of the strong solvent bands at about 730 and 1160 cm^{-1}, intensity and polarization measurements were difficult to obtain. [c] CH_3OH solution. [d] CH_2Cl_2 solution.

in the Raman spectrum; the corresponding number for the infrared spectrum is 23. The infrared and Raman spectra were obtained under identical conditions (neat liquid); so no problems due to solvent need be considered. This low ratio of coincidence (4 out of 21) is similar to that reported for cyclohexane (2 out of 14);[13] so the compound must be in the centrosymmetric chair conformation. The vibrational data, in conjunction with the nmr coupling constants,[6,14] are sufficient to describe the molecule as an extremely flattened chair. This conclusion is in agreement with the observation that a rate process ($\Delta G^{\ddagger} = 7.5$ kcal/mol) can be frozen out at extremely low temperatures.[15]

For the dispirodecane **2**, 7 coincidences were observed out of 17 possibilities in the 400–2000-cm^{-1} range. The number of infrared bands is limiting in this case. Although the coincidence ratio is higher than in the previous case, it is still consistent with a centrosymmetric chair conformation. The *R*-value analysis[7,16] shows that there is no flattening of the ring; so the conformation is best described as an undistorted chair. The barrier to ring reversal ($\Delta G^{\ddagger} = 10.9$ kcal/mol), in agreement with this conclusion, is very close to that of cyclohexane (10.2 kcal/mol).[17]

The 14 observed coincidences out of a possible 18 (the number of Raman bands) in the vibrational spectra of the deuterated dione **3** provide strong evidence for the noncentrosymmetric boat or twist-boat conformation. The coincidence ratio is impressively large when it is considered that the infrared spectrum was measured from a KBr pellet, and the Raman spectrum was obtained from CH_2Cl_2 and CH_3OH solutions. The conclusion that the molecule lacks a center of symmetry is in agreement with previous vibrational work,[4,5] but does not support the recent suggestion (appropriate only to the vapor phase)[9] that the molecule is in a chair.

The total number of infrared and Raman fundamentals can be calculated by group theory from knowledge of the symmetry class of the molecule. The symmetry of each vibration can also be determined in order to calculate the number of polarized Raman bands expected for each symmetry type. These calculations are summarized in Table IV for the three molecules under study. To determine the approximate number of observed fundamentals for **1** and **2**, all bands except those between 2000 and 2800 cm^{-1} and certain obvious overtones were counted. Because the C–D stretch fundamentals fall between 2000 and 2200 cm^{-1}, all observed bands except those above 2300 cm^{-1} were used for **3**-d_8. The bands assumed not to be fundamentals are rendered in parentheses in Tables I–III.

For 1,4-dimethylenecyclohexane, approximately 28 infrared bands and 27 Raman bands are considered to be fundamentals, and 16 of the Raman bands are polarized. Because of the absence of infrared data below 400 cm^{-1}, the count of infrared fundamentals may be short. On the other hand, some of the counted bands may be overtones or combinations. Any conclusions we make should therefore be based on large differences in the numbers of fundamentals. The Raman data should be given greater weight, since our range of observation is larger and overtones are much lower in intensity. Happily, the diene **1** presents a very straightforward case. The number of observed infrared and Raman vibrations, and the number of polarized Raman bands are very close to the expectation for the C_{2h} chair (Table IV): 28, 27, 16 observed *vs.* 27, 27, 15 predicted. The less symmetrical boat and twist forms predict a much larger number of fundamentals. The planar form, though not eliminated on the basis of number of fundamentals, is inconsistent with the number of polarized Raman bands (9 predicted *vs.* 16 observed).

The same ground rules, when applied to the dispiro compound **2**, give 23 infrared fundamentals (out of 25 observed peaks) and 30 Raman fundamentals (out of 30), of which 19 are polarized. The chair form predicts 36 infrared and Raman fundamentals and 20 polarized Raman bands, whereas the boat and twist forms again have a much larger expected number of bands. The infrared count is probably low because of the unobserved region below 400 cm^{-1}. The data, particularly from the more important Raman spectra, are consistent with the chair form.

The data for the dione **3**-d_8 are more difficult to treat in this manner. Only overtones and combination bands should be expected above about 2300 cm^{-1}. Below this point, 33 infrared peaks were observed from the KBr pellet, and a possible additional 5 from the CH_2Cl_2 solution. This number is far in excess of that possible for a chair, but it cannot differentiate between the D_2 (31) and C_2 (42) twist boats and the C_{2v} boat (32).

