

Short Communications

Raman Spectra of Crystalline
trans-1,2-DihalocyclohexanesHANS T. HORNTVEDT and
PETER KLÆBOE*Department of Chemistry, University of Oslo,
Oslo 3, Norway*

The conformational equilibria of the *trans*-1,2-dihalocyclohexanes (later called dihalocyclohexanes) have been studied in considerable detail. In the vapour and liquid phases these compounds form a mixture between a polar (*ee*) and an unpolar (*aa*) conformation. The conformational equilibrium is highly affected^{1,2} by the dielectric constant of the surrounding medium (solvent). Moreover, heavy halogen substituents favour *aa* and lighter halogens the *ee* conformers in the vapour and the liquid. This trend is further demonstrated by which conformer exists in the crystalline state. It was found that dichlorocyclohexane¹⁻³ existed in *ee*, whereas the dibromo,¹⁻³ chloroiodo,⁴ and bromoiodo⁵ compounds crystallized in the *aa* conformation. Having intermediately bulky halogens, bromochlorocyclohexane crystallized in *ee* at low temperatures³ and in *aa* at high pressure.⁶

The vibrational spectra of the dihalocyclohexanes are particularly interesting because the *ee* and *aa* conformers have largely their independent vibrational bands with quite few coincidences.³ In the monohalocyclohexanes⁷ several coincidences were observed, whereas in halogenated non-cyclic hydrocarbons most of the vibrational bands are common to the different conformers. For this reason we have attempted a careful attribution of the IR and Raman bands in the dihalocyclohexanes to the *ee*, *aa*, or *ee* + *aa* conformers. These results will be used as a basis for deriving force fields for the two conformers. In addition to the criteria used previously²⁻⁶ we have now

recorded the Raman spectra of dichloro-, bromochloro-, and dibromocyclohexane in the crystalline state at -180° . These data are given in the present communication, leading to a revised attribution for certain fundamentals.

Experimental. The samples of dichloro-, bromochloro-, and dibromocyclohexane were identical to those used in the previous studies.³ A cryostat, designed for 90° illumination technique,⁸ was employed in conjunction with the Cary 81 spectrometer and a Spectra Physics No. 125 A helium-neon laser. The samples were evaporated on a cold finger of copper kept at liquid nitrogen temperatures, annealed a few degrees below the freezing point and recooled to -180° before recording.

Results and discussion. The observed Raman frequencies of crystalline dichloro-, bromochloro-, and dibromocyclohexane are listed in Table 1 together with the liquid state³ values. Raman bands present in the liquid which definitely vanish in the crystals are equipped with asterisks. From our earlier results³ these Raman bands must be attributed to the *aa*, *aa*, and *ee* conformers in dichloro-, bromochloro-, and dibromocyclohexane, respectively. The Raman bands present in the crystals should belong to the stable conformers *ee*, *ee*, and *aa*, respectively, or attributed to coinciding bands of both conformers.

It is encouraging that the present attributions agree very well with our previous conclusions derived from IR data of the liquid and crystalline states and solvent effects observed in the IR and Raman spectra. In spite of the low symmetry of the dihalocyclohexanes, making all the vibrational bands allowed in IR as well as in Raman, the band intensities are frequently very different in the two media. Some of the earlier attributions were uncertain because of low IR band intensities or because of band overlap and indefinite solvent effects. Moreover, the four low frequency funda-

Table 1. Raman spectral data^a for the *trans*-1,2-dihalocyclohexanes.

