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VIBRATIONAL SPECTRA AND ROTATIONAL ISOMERISM OF HALO-METHANE SULPHONYL HALIDES: XCH_2SO_2Y (X = Cl, Br; Y = Cl, F)

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ABSTRACT

The infrared and Raman spectra of Cl—CH_2—SO_2Cl, Br—CH_2SO_2Cl, Cl—CH_2SO_2F and Br—CH_2SO_2F have been studied in the gaseous, liquid and solid states. A vibrational assignment of the observed frequencies is proposed for each molecule, and spectral evidence given for conformational isomers.

INTRODUCTION

In a series of studies on sulphonyl compounds, it has been shown that C—H bonds attached directly to a sulphonyl group are likely to take part in hydrogen bonding [1]. The extent of the effect clearly depends upon the substituents on both the S and C atoms. Intra- and inter-molecular hydrogen bonding can be an important factor in stabilizing a particular geometry of all possible isomers due to rotation about the C—S bond [2]. The interesting problems of internal rotation about the C—S bond, with polar substituents on both atoms, has been the subject of both theoretical [3] and experimental investigations [4, 5]. Infrared spectra of a number of R—SO_2Cl compounds recorded at different temperatures indicate that more than one conformation is present in the liquid phase.

The present report contains further experimental evidence from Raman spectra that confirms the presence of conformational isomers of CH_2Br—SO_2Cl in the liquid phase. On crystallization, some of the observed bands in the spectra of the liquid are "frozen out" in the spectrum of the solid, which suggests a preferred conformation on the solid. However, we were unable to observe a gradual intensity change in bands assigned to two different isomers with decreasing temperature. This can be interpreted as a clear indication that the conformation prevalent in the crystal structure is probably favored by packing forces due to specific intermolecular interactions, probably involving hydrogen bonding.

A vibrational assignment for all four molecules is given on the basis of a

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trans-conformation and correspondingly selected values of observed infrared and Raman bands are presented.

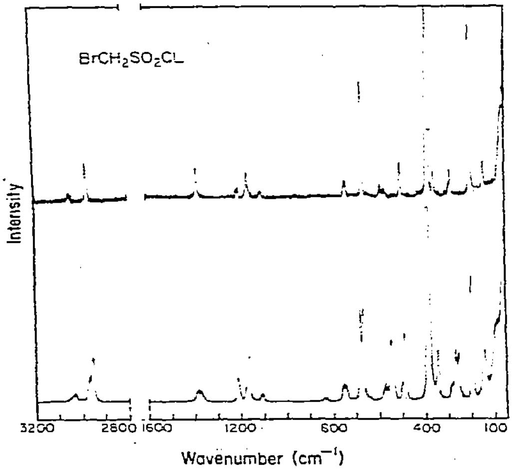
EXPERIMENTAL

$ClCH_2SO_2Cl$ (ClMSCl) was obtained from ICN Pharmaceutical, Inc. and distilled under reduced pressure (b.p. 80°C/24 mm Hg). $BrCH_2SO_2Cl$ (BrMSCl) was prepared from dibromomethane, sodium sulfite and PCl_5 following the procedure given by Truce et al. [6]. The product was distilled in vacuo (b.p. 94°C/21 mm Hg). The proton NMR spectrum shows a single peak at 3.9 ppm.

Chloro- and bromo-methanesulphonyl chlorides were fluorinated with sodium fluoride. In both cases, colourless liquids were obtained with boiling points at 70°C/13 mm Hg for $BrCH_2SO_2F$ (BrMSF) and 43°C/10 mm Hg for $ClCH_2SO_2F$ (ClMSF). The proton NMR spectra show a characteristic doublet at 3.21 ppm with J_{HF} = 6 Hz for $BrCH_2SO_2F$ and at 4.82 ppm with J_{HF} = 6 Hz for $ClCH_2SO_2F$.

Infrared spectra were recorded on a Perkin Elmer 621 grating spectrometer. Stoke's Raman scattering was obtained by excitation with a spectra Physics Argon ion laser Model 164 at 414.5 nm and 488 nm. Spectra were recorded with a Spex-1401 double spectrometer and an ITT Model FW-130 photomultiplier tube. The spectral slit width used was 5 cm^{-1}. Raman spectra of solids were recorded by crystallizing the liquids in a special cell cooled with liquid nitrogen.

Raman spectra of liquid and solid samples are presented in Figs. 1—4. Experimental frequencies, as well as calculated values, are listed in Tables 1 and 2.



