On the Molecular Structure of Malononitrile

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The structure of malononitrile molecule has been investigated by microwave spectroscopy[1], three kinds of isotopic species, $CHD(CN)_2$, $CD_2(CN)_2$, and $CH_2CNC^{15}N$, being used in addition to the normal one, $CH_2(CN)_2$. The CCN group was found to be bent slightly. However, as Dr. N. Muller pointed out in his private communication, the procedure of the analysis applied gave a mixed r_s and r_0 structure, that is, the positions of hydrogen and nitrogen atoms were determined by isotopic substitution, on the other hand those of carbon atoms were obtained from the first moment equation and the observed moments of inertia, because the isotopic atom ^{13}C was not available[2]. It would be therefore worthwhile to see whether the bent structure of the CCN group is established or not, in the r_0 structure including inertia defect. The reanalysis is made by fitting the calculated x-, y-, and z-moments with the observed by the least-squares method. The result is shown in Table I and the molecular structure obtained is listed in Table II. It is found within the mean deviation that the CCN group is bent by $3°40' \pm 2°54'$[3]. The bond lengths C–C and C≡N are nearer to those found in a number of other related molecules than those obtained in the previous paper, though the mean deviations attached are large enough to include the structural parameters determined by the previous analysis.

It is very difficult to estimate the errors in the molecular structure obtained. The effect of zero-point vibration is a serious factor in the determination of molecular structure by the spectroscopic method. The mean deviations given here are considered mostly due to the effect of zero-point vibration. The error in the observed moment of inertia is of minor importance, and was taken into consideration in the previous paper where the effect of zero-point vibration was ignored. The more detailed analysis will be made possible by using the ^{13}C species.

TABLE I. THE x-, y-, AND z-MOMENTS (amu Å^2)

	$CH_2(CN)_2$		$CH_2CNC^{15}N$		$CD_2(CN)_2$		$CHD(CN)_2$	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
$\sum m_i x_i^2$	1.4124	1.4102	1.4106	1.4102	2.9872	2.9847	2.1805	2.1856
$\sum m_i y_i^2$	170.3922	170.3574	175.1228	175.1228	170.3236	170.3574	170.3564	170.3574
$\sum m_i z_i^2$	22.7964	22.7991	23.0876	23.0877	27.4036	27.4065	25.1430	25.1374

TABLE II. MOLECULAR STRUCTURE OF MALONONITRILE

	r_0 structure	r_0 and r_s structure[a]
C–C	1.468 ± 0.034 Å	$1.480_3 \pm 0.0056$ Å
C≡N	1.167 ± 0.026 Å	$1.146_6 \pm 0.0064$ Å
C–H	1.088 ± 0.010 Å	$1.090_6 \pm 0.0034$ Å
∠CCC	$109°22' \pm 2°54'$	$110°24 \pm 24'$
∠HCH	$108°42' \pm 1°22'$	$108°26' \pm 26'$
∠CCN	$180° - (3°40' \pm 2°54')$ (outside)	$180° - (3°24' \pm 26')$ (outside)
Δ	0.333 ± 0.015 amu Å^2	0.3379 amu Å^2

a) See Ref. 1.

1) E. Hirota and Y. Morino, This Bulletin, 33, 158 (1960).
2) C. C. Costain, *J. Chem. Phys.*, 29, 864 (1958).
3) C. C. Costain and J. R. Morton, (ibid., 31, 389 (1959)) have shown that the C-C≡C group in propynal is bent by 1°36'.

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