

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.

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

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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

Table 1. Infrared and Raman spectral data of 1,3-dicyanopropane.

Infrared ^a	Liquid Raman	Infrared ^a - 70°	Solid Raman - 180°	Infrared high press. ^b	Interpretation
	2970 w,D ^c	2980 w			C-H str.
2955 vs		2960 s			C-H str.
2940 m,sd	2933 s,P	2929 m			C-H str.
2887 m	2894 m,P	2896 w			C-H str.
2832 w,sd	2838 w,P	2840 vw			C-H str.
2250 vs	2247 s P	2254 s			C≡N str.
		2246 s			
		2218 vw			¹² C≡ ¹⁵ N str.
2194 w,sd	2195 vw	2194 vw			¹³ C≡ ¹⁴ N str.
1455 s	1455 w,D	1460 s	1462 m	1467 s	CH ₂ scissor
		1455 w,sd			
		1437 vw,sd			
1427 s	1426 s,D	1430 vs	1422 m	1430 s	CH ₂ scissor
		1423 vw,sd			
		1417 vw,sd			
		1396 w		1398 w	
1365 m	1365 vw	* ^c		1365 vw,sd	AG CH ₂ wag
		1354 w,sd			
1353 m	1345 w,sd	1348 s	1347 w	1353 s	GG CH ₂ wag
		1337 vw,sd			
1332 s	1335 w,D	*	*	*	AG CH ₂ wag
1314 m	1314 vw	1315 s	1321 w	1319 m	GG CH ₂ wag
1297 m	1298 w,D	*	*	*	AG CH ₂ wag
1285 vw,sd	1289 w,sd	1288 vw		1283 w,sd	GG CH ₂ wag
1272 m	1274 w,P	1276 w	1263 m	1276 m	GG CH ₂ twist
		1250 vw			
1224 m	1224 w,P	*	*	*	AG CH ₂ twist
1190 w,sd	1190 vw,sd	1193 m	1186 w	1195 s	GG CH ₂ twist
		1189 m			
1180 w	1183 w,P	*	*	*	AG CH ₂ twist
1120 vw		1124 vw		1133 vw	GG CH ₂ twist
		1075 vw		1073 w	
1064 m,sd	1065 w,sd	1065 m	1065 w		GG asym. C-C str.
1054 m,sd	1055 w,sd,D	*	*	*	AA C-C str.
1044 m	1046 s,P	*	*	*	AG C-C str.
1020 m	1026 m,P	1025 m	1021 w	1032 m	GG sym. C-C str.
1007 m	1008 m,P	1010 m	1009 w	1011 m	GG sym. C-CN str.
997 m		*	*	*	AA C-CN str.
	969 w,P				
944 m	945 w,sdP	*	*	*	AG C-CN str./ CH ₂ rock
904 m	905 w,D?	903 m	902 w	910 m	GG CH ₂ rock
		898 w,sd			
888 w	891 w,sd	*	*	*	AA CH ₂ rock
870 m		872 m	866 vw	880 m	GG asym. C-CN str.
860 m	860 m, P	*	*	*	AG C-CN str./ CH ₂ rock
835 m	835 s, D	837 m	823 vs	848 w	GG CH ₂ rock
	825 s, P?		*		AG C-CN str.
	772 w, P	769 m		770 m	GG CH ₂ rock
757 s	753 vw, D?	754 s		756 m	GG
737 m		*		*	AA CH ₂ rock
583 m	585 w, P	585 m	581 w	597 m	GG CCC bend

Table 1. Continued.

564 w	566 w, sd, P	*	*	*	AA	CCC bend
535 w	532 vw, sd	537 m	533 vw	539 w	GG	CCC bend
507 m	508 m, P	*	*	*	AG	CCC bend
490 w ^d	490 vw	*				CCC bend
478 w ^d	480 vw	*	430 w	*	AA	CCC bend
382 w ^d		*		*		CCN bend
377 m	377 s D	376 m	377 s	381 w	GG	CCN bend
348 vw, sd	348 m	346 m	350 s	351 w	GG	CCC bend
338 s	340 m	*	*	*	AG	CCN bend
325 w, sd	325 w, sd	*	*	*	AG	CCN bend
240 w	245 w, D?	246 m	246 w		GG	CCN bend
212 m	213 w, D?	*	*		AG	CCN bend
175 w	173 w, D	178 m	172 m		GG	torsion
		150 w	148 w		GG	torsion

^a Weak IR bands outside the fundamental regions are omitted. ^b Approx. 20 kbar pressure and 40°. ^c Abbreviations: s, strong; m, medium; w, weak; v, very; sd, shoulder; bd, broad; P, polarized, D, depolarized; AA, *anti-anti*; AG, *anti-gauche* and GG, *gauche-gauche*; *, absent. ^d Observed only in amorphous solid at -70°.

uncertain IR counterparts and have assigned them as fundamentals. Moreover, four IR and Raman bands were detected below 338 cm⁻¹ (region not covered previously), which undoubtedly are low frequency bending or torsional modes.

