Table 1. Assignments of peaks in the ^1H NMR spectrum of the residue after destruction of $CuC_{10}H_{22}N_2O_2Cl_2$.

PPM (δ)	Degeneracy	Relative intensities	Assignment	
1.45	singlet	6	CH_3^a	
2.3	singlet	3	CH_3^c	Group
3.1	singlet	2	CH_2^b	I
3.15	triplet	1	CH_2^d	Group
3.8	triplet	1	CH_2^e	II

ketone, which would decompose to form the amine and mesityl oxide,[5] and as mesityl oxide would decompose to acetone in acidic solutions, it seems reasonable to claim the structure given in Fig. 1 as representative for the product obtained by the cited procedure.

The IR spectrum of the compound under discussion contains a band at 3225 cm^{-1}, not explicable in terms of a complex derived from the Schiff base of acetone and 2-aminoethanol, but close to the value observed for secondary amine complexes,[6] *e.g.* in triethylenetetramine copper(II) at 3195 and 3225 cm^{-1}, a fact which also lends support to the claimed structure.

1. Udovenko, V. V. and Artemenko, M. V. *Zh. Neorgan. Khim.* **4** (1959) 352; *Russ. J. Inorg. Chem.* **4** (1959) 156.
2. Udovenko, V. V., Sherstoboeva, M. A. and Stepanenko, O. N. *Ukr. Khim. Zh.* **35** (1969) 1248.
3. Curtis, N. F. *J. Chem. Soc.* **1960** 4409.
4. Curtis, N. F. and House, D. A. *Chem. Ind. (London)* **1961** 1708.
5. Cromwell, N. H. *Chem. Rev.* **38** (1946) 124.
6. Blight, M. M. and Curtis, N. F. *J. Chem. Soc.* **1962** 3016.

Received January 14, 1971.

Conformational Spectroscopic Studies of *trans*-1,2-Chloroiodocyclohexane

JORUN THORBJØRNSRUD and PETER KLÆBOE

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

Based upon our earlier work we have recently reinvestigated [2,3] the vibrational spectra of some *trans*-1,2-dihalocyclohexanes as liquids, dissolved in various solvents and as crystalline solids at low temperatures and under high pressures. It appears that the energy difference between the *ee* and *aa* conformation for these molecules is not very large in the liquid state. They crystallize [2] in the *ee* or *aa* conformations depending upon which halogens are attached to the ring; the dichloro in *ee*, dibromo in *aa*, whereas bromochlorocyclohexane can crystallize in both conformations.[2,3] We felt it would be of interest to extend these studies to other *trans*-1,2-dihalocyclohexanes to elucidate the steric and polar effects of the halogens upon the conformational stabilities. Moreover, we wanted so far as possible to assign the observed infrared and Raman bands to the *ee* or *aa* conformations and correlate the conformations with the vibrational spectra.

Attempts to prepare the corresponding bromoiodo- and diiodocyclohexane failed, but *trans*-1,2-chloroiodocyclohexane (CIC) could be prepared. To our knowledge this compound has not been studied previously, and the infrared and Raman spectra will be discussed in the present communication.

Experimental. Hypoiodous acid was added to cyclohexene and the formed 2-iodocyclohexanol reacted with phosphorus pentachloride dissolved in benzene. The reaction product was distilled three times under reduced pressure (b.p. 55° at 1 torr).

The infrared and Raman spectrometers have been described, additional infrared bands below 200 cm^{-1} were recorded on a Hitachi Perkin-Elmer F1S 3 spectrometer. A crystalline low temperature solid of CIC was finally achieved after prolonged annealing just below the melting point, but attempts to crystallize the compound under high pressure at room temperature were not successful.

