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The Molecular Structure of Methyl Isocyanide

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It is known from its Raman spectrum^{1a} and an earlier electron diffraction investigation² that the structure $\text{CH}_3\text{—N}\equiv\text{C}$: makes a larger contribution to the normal state of the methyl isocyanide molecule than the structure $\text{CH}_3\text{—}\dot{\text{N}}=\text{C}$:. If the latter structure were of much importance the C—N—C bond angle might differ somewhat from 180° . The infrared spectrum of the substance has been studied by Badger and Bauer,³ who pointed out that the absence of splitting of certain lines indicates that the molecule is linear. We have made an electron diffraction investigation of the substance with the improved technique

now available, and have verified that the molecule is linear or very nearly linear.

The samples used were prepared by Mr. David H. Brown from silver cyanide by the methods of Hartley and Gautier, and electron diffraction photographs were made and measured in the usual way. The photographs were much better than those obtained by Brockway, with seven measurable rings instead of three. The visual appearance of the photographs is represented by the sketched curve marked "Observed" in Fig. 1. The radial distribution integral calculated from this curve, also shown in Fig. 1, is seen to have principal peaks at 1.17, 1.43 and 2.59 Å. The first of these represents the shorter C—N bond distance with the C—H bond distance (1.09 Å.) unresolved. The effect of the latter on the position of the maximum should be small; we estimate it to be 0.01 Å., leading to 1.18 Å. for the shorter C—N bond distance. The peak at 1.43 Å. corresponds to the longer C—N bond distance and that at 2.59 Å. to the C—C distance.

The fact that the third distance is equal (to within 0.02 Å.) to the sum of the other two indicates that the C—N—C bond angle is close to 180° ; for 160° the value 2.57 Å. would be expected, and for 150° the value 2.52 Å. Assuming that the probable errors of the radial distribution values are about 1%, we see that it is not likely that the angle is less than 160° .

Simplified intensity curves calculated for various models are shown in the figure⁴; the C—H distance was taken as 1.09 Å. and the methyl carbon bond angles as tetrahedral throughout. Temperature factors for the C—H terms were introduced as described by Stevenson, Burnham and Schomaker.⁵ The other parameters of the models are the following

Model	H ₃ C—N, Å.	N—C, Å.	Angle C—N—C
A	1.44	1.18	180°
B	1.44	1.18	163°
C	1.44	1.18	156°
D	1.48	1.17	180°

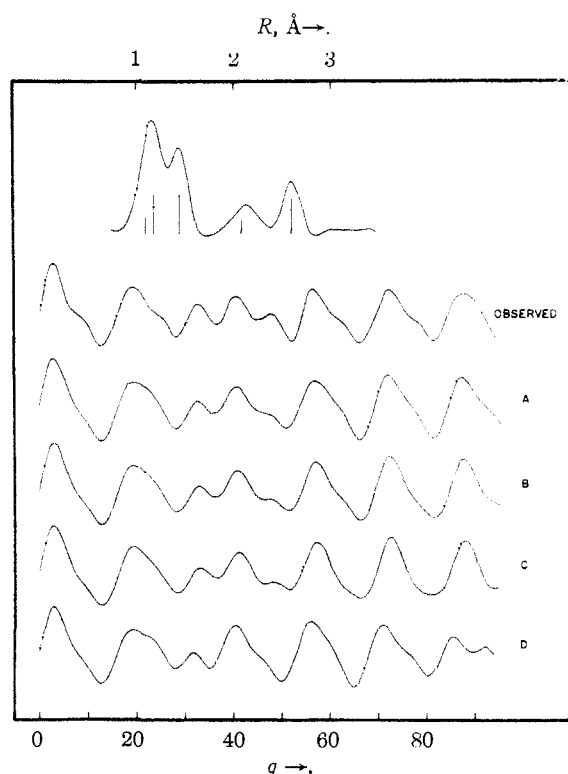


Fig. 1.—(Above) Radial distribution integral for methyl isocyanide, with lines indicating interatomic distances for the accepted structure. (Below) A curve representing the visual appearance of the photographs, and calculated simplified intensity curves for four models.

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(1a) A. Dadiou, *Ber.*, **64B**, 358 (1931).