Liquid ^b	C ₆ H ₁₀ Cl ₂ Solid	Cf. ^c	Liquid ^b	C ₆ H ₁₀ BrCl Solid	Cf. ^c	Liquid ^b	C ₆ H ₁₀ Br ₂ Solid	Cf. ^c
1446 s ^d	1443 s	<i>e,a</i>	1446 vs	1442 m	<i>e,a</i>	1444 vs	1440 m	<i>e,a</i>
1433 m	*	<i>a</i>	1431 s	*	<i>a</i>	1432 vs	1430 s	<i>a</i>
1360 vw			1359 vw	*	<i>a</i>	1359 s	1354 m	<i>a</i>
1342 s	1340 s	<i>e</i>	1339 s	1335 s	<i>e,a</i>	<i>1348 w</i>	<i>1340 w</i>	<i>a</i>
1332 w	1331 m	<i>e</i>	1333 w	1330 w	<i>e</i>	<i>1336 s</i>	*	<i>e</i>
1303 vw			1320 vw	*	<i>a</i>	1330 s	*	<i>e</i>
1283 m	1281 s	<i>e</i>	<i>1301 m^e</i>	*	<i>a</i>	1301 s	1300 m	<i>e,a</i>
1271 s	*	<i>a</i>	<i>1281 m</i>	<i>1279 m</i>	<i>e</i>	1280 vw		
1260 vw	1259 w	<i>e,a</i>	<i>1271 m</i>	*	<i>a</i>	1269 m	1264 m	<i>a</i>
1233 vw			1263 vs	*	<i>a</i>	1255 s	1251 s	<i>a</i>
1221 vw	1220 w	<i>e</i>	1226 m	*	<i>a</i>	1226 vw		
1213 vw			1217 s	1214 m	<i>e</i>	1197 vs	1190 vs	<i>a</i>
1203 s	1203 s	<i>e</i>	1203 s	1200 m	<i>e</i>	1178 m	1170 m	<i>a</i>
1136 m	*	<i>a</i>	1135 m	*	<i>a</i>	1159 m	*	<i>e</i>
1125 m	1123 m	<i>e</i>	1120 m	1118 m	<i>e,a</i>	1136 m	1136 m	<i>a</i>
1103 s	1104 m	<i>e</i>	1094 s	1095 m	<i>e,a</i>	1124 m	1121 m	<i>a</i>
1084 vw	1082 m	<i>e</i>	<i>1083 vw</i>	<i>1079 w</i>	<i>e</i>	1116 w	*	<i>e</i>
1065 vw			1061 m	*	<i>a</i>	<i>1086 s</i>	*	<i>e</i>
1051 s	1051 s	<i>e</i>	1049 s	1046 s	<i>e</i>	1074 vw		
1040 s	1040 s	<i>e</i>	1035 s	*	<i>a</i>	1058 m	1057 m	<i>a</i>
1033 m	*	<i>a</i>	1001 m	*	<i>a</i>	1047 s	*	<i>e</i>
1006 vw			976 s	976 s	<i>e</i>	1032 s	1029 s	<i>a</i>
981 s	980 s	<i>e</i>	938 w	938 w	<i>e</i>	999 w	996 m	<i>a</i>
942 m	942 m	<i>e,a</i>	906 s	908 m	<i>e,a</i>	971 m	*	<i>e</i>
910 m	911 m	<i>e</i>	<i>866 vs</i>	<i>866 m</i>	<i>e</i>	902 m	902 vw	<i>e,a</i>
871 m	870 m	<i>e,a</i>	843 vs	843 s	<i>e</i>	866 vs	862 vs	<i>a</i>
863 vw			819 s	*	<i>a</i>	840 s	*	<i>e</i>
845 s	845 s	<i>e</i>	805 vs	810 m	<i>e</i>	812 vs	806 vs	<i>a</i>
827 s	*	<i>a</i>	743 vs	739 s	<i>e</i>	802 vs	800 m	<i>a</i>
821 w	820 m	<i>e</i>	734 w	730 w	<i>e</i>	713 vw	712 w	<i>e,a</i>
806 s	802 vw	<i>e,a</i>	692 vs	689 vs	<i>e,a</i>	696 m	*	<i>e</i>
744 w	739 m	<i>e</i>	663 vs	*	<i>a</i>	685 m	*	<i>e</i>
735 vs	730 vs	<i>e</i>	652 m	*	<i>a</i>	651 vs	645 vs	<i>a</i>
700 vs	*	<i>a</i>	624 vw			540 s	535 s	<i>a</i>
616 w	*	<i>a</i>	584 s	*	<i>a</i>	493 vw		
514 w	511 m	<i>e</i>	541 vw	*	<i>a</i>	475 vs	472 vs	<i>a</i>
498 s	*	<i>a</i>	508 w	504 m	<i>e</i>	461 vw		
461 vw			485 vs	*	<i>a</i>	439 s	*	<i>e</i>
447 vs	446 s	<i>e</i>	461 w	*	<i>a</i>	425 vw		
384 vs	380 vs	<i>e</i>	443 s	443 s	<i>e</i>	408 vw		
375 m	371 s	<i>e</i>	368 vs	363 vs	<i>e</i>	364 s	359 s	<i>a</i>
361 w	*	<i>a</i>	345 vs	341 vs	<i>e</i>	337 m	*	<i>e</i>
331 w	329 m	<i>e</i>	318 s	315 m	<i>e</i>	321 m	320 m	<i>a</i>
307 vs	*	<i>a</i>	306 m	304 w	<i>e</i>	306 vs	*	<i>e</i>
283 m	280 m	<i>e</i>	263 vs	*	<i>a</i>	275 vw		
233 m	*	<i>a</i>	240 vs	236 m	<i>e</i>	236 s	233 vs	<i>a</i>
210 w	*	<i>a</i>	220 s	*	<i>a</i>	220 m	*	<i>e</i>
182 vs	180 s	<i>e</i>	186 s	*	<i>a</i>	175 vs	175 vs	<i>a</i>
164 m	163 vw	<i>e</i>	177 s	176 m	<i>e</i>	141 m	135 w	<i>a</i>
128 vw	128 w	<i>e</i>	150 s	147 m	<i>e</i>	120 s	*	<i>e</i>
112 vw	*	<i>a</i>	117 m	*	<i>a</i>	108 s	107 m	<i>a</i>

