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VIBRATIONAL SPECTRA AND CONFORMATIONS OF 1,3-DIBROMO-2,2-DIMETHYLPROPANE (DBDMP) AND 2,2-DI(FLUOROMETHYL)-1,3-DIFLUOROPROPANE (TFN)

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ABSTRACT

Two of the four possible conformers for DBDMP have been observed in the liquid phase. At low temperature DBDMP crystallizes in the GG conformation (C_2), and at high pressure in the AG conformation (C_1).

At least three of the possible six conformers have been observed for TFN. Two are in equilibrium at room temperature, and a third appears only in the matrix spectra deposited from a hot sample.

INTRODUCTION

In addition to their interesting conformational behaviour, halogenated neopentanes have the added feature that some, but not all, form plastic crystalline phases, which lie between the liquid and anisotropic crystalline phases, just as does the parent neopentane (ref. 1).

1-Chloro-2,2-dimethylpropane (ref. 2), 1,3-dichloro-2,2-dimethylpropane (DCDMP), (ref. 3), and 2-(chloromethyl)-2-methyl-1,3-dichloropropane (ref. 4) all form plastic crystals. DCDMP, the chloro analogue of 1,3-dibromo-2,2-dimethylpropane (DBDMP) which will be discussed here, crystallizes at low temperature in the GG conformation of C_2 symmetry and at high pressure in the AG conformation of C_1 symmetry. DCDMP has also been studied by electron diffraction (ref. 5), and molecular mechanics calculations have been carried out for compounds of the formula $C(CH_3)_2(CH_2X)_2$ (refs. 6,7).

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Neither 2,2-di(chloromethyl)-1,3-dichloropropane nor its bromo analogue forms a plastic crystal (ref. 8). Both form anisotropic crystals in which the molecule has D_{2d} symmetry; in the vapour and liquid states or in solution a conformer of S_4 symmetry also appears (refs. 9,10). Observation of only these 2 conformers agrees completely with molecular mechanics calculations (ref. 11) and electron diffraction results (ref. 10).

EXPERIMENTAL

Infrared spectra of the compounds were recorded in the vapour (TFN only), as liquids and solutions, in the plastic crystalline phase (TFN only), as low temperature and high pressure crystalline solids, and isolated in argon and nitrogen matrices deposited on a cold window from vapour mixtures at temperatures from 300 to 900 K (TFN) and to 700 K (DBDMP) using a Perkin-Elmer model 225 spectrometer, a Bruker model 114C FT-IR spectrometer, and a Displex unit from Air Products.

Raman spectra were recorded of the liquids, plastic crystalline phase (TFN only) and low temperature crystalline solids with a Dilor RT 30 triple monochromator with excitation by a Spectra Physics model 2000 argon ion laser.

RESULTS AND DISCUSSION

DBDMP ($C(CH_3)_2(CH_2Br)_2$)

Conformation and barriers

At low temperature the most stable conformer of DBDMP was found by NMR to be the GG (ref. 7). While the molecular mechanics calculations of Stølevik et al. (ref. 6) suggest that only 1.9 kJ/mol separates the three lowest energy conformers (GG, AG, AA), those of Whalon et al. with a different force field (ref. 7) give the same order but place the least stable AA form 6.4 kJ above the low energy GG. This is more consistent with our results as, even at 700 K, we find no evidence for a third conformer. Any thought that a third conformer might indeed be present but separated from the other two only by a small barrier disagrees

completely with the calculations which predict barriers between conformers of the order of 26 kJ/mol. Our own results, in which no change occured on prolonged annealing of the matrices at 34 K, serve only to establish that the barriers are at least 12 kJ/mol (refs. 12,13).

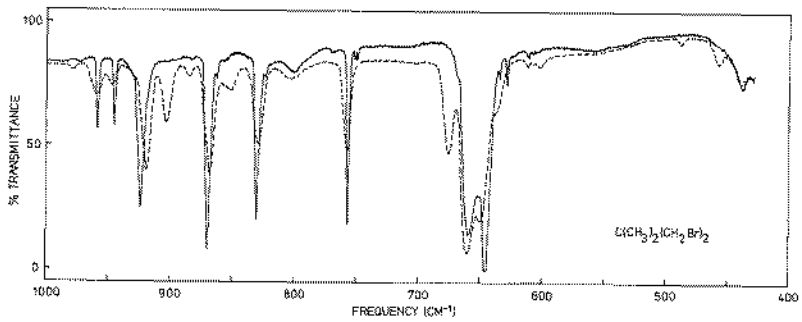

Fig. 1. Infrared spectrum of DBDMP (1000-400 cm^{-1}) as an amorphous solid (dashed curve) and as an anisotropic crystalline solid (solid curve) at 77 K.

