

The High Pressure Crystal of *trans*-1,2-Bromochlorocyclohexane

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Recently, we have reported the vibrational spectra of some *trans*-1,2-dihalo-cyclohexanes recorded in the liquid and solid states. The solid state infrared spectra were obtained at low temperatures and for *trans*-1,2-dichloro- and *trans*-1,2-dibromocyclohexane a high pressure crystalline solid was obtained by means of a high pressure cell with diamond windows.² It was observed that for these two molecules the conformation of the molecules were identical in the low temperature and

the high pressure crystalline solids, being *ee* and *aa* for the dichloro and the dibromo derivative, respectively.¹ We have now successfully obtained a high pressure solid of the third molecule: *trans*-1,2-bromochlorocyclohexane (BCC), and the infrared spectrum of this species will be presented in the present communication.

Experimental. The diamond cell, beam condenser, infrared spectrometer and experimental technique have been described previously¹ and the sample from the earlier study was used. We found that the sample crystallized readily at room temperature by applying high pressure. The infrared spectra of various crystalline samples of BCC were recorded: (a) the polycrystalline material first formed when the sample was pressurized; (b) a single crystal grown from the polycrystalline sample by manipulating the pressure^{1,2} and (c) crystalline material formed by simultaneous freezing and pressing. Moreover, the dichroic ratio of the

Table 1. Infrared spectral data of *trans*-1,2-bromochlorocyclohexane. (1600–200 cm⁻¹).

| Liquid | Solid | | Conformer | Liquid | Solid | | Conformer |
|---------|-----------------|---------------|--------------|------------|-----------------|---------------|--------------|
| | Low temperature | High pressure | | | Low temperature | High pressure | |
| 1455 w | 1460 m | 1461 m | <i>ee aa</i> | 906 vs | 907 vs | 906 s | <i>ee aa</i> |
| 1447 vs | 1448 s | 1443 vs | <i>ee aa</i> | 872 w | 868 w | | <i>ee aa</i> |
| 1435 vs | * | 1436 vs | <i>aa</i> | 862 vs | * | 869 s | <i>aa</i> |
| 1360 s | * | 1360 s | <i>aa</i> | 842 vs | 844 vs | * | <i>ee</i> |
| 1338 s | 1340 s | 1341 m | <i>ee aa</i> | 819 vs | * | 818 m | <i>aa</i> |
| 1330 m | 1328 m | * | <i>ee</i> | 815 vs | 815 vs | * | <i>ee</i> |
| 1321 s | * | 1320 m | <i>aa</i> | 806 vw | 802 w | * | <i>ee</i> |
| 1302 vw | 1301 vw | * | <i>ee</i> | 742 vs | 739 vs | 742 vw | <i>ee</i> |
| 1275 s | 1275 s | * | <i>ee</i> | 692 vs | 690 vs | 690 s | <i>ee aa</i> |
| 1264 s | * | 1268 s | <i>aa</i> | 663 s | * | 663 s | <i>aa</i> |
| 1253 s | 1256 s | * | <i>ee</i> | 630 w | 625 w | * | <i>ee</i> |
| 1227 m | * | 1224 m | <i>aa</i> | 584 vs | * | 580 s | <i>aa</i> |
| 1217 s | 1218 s | * | <i>ee</i> | 539 m | * | 539 m | <i>aa</i> |
| 1202 s | 1203 s | * | <i>ee</i> | 505 s | 508 s | * | <i>ee</i> |
| 1188 vs | * | 1183 s | <i>aa</i> | 484 m | * | 485 m | <i>aa</i> |
| 1178 s | 1178 vs | * | <i>ee</i> | 460 m | * | 460 m | <i>aa</i> |
| 1135 s | * | 1139 m | <i>aa</i> | 442 s | 443 s | * | <i>ee</i> |
| 1120 s | 1119 m | 1126 m | <i>ee aa</i> | 406 vw, bd | 400 vw | * | <i>ee</i> |
| 1094 w | 1096 m | 1096 vw | <i>ee aa</i> | 368 m | 365 m | 369 m | <i>ee aa</i> |
| 1062 w | * | 1062 w | <i>aa</i> | 344 m | 343 m | 340 m | <i>ee aa</i> |
| 1048 m | 1045 w | * | <i>ee</i> | 317 m | 316 m | * | <i>ee</i> |
| 1032 s | * | 1032 m | <i>aa</i> | 306 w | 305 m | * | <i>ee</i> |
| 1000 s | * | 1001 s | <i>aa</i> | 262 m | * | 262 m | <i>aa</i> |
| 976 s | 985 s | * | <i>ee</i> | 240 m | 238 m | * | <i>ee</i> |
| 937 w | 940 w | * | <i>ee</i> | 219 m | * | 220 m | <i>aa</i> |

s, strong; m, medium; w, weak; v, very; bd, broad and *, absent.