^a Only the region below 1500 cm⁻¹ is included. ^b Liquid state frequencies from Ref. 3.
^c Conformers: *e=ee*, *a=aa*, *e,a=ee+aa*. ^d Abbreviations: s, strong; m, medium; w, weak; v, very; *, absent. ^e Frequencies in italics are revised relative to Refs. 3 and 6.

mentals situated between 200 and 100 cm^{-1} for each compound were not previously recorded in IR and the attributions therefore particularly uncertain.

The low temperature Raman spectra of dichloro-, bromochloro- and dibromocyclohexane established the conformer of *ca.* 10 bands which were previously uncertain. Moreover, four, five, and five bands in the dichloro-, bromochloro-, and dibromocyclohexane, respectively, had earlier been attributed to the wrong conformer, and the frequencies are specified in Table 1 in italics. Some of these alterations involve modified correspondence between liquid and crystal bands, or between IR and Raman bands, always uncertain for close lying fundamentals. A few apparent anomalies were detected in which a crystalline state IR band vanished whereas the corresponding Raman band remained or *vice versa*. This feature is explained as overlapping *ee* and *aa* bands of which one conformer gives rise to strong IR intensity whereas the other conformer is intense in the Raman spectrum.

We believe that the vibrational spectra of the three dihalocyclohexanes have now been studied in more detail concerning conformational aspects than any other compounds of comparable complexity. Employing these data, force constant calculations for each conformer should be of considerable interest.

The authors are grateful to T. Torgrimsen for constructing the cryostat and for his help in the sample alignment.

1. Kozima, K., Sakashati, S. and Maeda, S. *J. Am. Chem. Soc.* **76** (1954) 1965.
2. Klæboe, P., Lothe, J. J. and Lunde, K. *Acta Chem. Scand.* **11** (1957) 1677.
3. Klæboe, P. *Acta Chem. Scand.* **25** (1971) 695.
4. Thorbjørnsrud, J. and Klæboe, P. *Acta Chem. Scand.* **25** (1971) 781.
5. Torgrimsen, T. and Klæboe, P. *Acta Chem. Scand.* **25** (1971) 1915.
6. Hornvedt, H. T. and Klæboe, P. *Acta Chem. Scand.* **25** (1971) 772.
7. Klæboe, P. *Acta Chem. Scand.* **23** (1969) 2641.
8. Levin, I. W. *Spectrochim. Acta A* **25** (1969) 1157.

Received October 19, 1972.

Substituted Propanes Part VIII. The Vibrational Spectra of 1,3-Dicyanopropane (Glutaronitrile)

J. THORBJØRNSRUD, O. H. ELLESTAD,
P. KLÆBOE and T. TORGRIMSEN

*Department of Chemistry, University of Oslo,
Oslo 3, Norway*

The IR spectra of 1,3-dicyanopropane (later called DCNP) as a liquid, as a low temperature crystal and as a complex with CuNO_3 were reported by Matsubara.¹ Force constant calculations for the three probable conformers were later carried out by Yamadera and Krimm.² It was concluded¹ that DCNP exists in a metastable conformer, probably *anti-gauche* (*AG*) upon rapid crystallization, and in a stable crystalline form *gauche-gauche* (*GG*) after annealing. In the liquid an additional conformer, *anti-anti* (*AA*) may be present, whereas the fourth staggered conformer *gauche-gauche*₁ (*GG*₁) with 1,3 parallel substituents should be sterically unfavourable.^{1,2}

We have recently studied³ the 1,2-dihalo as well as the 1,3-dihalo propanes by IR and Raman technique and have extended these investigations to include DCNP. Various spectral features not reported earlier have been included: (a) Raman spectra, including polarization data of the liquid and the low temperature crystal; (b) far IR spectra (400–50 cm^{-1}) of DCNP as a liquid and low temperature crystal; and (c) the IR spectrum of a high pressure (*ca.* 20 kbar) crystal at ambient temperature recorded by means of a high pressure diamond cell.

Experimental. DCNP from the K & K Laboratories was distilled under reduced pressure and the purity checked by gas chromatography. The IR, far IR, and Raman spectrometers, cryostats, diamond cell, beam condenser, and experimental technique have recently been described.³

Results and discussion. The IR and Raman frequencies observed for DCNP are listed in Table 1. A good correspondence was observed between the present IR and Raman frequencies of the liquid and the earlier IR values.¹ However, the previously assigned¹ fundamental at 1174 cm^{-1} was not detected. We observed Raman bands at 969, 825, and 772 cm^{-1} with no or with