The Microwave Spectrum of Hydroxyacetonitrile

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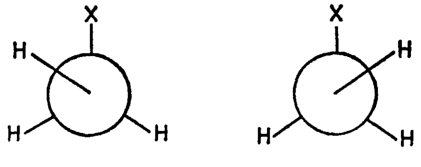
Summary Microwave spectra are reported for $HO{\cdot}CH_2{\cdot}CN$ and $DO{\cdot}CH_2{\cdot}CN$; the O–H and C≡N groups are found to adopt the *gauche* orientation with respect to each other.

RECENT microwave studies of prop-2-yn-1-ol[1,2] and prop-2-yn-1-thiol[3] have established that the most stable conformations are those in which the –OH or –SH bonds adopt the *gauche* orientation with respect to the acetylene groups.



Equivalent *gauche* forms. X = C≡C–H or C≡N

In addition to the usual pure rotational transitions these molecules also exhibit torsion–rotation transitions *via* the μ_c component of the dipole moment and from these the lowest torsional separations have been found to be 21·49 and 0·230 cm^{-1} for the alcohol and thiol respectively. Here we present a preliminary account of our microwave measurements on the related molecule hydroxyacetonitrile, $HO{\cdot}CH_2{\cdot}CN$, and its deuteriated derivative, $DO{\cdot}CH_2{\cdot}CN$.

$HO{\cdot}CH_2{\cdot}CN$ was prepared by the method of Gaudry[4] and $DO{\cdot}CH_2{\cdot}CN$ was best made directly in the waveguide cell by exchange with D_2O vapour. All spectra were observed in a Stark modulation spectrometer at room temperatures. Transitions due to both μ_a and μ_b dipole components were measured for the vibrational ground states and for the first excited torsional states of both $HO{\cdot}CH_2{\cdot}CN$ and $DO{\cdot}CH_2{\cdot}CN$. A selection of the measured lines is given in Tables 1 and 2.

TABLE 1

Measured line frequencies (*in* MHz) *for* HO·CH$_2$·CN

	$V = 0$	$V = 1$
$1_{01} \leftarrow 0_{00}$	9217·40	9213·10
$1_{11} \leftarrow 0_{00}$	37973·88	37998·11
$1_{10} \leftarrow 1_{01}$	29218·47	29244·34
$2_{02} \leftarrow 1_{01}$	18429·22	18420·69
$2_{12} \leftarrow 1_{11}$	17972·85	17969·12
$2_{11} \leftarrow 1_{10}$	18896·70	18887·71
$2_{11} \leftarrow 2_{02}$	29685·90	29711·30
$3_{03} \leftarrow 2_{02}$	27629·91	27616·93
$3_{13} \leftarrow 2_{12}$	26955·75	26950·29
$3_{12} \leftarrow 2_{11}$	28341·39	28327·65
$3_{12} \leftarrow 3_{03}$	30397·33	30422·23

TABLE 2

Measured line frequencies (*in* MHz) *for* DO·CH$_2$·CN

	$V = 0$	$V = 1$
$1_{01} \leftarrow 0_{00}$	8988·88	8985·65
$1_{11} \leftarrow 0_{00}$	34912·96	—
$1_{10} \leftarrow 1_{01}$	26389·51	26396·51
$2_{02} \leftarrow 1_{01}$	17971·45	17965·30
$2_{12} \leftarrow 1_{11}$	17513·76	17510·73
$2_{11} \leftarrow 1_{10}$	18444·36	18436·05
$2_{11} \leftarrow 2_{02}$	26862·35	26867·32
$3_{03} \leftarrow 2_{02}$	26941·68	26932·81
$3_{13} \leftarrow 2_{12}$	26266·62	26262·14
$3_{12} \leftarrow 2_{11}$	27662·06	27650·18
$3_{12} \leftarrow 3_{03}$	27582·77	27584·65

^{14}N quadrupole fine structure has been resolved in the $1_{01} \leftarrow 0_{00}$ transitions of HO·CH$_2$·CN and yields a value of $-3{\cdot}63$ MHz for the tensor component χ_{aa} in the ground vibrational state. The rotational constants derived from low J lines on a rigid rotor basis are given in Table 3 and consideration of these immediately confirms that the *gauche* conformation is also the favoured one here. Thus the quantity $I_C - I_A - I_B$ is calculated to be $-4{\cdot}0256$ a.m.u. Å^2 for the ground vibrational state and $-4{\cdot}0669$ a.m.u. Å^2 for the first excited torsional state. These figures may be compared to the value estimated for the *cis* or *trans* forms which is $-3{\cdot}2$ a.m.u. Å^2. The substitution co-ordinates of the hydroxy-proton ($a = 1{\cdot}437$, $b = 1{\cdot}002$, $c = 0{\cdot}671$ Å for $V = 0$) further substantiate the *gauche* conformation.

TABLE 3

Rotational constants (*in* MHz) HO·CH$_2$·CN

	$V = 0$	$V = 1$
A	33596·18	33621·23
B	4839·66	4836·20
C	4377·74	4376·90
DO·CH$_2$·CN		
A	30651·24	30658·01
B	4727·09	4724·16
C	4261·79	4261·50

Recently the direct torsion–rotation μ_c transitions in DO·CH$_2$·CN have been observed[5] near 16·8 GHz and an approximate treatment of frequency perturbations in the $J_{1,J-1} \leftarrow J_{0,J}$, μ_b, Q-branch lines of HO·CH$_2$·CN indicates that the lowest torsional splitting here is in the region of 3–5 cm^{-1}. It is thus very probable that the *cis–gauche* barrier in hydroxyacetonitrile is rather higher than the 90 cm^{-1} reported for prop-2-yn-1-ol.[2]

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