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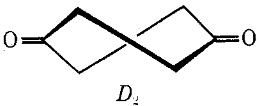
TABLE IV

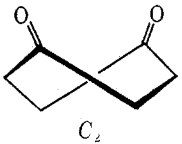
PREDICTED AND OBSERVED NUMBERS OF VIBRATIONAL FUNDAMENTALS

	1			2			3-d_8		
Symmetry group	Ir	R	P[a]	Ir	R	P[a]	Ir	R	P[a]
C_s ($3n - 6$)	54	54	54	72	72	72	42	42	42
C_{2h} (chair)	27	27	15	36	36	20	21	21	12
D_2 (symmetrical twist)	40	54	14	53	72	19	31	42	11
C_2 (tilted twist)	54	54	28	72	72	37	42	42	22
C_{2v} (boat)	41	54	15	55	72	20	32	42	12
D_{2h} (planar)	22	27	9	28	36	11	17	21	7
Observed	28	27	16	23	30	19	33/38[b]	25/27[c]	>12

[a] Number of polarized (totally symmetrical) Raman bands. [b] The first figure refers to data from the KBr pellet alone; the second includes additional bands observed in CH_2Cl_2 solution. [c] The first figure refers to data from CH_2Cl_2 solution alone; the second includes additional bands observed in CH_3OH solution.



D_2



C_2

The Raman data are not so useful in this context, because the solvent bands mask too many peaks. Of the 25 peaks observed in CH_2Cl_2 (27 when the two additional bands in CH_3OH are included) at least 12 are definitely polarized. Because polarization ratios could not be measured on some 10 peaks owing to solvent interference, the total number of polarized bands should greatly exceed the maximum number possible for the C_{2v} boat or the symmetrical D_2 twist boat. More reliable data on crystalline material was not possible because of fluorescence. Because the number of polarized peaks expected for the D_2 (11) or C_{2v} (12) forms and the C_2 form (22) is quite different, the method is potentially able to make the differentiation. We believe that our data point to the C_2 form, but a firm conclusion cannot yet be made.

Summary.—All evidence points to chair conformations for 1,4-dimethylenecyclohexane (1) and dispiro[2.2.2.2]decane (2). The diene exhibits 4 coincidences out of 21 possibilities, the dispiro compound 7 out of 17. The total number of fundamentals and the number of polarized Raman bands are consistent with the chair rather than with any of the less symmetrical boat or twist forms. Cyclohexane-1,4-dione-d_8 (3) has 14 coincidences out of a possible 18, so that a noncentrosymmetric boat or twist form is indicated. This conclusion is confirmed by the total number of infrared fundamentals. The number of polarized Raman bands points toward the tilted twist form (C_2), rather than the symmetrical twist (D_2) or the classic boat (C_{2v}). The present data are not unambiguous in this latter conclusion because many of the Raman bands are masked by solvent peaks. These conclusions refer to the dominant conformational form of each molecule. The presence of minor forms cannot be excluded.

Experimental Section

Infrared spectra were determined on a Beckman IR-9 spectrophotometer. Survey spectra were recorded at 200 cm^{-1}/min, and the frequency measurements were subsequently carried out at 8 cm^{-1}/min. The instrument was calibrated with a polystyrene film for each individual run. The liquids **1** and **2** were run as thin films on KBr plates. The dione **3** was run in a KBr pellet or in dilute CH_2Cl_2 solution. Frequencies of individual bands are accurate to ±1 cm^{-1}.

Raman spectra were determined on a laser Raman spectrophotometer described elsewhere,[18] using the 5141.7-Å emission of a 90-mW Argon ion Carlson Laboratory laser. Survey spectra were recorded initially, followed by redetermination of the frequency of each emission line at a slower scan rate or by manual variation of the monochrometer to determine maximum emission. Depolarization ratios were determined by maximizing the emission through a polarizing filter (parallel orientation) and then recording the spectrum again with the lens rotated 90° (perpendicular orientation). Intensities were determined either by photon counting at the emission maxima or by integration of the recorded spectra. The liquids **1** and **2** were examined without solvent in a 1-cm-diameter cell. The dione **3** was run as a 30% solution in CH_2Cl_2 and as a 25% solution in CH_3OH. The Raman spectra of the pure solvents were run prior to the determination of the dione spectrum. A solid disc of the dione gave only intense fluorescence. Frequencies of individual bands are accurate to ±1 cm^{-1}.

1,4-Dimethylenecyclohexane (**1**) was purchased from Chemical Samples Co. and used without further purification.

Dispiro[2.2.2.2]decane (**2**) was kindly supplied to us by Dr. J. L. Gosnell, Jr.[7]

Cyclohexane-1,4-dione-d_8 (**3**) was obtained by the acid-catalyzed exchange of the protons in cyclohexane-1,4-dione (Aldrich Chemical Co.) with D_2O according to the procedure of Wood, *et al.*[12] By this method, 0.3 g of PCl_5 was dissolved in 15 ml of D_2O, and the solution was added to 6.0 g of the dione. The reaction was stirred at room temperature for 8 days and extracted into CH_2Cl_2. The solution was dried ($MgSO_4$) and evaporated to dryness. The recovered product was subjected to four such exchanges. The final product was 98.2% deuterated (85% d_8, 15% d_7 by mass spectrometry), mp 78–79° (lit.[12] mp 78–79°).

Registry No.—**1,** 4982-20-1; **2,** 24518-94-3; **3**-d_8, 23034-25-5.

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