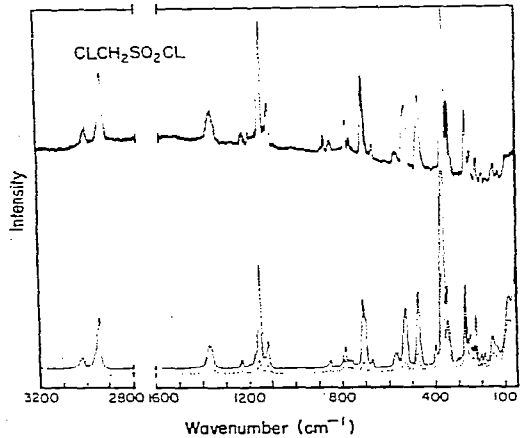
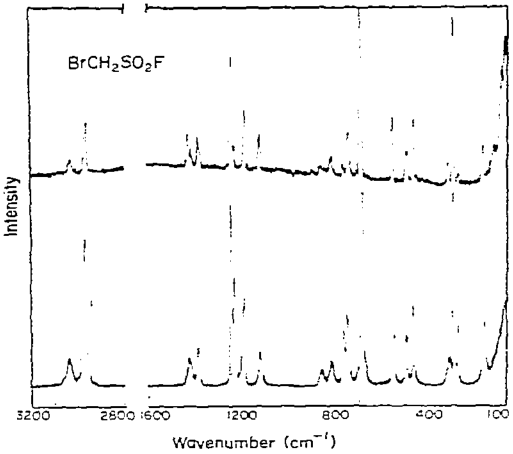


Fig. 1. Raman spectra of liquid (lower traces) and solid (upper traces) $BrCH_2SO_2Cl$.

Fig. 2. Raman spectra of liquid and solid $ClCH_2SO_2Cl$.



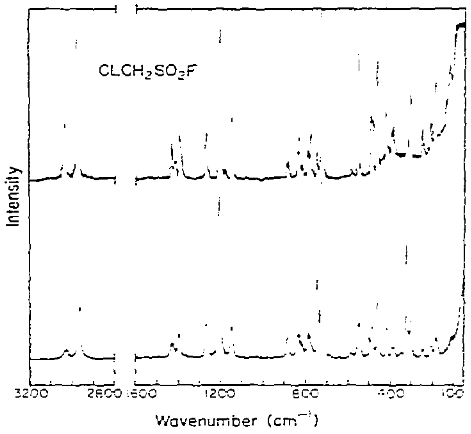


Fig. 3. Raman spectra of liquid and solid $BrCH_2SO_2F$.

Fig. 4. Raman spectra of liquid and solid $ClCH_2SO_2F$.

TABLE 1

Observed and calculated vibrational frequencies for $ClCH_2SO_2F$ and $BrCH_2SO_2F$

No.	$ClCH_2SO_2F$			$BrCH_2SO_2F$			Assignment
	IR[a]	Raman (Solid)	Calculated	IR[a]	Raman (Solid)	Calculated	
1	2965 (l)	2970 s	2986	2968 (l)	2970 m	2968	C—H stretch
2	1398 (g)	1395 m	1440	1391 (g)	1385 w	1430	CH_2 scissor
3	1268 (g)	1266 m	1267	1246 (g)	1242 ms	1248	CH_2 wag
4	1213 (g)	1200 s	1184	1190 (g)	1188 m	1175	SO_2 stretch
5	882 (g)	882 w	837	853 (g)	851 w	824	S—F
6	791 (g)	780 w	749	758 (g)	757 w	760	C—S
7	723 (g)	722 vs	690	678 (g)	681 s	624	C—X
8	544 (g)	550 ms	544	545 (g)	544 m	541	SO_2 scissor
9	486 (g)	486 m	491	490 (l)	488 m	489	SO_2 wag
10		325 vs	270		284 s	241	C—S—F bend
11		186 w	166		156 w	130	X—C—S bend
12	3030 (l)	3032 ms	3050	3037 (l)	3039 w	3047	C—H stretch
13	1442 (g)	1434 w	1438	1445 (g)	1425 w	1429	SO_2 stretch
14	1150 (l)	1150 m	1180	1118 (l)	1116 w	1118	CH_2 twist
15	835 (g)	834 w	807	808 (g)	808 w	773	CH_2 rock
16	450 (g)	456 m	435	453 (l)	454 m	436	SO_2 twist
17		306 m	316		304 w	315	SO_2 rock

[a] l = liquid; g = gas; s = strong; m = medium, w = weak.

