The Molecular Structure of 4-Methoxy-2,6-dimethylbenzonitrile *N*-Oxide

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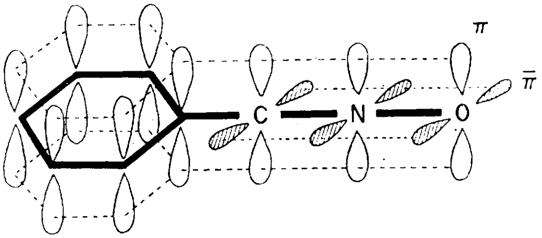
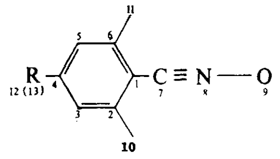
ALIPHATIC and aromatic amine *N*-oxides have been studied by means of *X*-ray analysis and electronic and i.r. absorption spectra,[1] but there is no report on the *X*-ray analysis of the molecular structure of aromatic nitrile *N*-oxide. Various physicochemical studies[2] of substituted benzonitrile *N*-oxides have shown that the CNO group has a character of a partial triple-bond consisting of π and $\bar{\pi}$ systems as shown in the Scheme. As a result, the N→O dative bond length (R_{NO}) becomes relatively short. The present work was undertaken to confirm the electronic structure of benzonitrile *N*-oxide from a structural standpoint and to obtain information on the crystal structure by *X*-ray methods.



SCHEME

Three 4-substituted 2,6-dimethylbenzonitrile *N*-oxides were synthesized[2b] and the crystal structures were determined at room temperature. The crystal structure of (I) at about − 140° has been also established, from which the molecular structure was deduced. Studies on (II) and (III) at low temperature are in progress.



(I) R = OMe
(II) R = Me
(III) R = Br

The crystal data of (I) were obtained by using Cu-K_α radiations: $C_{10}H_{11}NO_2$, M = 177, monoclinic, a = 8·36, b = 12·76, c = 9·01 Å, β = 110°38′, U = 899 Å^3, D_m = 1·260 g.cm.$^{-3}$ (at 25°), Z = 4, D_c = 1·259 g.cm.$^{-3}$ (at 25°), space group $P2_1/c$.

The intensities of 650 observed reflexions were collected by integrated low-temperature Weissenberg photographs, consisting of $(h0l)$ — $(h6l)$ and $(0kl)$ — $(3kl)$. The structure was solved by the Patterson functions and so-called "rigid-body"[3] least-squares techniques, and refined by the full-matrix least-squares methods by using individual anisotropic temperature factors (except hydrogen atoms). With hydrogens included, the final R-value was 7·5%.

Details of the molecular structure are as follows: bond lengths (Å)

C(1)–C(2)	1·390	C(2)–C(3)	1·401
C(3)–C(4)	1·400	C(4)–C(5)	1·394
C(5)–C(6)	1·385	C(6)–C(1)	1·410
C(1)–C(7)	1·435	C(7)–N(8)	1·147
N(8)–O(9)	1·249	C(2)–C(10)	1·518
C(6)–C(11)	1·517	C(4)–O(12)	1·363
O(12)–C(13)	1·436		

bond angles (degrees)

C(1)–C(2)–C(3)	118·9	C(2)–C(3)–C(4)	119·0
C(3)–C(4)–C(5)	121·6	C(4)–C(5)–C(6)	119·9
C(5)–C(6)–C(1)	118·3	C(6)–C(1)–C(2)	122·3
C(2)–C(1)–C(7)	120·2	C(6)–C(1)–C(7)	117·5
C(1)–C(7)–N(8)	173·8	C(7)–N(8)–O(9)	178·3
C(1)–C(2)–C(10)	123·0	C(3)–C(2)–C(10)	118·2
C(1)–C(6)–C(11)	121·4	C(5)–C(6)–C(11)	120·4
C(3)–C(4)–O(12)	122·9	C(5)–C(4)–O(12)	115·5
C(4)–O(12)–C(13)	118·3		

The averaged standard-deviations in bond lengths and bond angles are 0·008 Å and 0·6°, respectively. Bond lengths and bond angles of hydrogen atoms are also reasonable. The molecule is planar within experimental error, but the carbon atom of the methoxy-group is slightly out of the molecular plane (0·14 Å), and –CNO is bent a little in that plane. However, on the basis of molecular packing in crystalline state, it is supposed that –CNO in the free state may be linear just like the structure of fulminic acid.[4]

Molecular dimensions determined here seem to be reasonable compared with the bond order obtained by molecular orbital (MO) calculation.[2] Especially R_{NO} is quite short (1·249 Å). This is consistent with the values[2] (1·27—1·21 Å), in the order of magnitude, estimated by using the relations between bond order and bond length, and between N–O stretching frequency and bond length. In addition, the fact that the present R_{NO} value is larger than that (1·207 Å) of fulminic acid is also theoretically acceptable, since MO calculation led to the same conclusion.[2b]

(*Received, July 22nd,* 1968; *Com.* 977.)

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[1] E. Ochiai, "Aromatic Amine Oxides", Elsevier, Amsterdam, 1967.

[2] (a) T. Kubota, M. Yamakawa, M. Takasuka, K. Iwatani, H. Akazawa, and I. Tanaka, *J. Phys. Chem.*, 1967, **71**, 3597; (b) M. Yamakawa, T. Kubota, H. Akazawa, and I. Tanaka, *Bull. Chem. Soc. Japan*, 1967, **40**, 1600; *ibid.*, 1968, **41**, 1046.

[3] C. Scheringer, *Acta Cryst.*, 1963, **16**, 546.

[4] M. Winnewisser and H. K. Bodensch, *Z. Naturforsch.*, 1967, **22a**, 1724.