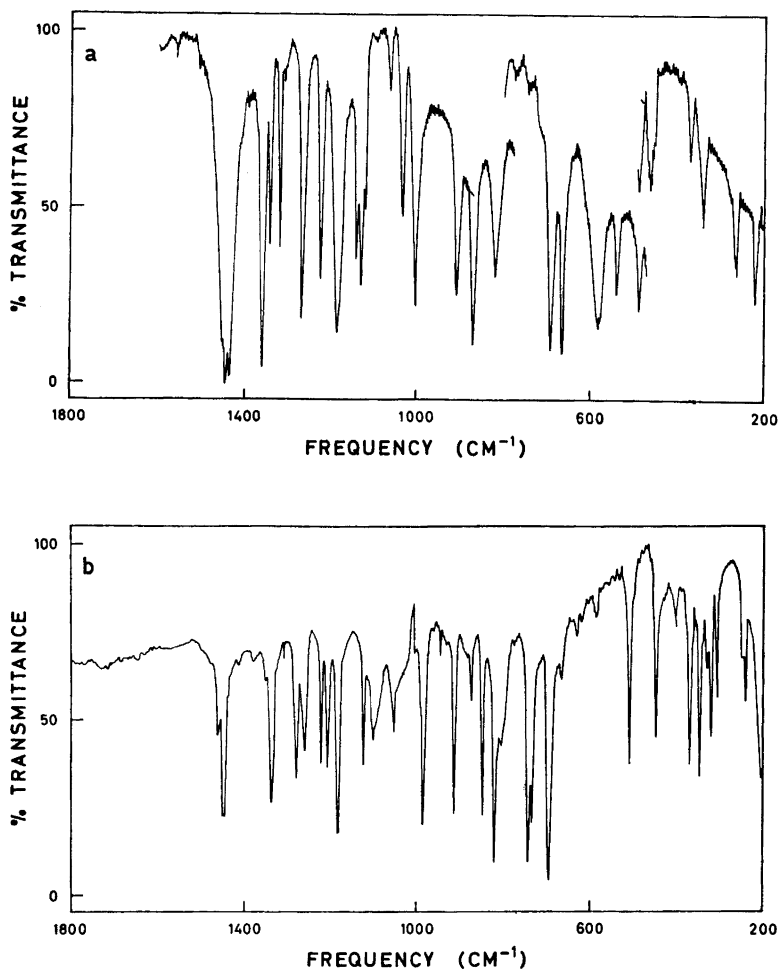


Fig. 1. The infrared spectra (1800–200 cm^{-1}) of crystalline *trans*-1,2-bromochlorocyclohexane; upper curve: single crystal at *ca.* 20 kbar pressure, lower curve: polycrystalline solid at -160° .

various infrared bands were determined on the single crystal, using polarized radiation from the P.E. gold grid polarizer.

Results and discussion. The infrared spectrum of a high pressure single crystal of BCC together with the corresponding low temperature spectrum are shown in Fig. 1. The observed frequencies of the stronger bands below 1500 cm^{-1} , considered

to be fundamentals, are listed in Table 1 and compared with the liquid and the low temperature frequencies. It is immediately apparent from Fig. 1 and Table 1 that there is general non-coincidence between the high pressure and the low temperature spectra. Since the low temperature solid is present¹ in the *ee*-conformation, the high pressure solid clearly exists in the *aa*-conformation. No appreciable variation

between the single crystal and the polycrystalline spectra were observed and we therefore conclude that BCC crystallizes in the *aa* conformation under high pressure at ambient temperature.

The present results for BCC are in sharp contrast with our previous data for the *trans*-1,2-dichloro- and *trans*-1,2-dibromocyclohexane¹ as well as the halo cyclohexanes,⁴ since they all crystallize in the same conformation at low temperatures and under high pressure. Thus, for BCC the stabilities of the *ee* and the *aa* crystalline solids are evidently very similar. This is not surprising since this molecule is a hybrid between the dichloro and the dibromo compounds which crystallize^{1,4} in *ee* and *aa* conformations, respectively. It is interesting to compare the result for BCC with those obtained⁵ for 1,1,2,2-tetrachloroethane giving the *trans* conformation at high pressure and *gauche* at low temperatures. The tetrabromoethane, however, could crystallize in *trans* or *gauche* at low temperatures or high pressure according to the experimental procedure.⁵ Using a simultaneous freezing and pressing an *ee* crystal of BCC was obtained, which slowly changed to *aa* at room temperature during the recording.

The spectrum of BCC in the *aa* conformation obtained for the first time were in good agreement with our earlier assignments¹ for this molecule. However, a few discrepancies were observed for bands which were assigned to one conformer and now turn out to be common for both conformers or *vice versa*.

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Magnetic Properties of (Acylloximato)copper(II) Complexes. Studies in Magnetochemistry 26*

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The constitution of (benzoin oximato)-copper(II), first described by Feigl,^{1,2} has been discussed in some publications.³⁻⁷ The structure shown in Fig. 1 A has been

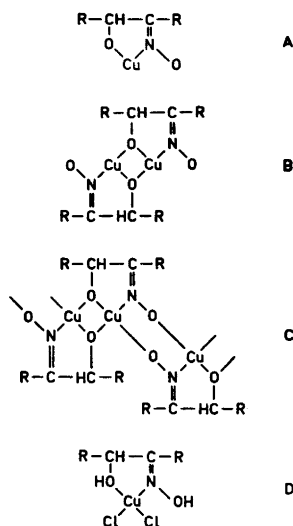


Fig. 1. The structures proposed for the copper complexes.

proposed, and some authors^{5,7} suggest a polymerisation resulting in four-coordinated copper. However, as the complex is insoluble in all common solvents, it has neither been possible to determine the molecular weight, nor to prepare single crystals for X-ray analyses, and it has so far not been possible to prove these assumptions by X-ray evidence. The X-ray powder photos of the compound show, that the substance is microcrystalline; only very diffuse lines appear.

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