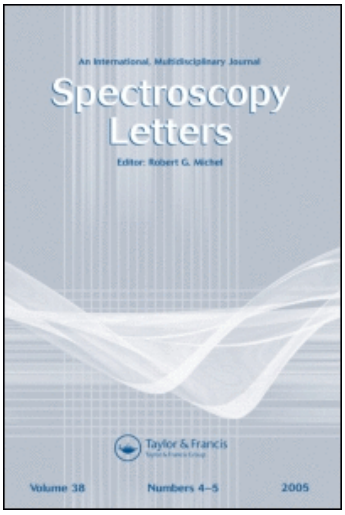

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Conformational Analysis of 3-Metbylbutyronitrile

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CONFORMATIONAL ANALYSIS OF 3-METHYLBUTYRONITRILE

Keywords: 3-Methylbutyronitrile, Conformational analysis, Normal coordinate analysis, Vibrational spectra, Molecular mechanics calculations

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ABSTRACT

Infrared and Raman spectra were obtained for 3-methylbutyronitrile and were interpreted with the aid of normal coordinate calculations. The presence of both possible conformers was verified in this way. Molecular mechanics calculations were made for both conformers, and structural and energy data were obtained.

INTRODUCTION

Rotational isomerism has been shown to exist in alkynes, such as 1-pentyne,[1] 1-hexyne,[2] and 4-methyl-1-pentyne,[3] and in nitriles, such as n-propyl cyanide[4] and n-butyl cyanide.[5] n-Propyl cyanide is similar in structure to 1-pentyne and both exhibit rotational isomerism, with the two conformers of the nitrile having properties very close to those of the alkyne. 3-Methylbutyronitrile and 4-methyl-1-pentyne can both be written as $X{\equiv}C\text{-}CH_2CH(CH_3)_2$, with X = N or CH, so the conformational and vibrational behavior of this nitrile has been studied in order to compare it with the corresponding alkyne.

EXPERIMENTAL

Infrared spectra were obtained with a Nicolet MX-1 FTIR spectrometer. Raman spectra were obtained with a SPEX Ramalog system equipped with a Spectra-Physics model 2020 argon ion laser. The 514.5 nm line was used at ca. 115 mw power, with the sample contained in a 1 ml cell. The sample was obtained from ICN Pharmaceuticals.

CALCULATIONS

Normal coordinate calculations were made with a Prime 9955 computer. The computer programs written by

Schachtschneider[6], were used for calculation of the G matrix (GMAT) and for solution of the vibrational secular equation (VSEC). The molecular mechanics program was written by Allinger and Yuh and converted by Petillo to run on a microcomputer (MICROSOFT FORTRAN v3.20)[8].

RESULTS AND DISCUSSION

3-Methylbutyronitrile can exist in only two spectroscopically distinguishable stable conformations, one with four carbons coplanar (C_1 symmetry) and one with only three carbons coplanar and the two methyl groups projected out of that plane (C_s symmetry). The C_1 conformer should be the low-energy form.

Infrared spectra of 3-methylbutyronitrile are very similar to those of 4-methyl-1-pentyne, and there is little doubt that both conformers exist. Therefore, normal coordinate calculations were made for both conformers in order to make a complete vibrational assignment. Force constants were transferred from a force field determined for propionitrile and the two conformers of butyronitrile,[5] supplemented by three force constants of the substituted group transferred from a branched alkane force field.[9] These force constant values were used without modification. Observed and calculated wavenumbers for both conformers are listed in Table 1. Assignment of the bands to

TABLE 1

Observed and calculated wavenumbers for 3-methylbutyronitrile

Obs. cm^{-1}	Calc. cm^{-1} C_1	Calc. cm^{-1} C_s	Obs. cm^{-1}	Calc. cm^{-1} C_1	Calc. cm^{-1} C_s
	2980	2980	--	987	--
2980	2978	2978	970	-	969
	2978	2978	957	965	963
	2976	2976	930	939	947
2927	2945	2945	912	905	-
	2904	2905	891	-	901
2902	2895	2895	878	880	-
	2895	2895	866	-	861
2878	2879	2879	815	804	-
--	1479	1479	783	-	791
	1467	1467	611	-	618
1466	1462	1462	539	539	-
1450	1458	1458	426	439	-
	1439	1439	412	-	406
1425	--	1414	377	-	374
--	1403	--	355	367	355
1390	1388	1385		349	
1372	1378	1378	340	341	343
1342	--	1330	161	156	144
--	1316	--	-	77	74
1282	1283	1269			
1234	1219	1223			
1170	1153	1184			
1124	--	1128			
1114	1112	--			
1095	1096	1095			

TABLE 2

Molecular mechanics results for 3-methylbutyronitrile

Property	Value
≡CCCC dihedral angle	
C_1 conformer	-173.6°, 63.9°
C_s conformer	- 62.4°, 62.4°
Relative energy (cal/mole)	
C_1	0
C_s	110
Bond lengths (Å)	
C≡N	1.164
≡C-C	1.469
C-C	1.538 - 1.539
C-H	1.114
Dipole moment (D)	3.40
Internal rotational barrier (kcal/mole)	
$C_1 \longrightarrow C_s$	4.2

normal modes (in terms of symmetry coordinates) is available from the author. Table 1 shows that seven bands are assigned solely to the C_1 conformer and nine bands are assigned solely to C_s. The presence of both conformers is therefore necessary to explain the spectra, just as was the case for the alkyne.

Molecular mechanics calculations were also made for both conformers of 3-methylbutyronitrile. The energy difference between conformers was calculated to be only 110 cal/mole, which corresponds to a 71% concentration of the C_1 conformer (with a statistical weight of 2) and a 29% concentration of the C_s conformer. Other results of the molecular mechanics calculations are given in Table 2, which shows the two conformers to have structures similar to those of 4-methyl-1-pentyne. Complete structural parameters are available from the author.

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