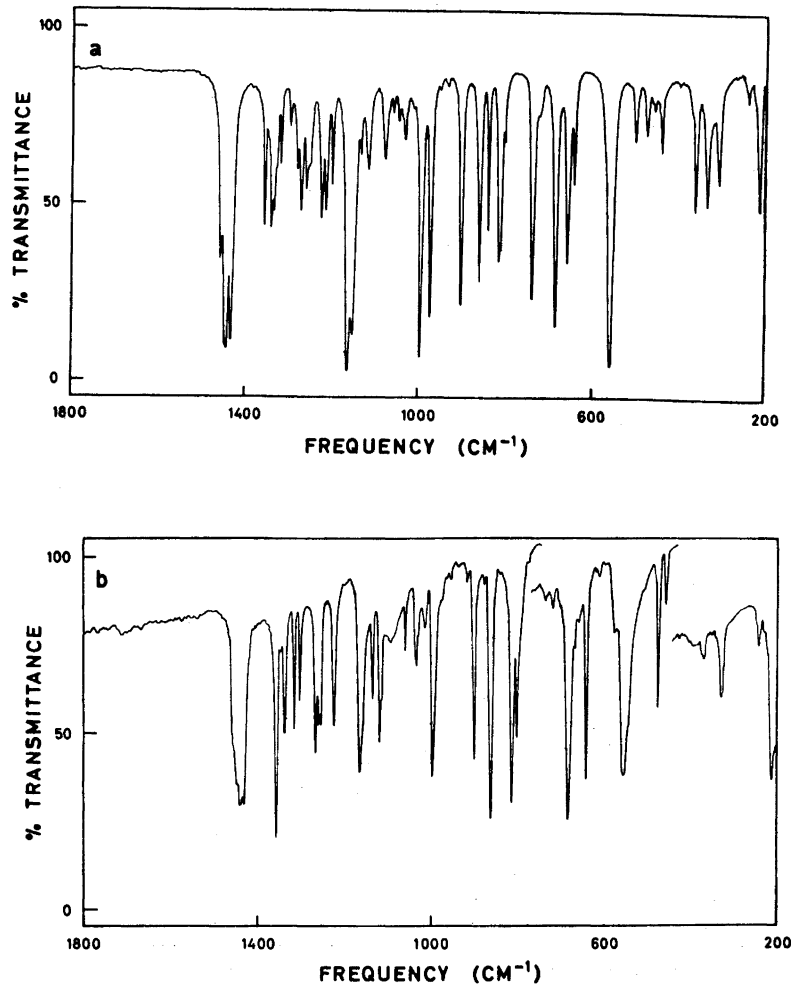

Fig. 1. The infrared spectra (1800—200 cm^{-1}) of *trans*-1,2-chloroiodocyclohexane; upper curve: liquid, cell thickness 0.1 (400—200 cm^{-1}) and 0.025 mm; (1800—400 cm^{-1}); lower curve: polycrystalline solid at —70°, cell thickness *ca.* 0.05 mm.

Results and discussion. The infrared spectra of CIC as a liquid and as a crystalline solid at *ca.* —70° in the fundamental frequency region 1800—200 cm^{-1} are shown in Fig. 1. A list of the observed infrared and Raman frequencies are given in Table 1. In addition to the spectra of liquid CIC, infrared and Raman spectra were recorded of CIC dissolved in CCl_4 and CH_3CN. Large relative variations in the band intensities were observed since the *ee* (*aa*) conformation is stabilized in polar (unpolar) solvents. Bands which increase or decrease in polar solvents are denoted *i* or *d* and are assigned [1,2] to the *ee* or *aa* conformations, respectively. It appears from Table 1 that the *ee* bands disappear in the crystalline state whereas the *aa* bands remain, demonstrating that CIC crystallizes in the *aa* conformation at low temperatures.

Very uncertain estimates of the infrared and Raman band intensities suggest that

Table 1. Infrared and Raman spectral data of *trans*-1,2-chloroiodocyclohexane.

Infrared		Raman	Conformer[a]	Infrared		Raman	Conformer[a]
Liquid	Solid −70°C	Liquid		Liquid	Solid −70°C	Liquid	
		2972 sd	*ee aa*	996 vs d	996 vs	997 m d	*aa*
2940 vs[b]	2938 s	2942 s	*ee aa*	973 vs i	*	974 s i	*ee*
		2900 m	*ee aa*	951 vw	952 vw		
2859 vs	2851 s	2859 m	*ee aa*	933 vw	932 vw	932 vw	
		2842 sd	*ee aa*		915 vw		
2780 vw				902 s	900 s	902 m	*ee aa*
	2700 vw			860 s	861 vs	864 s d	*aa*
2660 vw	2660 vw			840 m i	*	840 m i	*ee*
1458 m	1458 m	1458 sd	*ee aa*	814 s	812 vs	815 s	*ee aa*
	1448 m			809 m i	*		*ee*
1442 vs	1439 s	1442 m	*ee aa*	802 w	801 s	802 s d	*aa*
1432 vs d	1430 s	1431 m d	*aa*	738 s i	738 vw	738 m i	*ee*
1355 m d	1355 vs	1356 vw	*aa*	720 w	718 vw		
1339 m	1337 m		*ee aa*	684 vs d	682 vs	685 s d	*aa*
1331 m	*	1332 m i	*ee*		668 vw		
1327 w	*		*ee*	655 s i	659 vw	656 s i	*ee*
1317 w d	1315 m		*aa*	640 m d	640 s	642 vs d	*aa*
1295 vw	1300 m	1297 w d	*aa*		573 w		
1279 w	*	1279 sd	*ee*	557 vs d	558 s	559 s	*aa*
1270 m	1265 m	1270 sd	*aa*	500 w i	*	500 w	*ee*
1257 m d	1258 m	1259 s	*aa*	475 w d	476 s	476 s	*aa*
1250 w i	1250 m	1248 sd	*ee aa*	458 vw	458 w	459 m	*ee aa*
1221 m d	1222 m	1223 m d	*aa*	440 w i	*	441 m	*ee*
1211 m i	*	1212 sd	*ee*		370 vw	372 vw	*ee aa*
1198 m	*	1200 m i	*ee*	361 m i	*	361 s i	*ee*
1161 vs	1163 s	1162 s d	*aa*	334 m d	331 w	334 s	*aa*
1150 vs i	*	1152 s i	*ee*	306 m	*	306 m i	*ee*
1131 w	1133 m	1133 w d	*aa*	240 w	242 vw	240 s	*aa*
	1118 m	1120 m	*ee aa*	213 m	212 w	213 s i	*ee aa*
1113 w	1112 m					196 vw	*aa*
1076 w	*	1077 w i	*ee*	170 w		171 w i	*ee*
1058 vw	1058 w	1058 w d	*aa*	142 w d		144 w d	*aa*
1046 w i	*	1047 s i	*ee*	112 w		112 vw	*ee*
1031 w d	1031 w	1032 s d	*aa*				