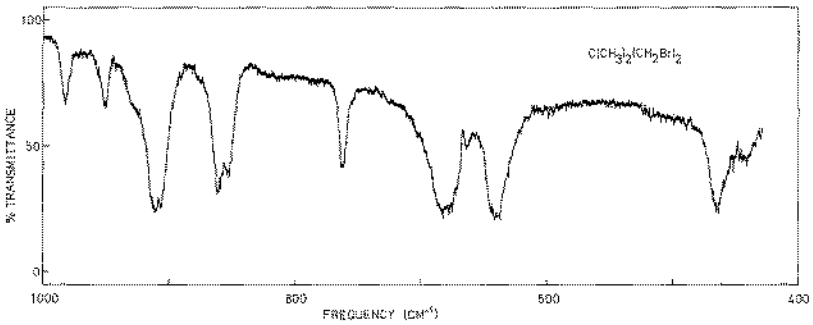

Fig. 2. Infrared spectrum of DBDMP (1000-400 cm^{-1}) as a crystalline solid at ca. 25 kbar.

Normally we would not be able to be as confident about the absence of a third conformer, but, just as with DCMP, the low temperature and high pressure crystals did not contain the same conformer (see Figures 1 and 2).

Based on polarization data, normal coordinates calculations, the NMR results and the molecular mechanics calculations, we can confidently assign the two conformers as GG at low temperature and AG at high pressure, which is exactly what was found in DCDMP. Since we thus can see the spectrum of each of these conformers completely, it is quite obvious that we are not burdened with extra, unexplained bands.

Energies

From Raman spectra recorded at various temperatures and from matrices deposited over a wide temperature range, energy differences of 5.5 ± 0.4 kJ/mol in the liquid and 3.8 ± 0.4 kJ/mol in the vapour were calculated.

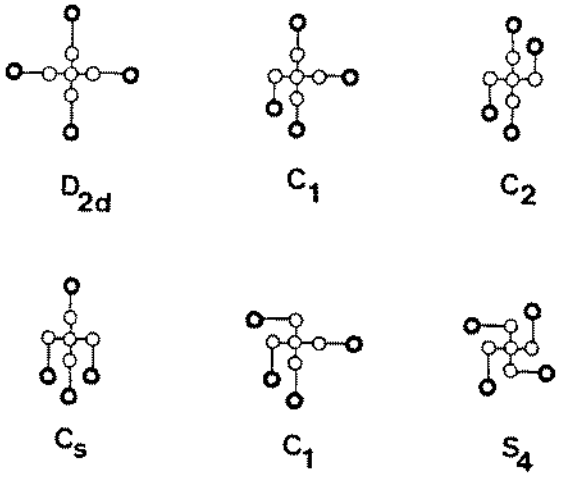

Fig. 3. Possible conformers for TFN.

Plastic crystal

Although the presence of a plastic crystalline phase was never detected at low temperature, as the high pressure crystal was being melted a phase having the characteristic appearance of a plastic crystal was twice seen in the diamond cell.

2,2-DI(FLUOROMETHYL)-1,3-DIFLUOROPROPANE (TFN) ($C(CH_2F)_4$)

In contrast to its chloro and bromo analogues, TFN does form a plastic crystal (ref. 14). Also in contrast to the other two compounds, molecular mechanics calculations on TFN (ref. 11) make it clear that the other four possible conformers which are not acceptable for the chloro, bromo, and iodo analogues must be considered. These conformers, of symmetry C_1, C_1, C_2 and C_s may be present even though they contain, respectively, 1, 1, 2, and 3 parallel 1,3 interactions. Figure 3 shows the six possible conformers, and group theory predictions for the various conformers are shown in Table 1.

TABLE 1
Symmetry Species and Vibrational Activity for TFN

Conformer Symmetry	Vibrational Representation
D_{2d}	$7a_1$ + $4a_2$ + $5b_1$ + $7b_2$ + 11e R,p ia R,dp ir,R,dp ir,R,dp
S_4	11a + 12b + 11e R,p ir,R,dp ir,R,dp
C_1	45a ir,R,p
C_2	23a + 22b ir,R,p ir,R,dp
C_s	25a' + 20a" ir,R,p ir,R,dp

abbreviations: R, Raman; IR, infrared; p, polarized; dp, depolarized; ia, inactive.