TABLE 2

Observed and calculated vibrational frequencies for $ClCH_2SO_2Cl$ and $BrCH_2SO_2Cl$

No.	$ClCH_2SO_2Cl$			$BrCH_2SO_2Cl$			Assignment
	IR^a	Raman (Solid)	Calculated	IR^a	Raman (Solid)	Calculated	
1	2949 (l)	2948 ms	2941	2966 (l)	2966 m	2976	CH stretch
2	1385 (g)	1385 m	1460	1378 (g)	1381 m	1450	CH_2 scissor
3	1246 (g)	1242 w	1256	1209 (g)	1208 w	1244	CH_2 wag
4	1175 (g)	1170 s	1180	1174 (g)	1168 m	1181	SO_2 stretch
5	727 (g)	728 ms	761		741	756	C—S
6		691 w	679		669	633	C—X
7	589 (l)	590 w	565		570 w	536	SO_2 scissor
8	490 (g)	490 ms	514	490 (g)	494 m	511	SO_2 wag
9		384 vs	374		384 vs	375	S—Cl stretch
10		244 m	203		199 s	174	C—S—Cl bend
11		169 w	146		140 m	124	X—C—S bend
12	3026 (l)	3025 w	3042	3046 (l)	3047 w	3046	C—H stretch
13	1416 (g)	1394 (sh)	1394	1425 (g)		1395	SO_2 stretch
14	1136 (g)	1134 w	1134	1106 (l)	1108 w	1105	CH_2 twist
15	808 (g)	804 m	751	828 (g)		765	CH_2 rock
16		354 m	379		347 m	390	SO_2 twist
17		284 ms	284		286 w	288	SO_2 rock

^{a}l = liquid; g = gas; s = strong; m = medium; w = weak.

RESULTS AND DISCUSSION

Molecular geometry and GF calculations

The molecular structure of these molecules has not yet been published. For the G matrix computations, bond lengths and bond angles were transferred from the structures of CH_3SO_2Cl and CH_3SO_2F [7]. The geometry and compliance constants for the S—C—X group were taken from previous work on halomethanes. Compliance constants for the $—CH_2SO_2X$ group are those obtained for CH_3SO_2Cl, CH_3SO_2F [8] and $CH_2(SO_2Cl)_2$ [9] without any further refinement. Therefore, only an approximate correlation between observed and calculated values is expected. This calculation serves the only purpose of producing information complementary to experimental data for vibrational assignment. Calculated values are listed in Tables 1 and 2.

Due to internal rotation about the central C—S bond, several potential minima are possible in the potential energy surface of a halomethane sulphonyl halide. They give rise to possible different molecular conformations, i.e. staggered (*trans* or *gauche* in relation to the spatial location of the halogens) and eclipsed forms. Hargittai and collaborators [7] have studied conformational properties of a number of sulphone molecules in the gas phase.

Their observations favor a staggered form for derivatives with no double bond other than those of the sulfone group attached to the C—S axis. A GF calculation of both *trans* and *gauche* forms was done during this work leading to similar numerical values. Small differences are overbalanced by the approximations in the F matrix and could not be brought into the trans/gauche discussion. For convenience, the results for the *trans* form only are listed in the tables.

The Raman spectra presented in Figs. 1—4, show unequivocal evidence of rotational isomerism: broad band shapes in the liquid phase and changes in relative intensities of certain bands upon transition from liquid to solid phase. Of all four molecules studied, $BrCH_2SO_2Cl$ is the most evident case for at least two main conformations of similar population in the liquid phase, and of one predominant conformation in the crystal structure. Undoubtedly, packing forces, hydrogen bonding in particular, play an important role in determining the molecular geometry. It is not unreasonable to suggest that the more symmetric *trans* form (C_s) would prevail in the solid with predominant SO---H hydrogen bonding in the crystal structure.

To illustrate the changes observed in the RS of BrMSCl, let us examine the 600—700 cm^{-1} region of the spectra. The only vibrational frequency expected in this region is the C—Br stretching mode. In the liquid a very well defined "doublet" is observed at 668 cm^{-1} and 679 cm^{-1}, with similar relative intensities. These two frequencies are assigned to the C—Br stretching vibrations of two different conformational isomers (most likely the *trans* and *gauche* forms of BrMSCl). Since the relative intensities are equal, a 1:1 mixture of the isomers can be assumed. The RS of the crystal, however, shows only one Raman band at 669 cm^{-1}, clearly indicating that one conformation alone is present in the solid. Similar changes in the RS of BrMSCl were observed for C—H stretching vibrations in the 3000 cm^{-1} region.

VIBRATIONAL ASSIGNMENT

CH_2 Vibrations

These characteristic vibrational frequencies need not be discussed in detail. However, what could be called a "reverse mass effect" is clearly observed for C—H stretching vibrational frequencies. In effect, both the symmetric and the antisymmetric vibrational frequencies increase in value if a Cl atom is substituted by a Br atom, in defiance of a mass increase of the $—CH_2X$ group. The same "anomaly" is observed when the vibrational spectra of CH_2Cl_2 and CH_2Br_2 are compared [10]. To account for this effect, a larger force constant for the C—H bond in $—CH_2Br$ with respect to that in $—CH_2Cl$ ought to be assumed. An increase in the value of the stretching force constant of a given chemical bond means a more covalent bond (more electron-sharing) [11]. This is in keeping with the traditional explanation of a more polar (less covalent) bond in $—CH_2—Cl$ than in $—CH_2Br$, due to inductive effect.