The IR and Raman bands vanishing in the crystal (equipped with asterisks in Table 1) reveal that our solid was identical to Matsubara's stable crystal, established as GG from similarities with the CuNO₃ complex.¹ Moreover, among four different 1,3-dihalopropanes investigated, all crystallized in the GG conformer at low temperature.³ We never crystallized the metastable solid (supposedly¹ AG) probably because of too slow cooling rate⁴ in our IR and Raman cryostats.

As apparent from Table 1, the IR frequencies of the high pressure crystal were essentially identical to those obtained at low temperature when the unfavourable conditions (wide slits, high gain, and slow scan) of the former is taken into account. Accordingly, DCNP crystallizes in GG under high pressure. We have recently observed that 1,3-diiodopropane crystallized in GG at low temperature, but in AA under high pressure.³ That compound, like DCNP, formed a metastable crystal upon rapid cooling, but with molecules in the AA conformation.⁵ For DCNP, however, the thermodynamically stable conformer in the crystals formed at -70° and at 20 kbar (ca. 50°) was in both cases GG.

It can be seen from Table 1 that many of the strong IR and Raman bands of liquid DCNP (e.g. 1365, 1332, 1297, 1224, 944, 860, 737, and 338 cm⁻¹ in IR, and 1046, 825, and 508 cm⁻¹ in Raman) vanish in the crystal spectra. Great precautions should be exercised when the conformational abundance is inferred from vibrational band intensities. However, these results clearly demonstrate that the GG and the "metastable crystal" conformer (presumably AG¹) are present in comparable concentrations in liquid DCNP at room temperature. In the corresponding 1,3-dihalopropanes the GG conformer is present in large excess in the liquids.³ The fact that some of the Raman bands appear depolarized (1335 and 1298 cm⁻¹) and one band is IR inactive (825 cm⁻¹) might suggest C_{2v} symmetry (AA) for the second abundant conformer in DCNP. However, the greater stability of the *gauche* conformer compared to *anti* in butyronitrile⁶ indicates AG as more stable than AA in DCNP. Dipole measurements⁷ of DCNP can be interpreted in the same direction and we have therefore followed the earlier authors,^{1,2} attributing the two abundant conformers to GG and AG as apparent from Table 1. A few vibrational bands are attributed to the less stable, more symmetric conformer AA. The spectra as well as the force constant calculations² reveal a large overlap between vibrational bands of different conformers for this molecule.

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The Phase Diagrams of the Systems NaCl-MgCl₂ and KCl-MgCl₂

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As a part of our investigations of the physicochemical properties of the magnesium chloride-calcium chloride-alkali chloride electrolyte for the production of magnesium, the phase diagrams of the two systems NaCl-MgCl₂ and KCl-MgCl₂ have been reinvestigated.

The methods used in the investigation were: Thermal analysis, differential thermal analysis, and X-ray diffraction studies at room temperature. These methods and techniques have been described in previous papers¹⁻³ from this institute.

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The chemicals NaCl, KCl, and MgCl₂ were the same as used in the density measurements on molten mixtures in the same systems.⁴ The two phase diagrams are presented in Figs. 1 and 2.

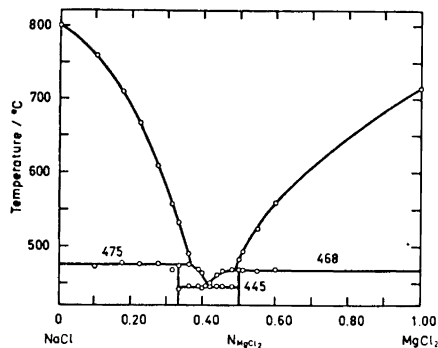


Fig. 1. The phase diagram of the system NaCl-MgCl₂.

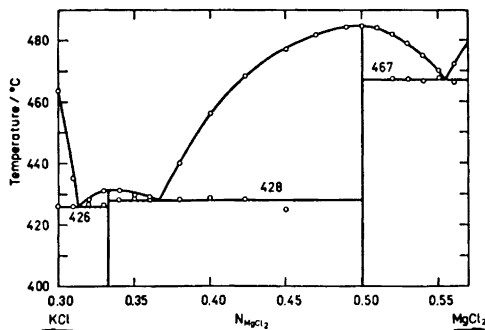
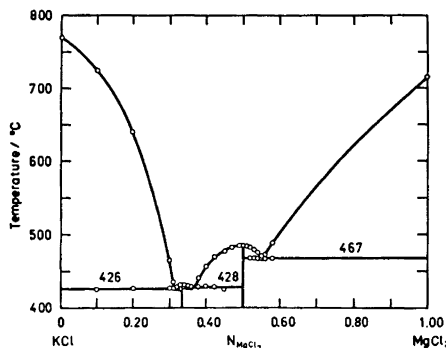


Fig. 2. a. The phase diagram of the system KCl-MgCl₂; b. The main part of the phase diagram KCl-MgCl₂.