Most abundant conformer

First, from the fact that the stronger bands present in the vapour and liquid persist upon crystallization at low temperature, it can be seen that it is the most abundant conformer which is present in the crystal. We think it most unlikely that this conformer is either of the two with high symmetry (D_{2d} and S_4). Below 1500 cm^{-1} the first is expected to have 6 polarized and 4 depolarized Raman fundamentals which have no infrared counterparts; the second should have 9 polarized bands without infrared counterparts. Both should also have 15 depolarized Raman fundamentals with infrared counterparts. Of the 25 Raman bands below 1500 cm^{-1} for which polarization data are available, 20 are polarized. This is far too many for either D_{2d} or S_4. Furthermore, all but 5 of these bands have infrared counterparts. Thus the persistent conformer must be of symmetry C_1 (2 possibilities), C_2, or C_s.

Second conformer

Next we consider the conformer (or conformers) which disappears upon crystallization. That lone conformer (or one of the conformers) almost certainly has D_{2d} or S_4 symmetry inasmuch as three of the disappearing bands (at 818, 790, and 393 cm-) are polarized and have no infrared counterparts. There is probably only one disappearing conformer as only about 17 bands disappear. However, our normal coordinate results place only one fundamental of the proper symmetry near 800 cm^{-1} for either D_{2d} or S_4. Thus, postulation of a single disappearing conformer requires explaining one of the two bands near 800 cm^{-1} as an overtone or combination of the proper symmetry enhanced by Fermi resonance. The high pressure crystal apparently contains the conformer which disappears at low temperature. Furthermore, the barrier (or barriers) between the two (or three) conformers discussed thus far must be low (5 or 6 kJ/mol) inasmuch as bands due to the disappearing conformer are not present in the argon matrix and appear with diminshed intensity (relative to solution spectra) in the nitrogen matrix. In other words, even as the sample is cooling on the cold window, the less stable conformer is being lost. Further, when the nitrogen matrix is annealed at 35 K, the bands of the less stable conformer quickly vanish.

High temperature conformer

Finally, in the matrices deposited from samples at 450 K and 900 K, we see bands which are not seen in the 300 K deposition and thus must be due to yet another conformer. Clearly, the energy of this conformer differs more greatly from the low energy form than do those seen at lower temperature. The barrier of its conversion to the other forms is also large enough that it can be trapped. However, it quickly disappears when the matrix is annealed at 34 K suggesting a barrier of 7 or 8 kJ/mol. For a portion of the matrix spectra, see Fig. 4. We note that these barriers are much lower than those calculated which are of the order of 20 kJ/mol.

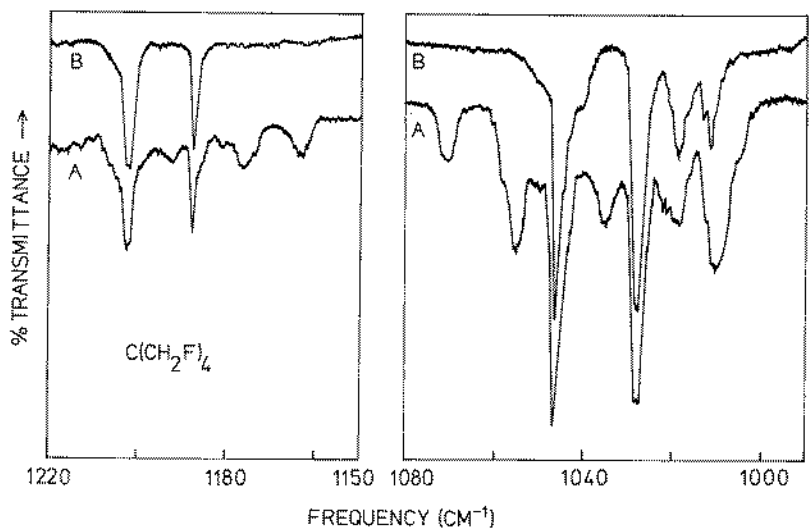

Fig. 4. Infrared spectrum of TFN isolated in a nitrogen matrix before (A) and after (B) annealing at 34 K for 70 minutes.

CONCLUSIONS

We have demonstrated that DBDMP has a plastic phase, that the barrier between the two conformers seen is quite high, and that the same conformer is not present in the low temperature and high pressure crystals. In TFN the barriers are much lower. At least

three conformers have been observed; the barrier separating the lower energy forms is somewhat less than that between the high and low energy forms.

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