[a] The bands assigned to a conformation are considered to be fundamentals.
[b] Abbreviations: s, strong; m, medium; w, weak; v, very; sd, shoulder; bd, broad; i and d, increased and decreased intensities in polar solvents, respectively.

the *aa* is more abundant than the *ee* conformer in the pure liquid. Moreover, the crystallization of CIC in the *aa* conformation supports the earlier conclusions [1,2] that the *aa* conformation becomes increasingly stable with heavier halogen substituents. Unfortunately, unlike the other *trans*-1,2-dihalocyclohexanes studied,[2] we were not able to determine the high pressure crystalline conformation of CIC which might not be the same as the low temperature conformation.[3]

The observed vibrational bands in Table 1 are assigned to the *ee*, *aa* or *ee*+*aa* conformations in agreement with our earlier work,[2] but for some bands the data are not conclusive. However, the spectral data agree very well with those of the other *trans*-1,2-dihalocyclohexanes.[2] It appears that comparatively few *ee* and *aa* bands coincide for these molecules. As reported earlier [2] we consider the *ee* bands at 738 and 655 cm^{-1} and the *aa* bands at 640 and 557 cm^{-1} to be connected mainly with the

four C–hal stretching vibrations [4] in the present molecule.

We are indebted to K. Ruzicka for synthetic work and to O. H. Ellestad at the Chemical Laboratory V, H. C. Ørsted Institute, Copenhagen, for recording the far infrared spectra.

1. Klæboe, P., Lothe, J. J. and Lunde, K. *Acta Chem. Scand.* **11** (1957) 1677.
2. Klæboe, P. *Acta Chem. Scand.* **25** (1971) 695.
3. Horntvedt, H. T. and Klæboe, P. *Acta Chem. Scand.* **25** (1971) 772.
4. Altona, C., Hageman, H. J. and Havinga, E. *Spectrochim. Acta* **A 24** (1968) 633.

Received February 2, 1971.

Force Fields of the Methylammonium Halides in the α-Phases

G. BORCH

Chemistry Department A, The Technical University of Denmark, DK-2800 Lyngby, Denmark

and

U. ANTHONI and P. H. NIELSEN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

In a recent communication by Whalley [1] it was pointed out that the infrared spectra of the α-phases (stable at room temperature) of methylammonium chloride, bromide, and iodide cannot be interpreted except by taking into account the orientational disorder of the cations of C_{3v} symmetry in the tetragonal field produced by the halide ions. It was shown that the vibrations of species A_1 are almost independent of this disorder and appear as sligthly perturbed fundamentals in the infrared spectra. In contrast, the vibrations of species **E** couple to give several infrared-active combinations. Owing to overlap these appear as broad, Gaussian absorption bands. This difference in shape is clearly observed in the infrared spectra of the methylammonium halides and three deuterated compounds.[2,3]

A harmonic force field for organic ammonium compounds has not yet been described, but is needed as a basis for study of the vibrational spectra of hydrazinium compounds.[4] In the light of the foregoing discussion it follows that only the experimental frequencies of species A_1 of the methylammonium halides can be considered suitable for developing such a force field. The maxima of the bands of species E are produced by superposition of many sub-bands and should be considered only rough approximations to the frequencies of the fundamental vibrations of the isolated methylammonium ion. However, a comparison of the infrared spectra of the α- and the γ-phases of the four isotopic species of methylammonium chloride [3] shows that the main effect of orientational disorder on the absorption bands of species **E** is to broaden the bands without changing the position of the maxima. The fundamentals of species **E** have therefore been included in the experimental material used for determination of the force fields.

The geometry of methylammonium chloride [5] and bromide [6] is partly known, but comparable data do not exist for the iodide. Therefore, all calculations have been carried out assuming tetrahedral bond angles and identical bond lengths: C–H = 1.093 Å, N–H = 1.011 Å, and C–N = 1.465 Å. The methylammonium ion was described in terms of C_{3v} symmetry, *i.e.* with the irreducible representation $5A_1 + A_2 + 6E$. The torsional vibration of species A_2 was omitted in the normal coordinate analyses. The fundamental frequencies (Table 2) were taken from the paper by Theoret and Sandorfy.[3]

The symmetry coordinates were constructed from the internal coordinates (Table 1) in the usual way. The two angle deformation redundants of species A_1 were removed automatically during the calculations. The final force constants for the three methylammonium halides are listed in Table 1. Most of the force constants change regularly from the chloride to the iodide. The decreasing strength in the $N^+-H\cdots X^-$ hydrogen bond in the sequence X = Cl, Br, I is reflected in increasing values of K_r' and decreasing values of $H_{\alpha'}$, $H_{\beta'}$, and K_R.