$—SO_2—$ Group frequencies

Stretching vibrations of the $—SO_2—$ group are easily identified in the spectra. The antisymmetric vibration gives rise to a strong infrared band, which is always observed in the gas phase for all four compounds, at about 1430 cm^{-1}. As previously observed for $CH_2(SO_2Cl)_2$, $CD_2(SO_2Cl)_2$ and other $—SO_2—$ derivatives [1], the corresponding Raman band is weak, broad and depolarized, Deuteration has shown [1] that the SO_2 antisymmetric stretch is higher in frequency than the $—CH_2—$ scissoring vibration. The symmetric SO_2 vibration is reasonably strong, polarized and characteristic in all RS at about 1190 cm^{-1} (see Figs. 1—4).

SO_2 group deformation vibrations have been assigned mainly on the basis of calculated frequencies as listed in Tables 1 and 2. SO_2 deformations are observed for all four molecules in the very specific range 280 cm^{-1} to 600 cm^{-1}, and therefore, they do not overlap with the skeletal deformations, normally recorded at even lower frequencies. The only exception is in ClMSF where the skeletal deformation C—S—F is observed at 325 cm^{-1}, which could not be mistaken due to its large relative intensity in the RS.

S—X Stretching vibrations

The S—Cl stretching vibration is, as in all sulphonyl chloride derivatives, the most intense band in the RS, and for both BrMSCl and ClMSCl, is recorded at 384 cm^{-1}. In $CH_2(SO_2Cl)$, the S—Cl stretch is observed at 397 cm^{-1} and in CH_3SO_2Cl, at 374 cm^{-1}. Its largest change in polarizability is clearly related to the motion of the two "soft" atoms S and Cl. This also explains a relatively large Raman intensity of the skeletal deformations involving the C—S—Cl group, at 244 cm^{-1} for ClMSCl and 199 cm^{-1} for BrMSCl. The stretching vibration of the much more polar S—F bond is seen mainly in the infrared spectrum as a band of medium intensity while in the RS it is observed as a weak band at 882 cm^{-1} for ClMSF and 851 cm^{-1} for BrMSF.

The lowest frequency value assigned corresponds to the bending vibration of the X—C—S group (X = Br, Cl). In the present assignment, we have not included the torsional vibration, which was also excluded from the set of internal coordinates in our calculations. This is due to the fact that both rotating parts are asymmetric rotors. This particular frequency should be observed below the value of the skeletal vibration and its relative intensity is probably quite low.

CONCLUSION

Vibrational assignment of fundamental vibrational frequencies is proposed for $BrCH_2SO_2Cl$, $ClCH_2SO_2Cl$, $BrCH_2SO_2F$ and $ClCH_2SO_2F$. The present description of the vibrational spectra of these molecules is based on IR and Raman data in all three phases, a GF calculation for each molecule and characteristic group frequencies for a larger series of sulphonyl derivatives. IR and RS of liquid samples of BrMSCl, ClMSCl, BrMSF and ClMSF clearly indicate the presence of more than one rotational isomer, since the number of bands with relative intensities proper of fundamental vibrations is greater than the 18 expected for these molecules. On crystallization, the BrMSCl produce a "clean" spectrum (see Fig. 1) where a number of bands have "frozen out," suggesting the presence of one predominant isomer in the crystal packing. This is not observed for the other three molecules, the isomers of which seem to coexist at low temperatures. A variable-temperature Raman study was also attempted for $BrCH_2SO_2Cl$. The experiment was carried out using the technique of Miller and Harvey [12]. No gradual change of the relative intensity of Raman bands was observed with decrease in temperature. An abrupt change occurred at temperatures below the freezing point upon crystallization. Several attempts were made in a temperature range of 60°C to −50°C. All these compounds form a supercooled liquid before forming a crystal structure. Packing forces most probably induce a particular conformation for $BrCH_2SO_2Cl$ in the crystal structure, but this crystal order does not seem to be followed by $ClCH_2SO_2$, $BrCH_2SO_2F$ and $ClCH_2SO_2F$.

For the other three molecules, important changes are observed between the RS of the liquid and the solid. However, in all cases more than one conformation seems to coexist in the solid crystals. It should be noted that we never obtained a complete crystallization of the ClMSCl, and this particular compound behaves as a supercooled liquid at low temperatures. This anomaly of ClMSCl was also reported in low temperature IR studies [5].

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