CHEMISTRY LETTERS, pp. 951-952, 1982.

INFRARED AND RAMAN SPECTROSCOPIC STUDIES ON MOLECULAR CONFORMATIONS OF $F(CH_2)_nF$ (n=3-6)

Hiroatsu MATSUURA,* Masaaki SAKAKIBARA,† and Hiromu MURATA
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Naka-ku, Hiroshima 730
†Faculty of General Education, Tottori University, Koyama-cho, Tottori 680

The infrared and Raman spectra of $F(CH_2)_nF$ (n=3-6) were measured and analyzed on the basis of the normal coordinate treatment. The spectral analyses indicated that the molecule in the solid state takes the *gauche-gauche* conformation for n=3, *gauche-trans-gauche'* for n=4, *gauche-trans-trans-gauche* for n=5, and *gauche-trans-trans-trans-gauche'* for n=6.

In a series of our previous studies,[1-3] the vibrational spectra of $X(CH_2)_nX$-type molecules (X=Cl, Br, and I; n=4-6) have been thoroughly studied in relation to the molecular conformations. The conformations of the n=3 members (X=Cl, Br, and I) have also been the subject of a detailed study.[4] In the present work, the infrared and Raman spectra of the fluorine analogues, $F(CH_2)_nF$ (n=3-6), were measured and analyzed, to complete the study of the molecular conformations of a series of $X(CH_2)_nX$-type molecules. In analyzing the spectra, normal coordinate treatment has been utilized to establish the assignments of the observed bands.

Samples of $F(CH_2)_nF$ were prepared by treating $Br(CH_2)_nBr$ or $Cl(CH_2)_nCl$ with KF. The normal coordinate treatment was carried out by using a computer program MVIB.[5] The force constants determined previously[6] from the experimental wavenumbers for 1-fluoro-n-alkanes[7] were used, without further modification, to calculate wavenumbers and modes of the normal vibrations for $F(CH_2)_nF$.

For $F(CH_2)_3F$, some of the bands observed in the liquid state disappear on solidification, indicating that only the most stable rotational isomer persists in the solid state. The results of the normal coordinate treatment for the four possible conformers, *trans-trans* (TT), *trans-gauche* (TG), *gauche-gauche* (GG), and *gauche-gauche'* (GG'), clarify that the solid-state bands are all consistent with the calculated wavenumbers for the GG conformer. Examination of the liquid-state spectra reveals that the TG and TT conformers are coexisting in this state along with the GG conformer.

Comparison of the infrared and Raman spectra of $F(CH_2)_4F$ in the solid state proves that their activities are mutually exclusive. This indicates that the molecule has a center of symmetry and accordingly its conformation is either TTT (C_{2h}) or GTG' (C_i). The calculated results readily show that the molecule is in the GTG' conformation in the solid state. The molecule may assume many conformations in the liquid state. The Raman and infrared spectra of this molecule in the

liquid and solid states are shown in Fig. 1.

For $F(CH_2)_5F$ and $F(CH_2)_6F$, the molecule takes the GTTG and GTTTG' conformations, respectively, in the solid state. The latter clearly exhibits the infrared and Raman activities of mutual exclusion.

Table 1 summarizes the conformations of the series of $X(CH_2)_nX$-type molecules established in this and previous works.[1-4] The results lead to a general interpretation of conformational stabilities for α,ω-dihalogeno-*n*-alkanes that the *gauche* conformation about the XCH_2-CH_2C axis is more stabilized in shorter members and that the *trans* conformation about the same axis is more stabilized when X is a heavier atom. The shortest member that assumes the all-*trans* conformation is the one with n=3 for the iodides, n=5 for the bromides, and n=6 for the chlorides. It should be remarked that, for the fluorides, the molecule does not take the all-*trans* conformation even for n=6.

Table 1. Conformations of $X(CH_2)_nX$ in the solid state

X	$X(CH_2)_3X$		$X(CH_2)_4X$		$X(CH_2)_5X$		$X(CH_2)_6X$	
	Conf.	Ref.	Conf.	Ref.	Conf.	Ref.	Conf.	Ref.
F	GG	This work	GTG'	This work	GTTG	This work	GTTTG'	This work
Cl	GG	4	GTG'	1	TTTG	3	TTTTT	3
Br	GG	4	GTG'	1	TTTT	3	TTTTT	3
I	GG,TT[a]	4	GTG',TTT[b]	2	TTTT	2	TTTTT	2

a) At high pressure. b) Metastable.

References

1) H. Matsuura, S. Imazeki, Y. Ogawa, M. Sakakibara, I. Harada, and T. Shimanouchi, Bull. Chem. Soc. Jpn., 52, 2512 (1979).
2) M. Sakakibara, H. Matsuura, and H. Murata, J. Mol. Struct., 55, 21 (1979).
3) M. Sakakibara, Y. Yonemura, Z. Tanaka, H. Matsuura, and H. Murata, J. Mol. Struct., 70, 169 (1981).
4) J. Thorbjørnsrud, O.H. Ellestad, P. Klaboe, and T. Torgrimsen, J. Mol. Struct., 15, 61 (1973).
5) H. Matsuura and M. Tasumi, in "Vibrational Spectra and Structure," ed by J.R. Durig, Vol. 12, Elsevier, Amsterdam, to be published.
6) T. Shimanouchi, H. Matsuura, Y. Ogawa, and I. Harada, J. Phys. Chem. Ref. Data, 9, 1149 (1980).
7) G.A. Crowder and H.-K. Mao, J. Mol. Struct., 18, 33 (1973); 23, 161 (1974).

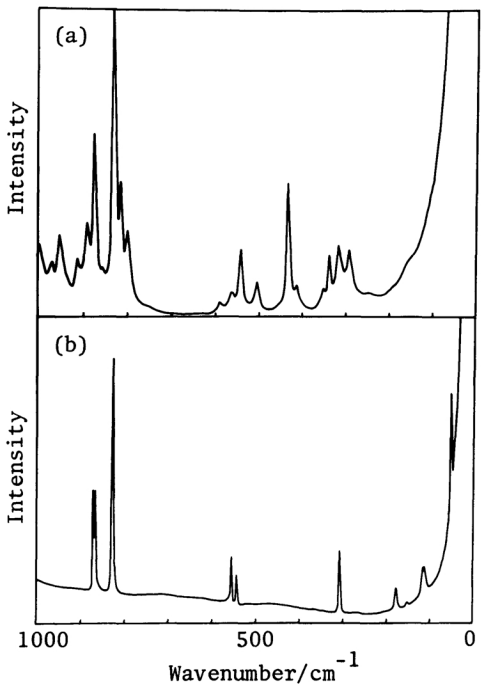

Fig. 1. Raman spectra of $F(CH_2)_4F$. (a) Liquid state and (b) solid state.

(Received March 26, 1982)