(2) L. O. Brockway, *THIS JOURNAL*, **58**, 2516 (1936).

(3) R. M. Badger and S. H. Bauer, *ibid.*, **69**, 303 (1937).

(4) The curves were calculated by an equation differing somewhat from that which we have used heretofore; this equation and a brief discussion of the radial distribution integral are given by R. A. Spurr and V. Schomaker, *THIS JOURNAL*, **64**, 2693 (1942).

(5) D. P. Stevenson, H. D. Burnham and V. Schomaker, *THIS JOURNAL*, **61**, 2922 (1939).

Curves C and D (Brockway's model) are unsatisfactory; C does not show the shelves for the 5th and 6th rings, and D makes the 4th ring much less pronounced than observed. A and B are about equally satisfactory. We conclude from this, as from the radial distribution integral, that the deviation from linearity is not greater than about 20°.

The observed frequency of the normal mode of oscillation corresponding mainly to bending of the CNC chain is 290 cm.⁻¹, and the corresponding force constant⁶ has the value 0.205×10^{-11} erg radian⁻². The zero-point energy $h\nu$ for this degenerate oscillation corresponds to a root-mean-square deviation of 9.6° of the C—N—C angle from 180°, and the equipartition energy $2kT$ at room temperature corresponds to the somewhat larger value 11.4°. The model indicated by the spectroscopic data would hence give a calculated intensity curve lying between A and B, and somewhat closer to B than to A. The electron diffraction photographs are accordingly compatible with this model.

The quantitative comparison of model A with the measured ring diameters leads to the C—N interatomic distances H₃C—N = 1.44 and N—C = 1.18 Å., in essential agreement with the radial

distribution values. From these the average C—C distance is calculated, with consideration of the bending oscillation, to be 2.59 Å.

The H₃C—N value 1.44 Å. (which is 0.04 Å. smaller than that reported by Brockway) differs from the single-bond radius sum by only 0.03 Å., whereas the observed H₃C—C distance in methyl cyanide is 0.05 Å. smaller than the radius sum.⁷ This indicates that hyperconjugation of the methyl group and the triple bond is smaller for the isocyanide than for the cyanide, which is reasonable in view of the fact that the corresponding structure H⁺CH₂=N⁺=C:— for the isocyanide has an unstable distribution of charge.

An explanation in terms of resonance can be given of the fact that the observed bending frequency of methyl isocyanide, 290 cm.⁻¹, is much smaller than that, 376 cm.⁻¹, for methyl cyanide, and that the bending force constants computed from the oscillational frequencies, 0.205×10^{-11} and 0.320×10^{-11} erg radian⁻², respectively, are similarly related. The force constant for the cyanide represents essentially the resistance to bending of a single bond and triple bond. In the case of the isocyanide the structure $\text{H}_3\text{C} \backslash \text{N}=\text{C}:$, for which the bent configuration is the stable one, makes an increasing contribution to the normal electronic state as the molecule deviates by increasing amount from linearity, and the resultant increase in resonance energy lowers the wings of the electronic-energy curve, leading to a smaller force constant and oscillational frequency.

We thank Dr. V. Schomaker for his assistance and advice during this work.

Summary

The electron diffraction study of methyl isocyanide shows the molecule to be linear, with interatomic distances H₃C—N = 1.44 ± 0.02 Å. and N—C = 1.18 ± 0.02 Å.

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(7) L. Pauling, H. D. Springall and K. J. Palmer, *THIS JOURNAL*, **61**, 927 (1939).

TABLE I

Max.	Min.	$q_{\text{obs.}}$	q_A	$q_A/q_{\text{obs.}}$
	1	12.7	13.0	(1.02)
1		19.2	19.3	1.005
	2	28.1	28.1	1.000
2		32.5	32.6	1.003
	3	36.4	35.8	0.983
3		40.2	40.6	1.010
	4	44.4
4		47.5
	5	51.4	50.9	0.991
5		56.5	56.7	1.003
	6	65.6	65.9	1.004
6		71.8	71.9	1.002
	7	80.9	81.2	1.003
7		87.5	87.0	0.994

Average 1.000

(6) J. W. Linnett, *J. Chem. Phys.*, **8**, 91 (1940).