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## The Structures of 4-Methoxy-2,6-dimethylbenzointrile *N*-Oxide (I), 4-Bromo-2,6-dimethylbenzointrile *N*-Oxide (II) and 2,4,6-Trimethylbenzointrile *N*-Oxide (III)

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### Abstract

The crystal structures of (I), (II) and (III) have been determined at 130 K (I) and 295 K (II, III). (I) is monoclinic, space group  $P2_1/c$ ,  $a = 8.36$  (1),  $b = 12.76$  (2),  $c = 9.01$  (1) Å,  $\beta = 110.6$  (5)°,  $Z = 4$ . (II) is monoclinic, space group  $P2_1/c$ ,  $a = 8.942$  (1),  $b = 7.040$  (1),  $c = 16.966$  (2) Å,  $\beta = 121.16$  (1)°,  $Z = 4$ . (III) is monoclinic, space group  $C2/c$ ,  $a = 8.771$  (1),  $b = 15.124$  (3),  $c = 7.070$  (1) Å,  $\beta = 105.25$  (1)°,  $Z = 4$ . The structures were refined by the least-squares method to  $R$  indices of 0.071 (862 reflexions) for (I), 0.076 (974) for (II), and 0.163 (383) for (III). The details of the molecular structure of (III) were not obtained because of the disordered structure. The N–O dative bond lengths are 1.249 (7) and 1.237 (10) Å in (I) and (II), respectively, which are shorter than those in trimethylamine *N*-oxide (1.388 Å) and pyridine *N*-oxide derivatives (in the range of 1.28–1.30 Å). The bond  $-C\equiv N\rightarrow O$  is considered to be linear, like those of fulminic acid and acetonitrile *N*-oxide. The hydrogen bonds between the O atom of the *N*-oxide group and the C atom in the benzene ring are weak compared with those found in crystals of pyridine *N*-oxide derivatives.

### Introduction

Various physico-chemical studies of substituted benzonitrile *N*-oxides (Kubota, Yamakawa, Takasuka, Iwatani, Akazawa & Tanaka, 1967; Yamakawa, Kubota & Akazawa, 1967; Yamakawa, Kubota, Akazawa & Tanaka, 1968; Bastide, Maier & Kubota,

1976) have revealed that the  $-C\equiv N\rightarrow O$  groups in benzonitrile *N*-oxides have the character of a partial triple bond, consisting of  $\pi$  and  $\bar{\pi}$  systems (Fig. 1), and that the N–O dative bond lengths are, hence, shorter than those in aliphatic and aromatic amine *N*-oxides.

The structures of trimethylamine *N*-oxide (Caron, Palenik, Goldish & Donohue, 1964) and pyridine *N*-oxide derivatives were investigated, but no structures of benzonitrile *N*-oxides have been reported. The structure analyses of the three compounds were undertaken to confirm the electronic structure of benzonitrile *N*-oxide from a structural standpoint. The structure of (I) has been reported in a preliminary form by Shiro, Yamakawa & Kubota (1968).

### Experimental

Crystals of each compound were obtained from a methanol solution. Crystal data are given in Table 1.

Three-dimensional intensity data for (I) were collected at 130 K on integral Weissenberg photographs with Ni-filtered Cu  $K\alpha$  radiation ( $h0l$ – $h6l$  and  $0kl$ – $3kl$ ). Intensities were measured on a densitometer and those in the upper layer were corrected for spot size. Intensity

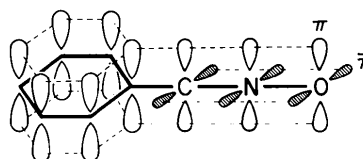


Fig. 1. Schematic  $\pi$ -resonance systems of benzonitrile *N*-oxide.

data of (II) and (III) were collected at 295 K on a diffractometer equipped with a scintillation counter and pulse-height analyser. Intensities were measured by the  $\theta$ - $2\theta$  scan technique with Zr-filtered Mo  $K\alpha$  radiation. Each reflexion was integrated in 80 steps at an interval of  $0.01^\circ \text{ s}^{-1}$ . Backgrounds were counted for 20 s on both sides of the reflexion. Lorentz and polarization corrections were applied, but no correction was made for absorption.

### Structure determination and refinement

#### 4-Methoxy-2,6-dimethylbenzotrile *N*-oxide

The structure was solved by a constrained least-squares method, the coordinates of the center of mass, the orientation angles of the molecule (treated as a rigid-body), and the rotation angle of the methoxy group being used and refined (rigid-body least-squares method). Several sets of initial values of the parameters were assigned by inspection of the vector map and selected on the basis of packing considerations; one of these sets led directly to the correct structure. After the positional and isotropic thermal parameters of all the non-hydrogen atoms had been refined by the full-matrix least-squares method, a difference electron density map revealed all the H atoms in stereochemically reasonable positions. The coordinates and overall temperature factor of the H atoms were fixed in the subsequent refinements. After anisotropic refinement of the non-hydrogen atoms, a difference electron density map showed no significant peaks other than those due to the H atoms. The final  $R$  value, where  $R = \sum |\Delta F| / \sum |F_o|$ , converged to 0.071 for 862 reflexions.\*

#### 4-Bromo-2,6-dimethylbenzotrile *N*-oxide

The structure was solved by the heavy-atom method. After refinements by the block-diagonal least-squares method, all the H atoms were located and verified as for (I). The final refinement reduced the  $R$  value to 0.076 for 974 reflexions.\*

#### 2,4,6-Trimethylbenzotrile *N*-oxide

Systematic absences indicated the space group to be  $Cc$  or  $C2/c$ . The latter centrosymmetric one was initially assumed, which would mean that the molecules lie on twofold axes. The structure was solved by rigid-body least-squares refinement for the  $y$  coordinate of

\* Lists of structure factors and thermal parameters for (I), (II) and (III) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34144 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal data for (I), (II) and (III)*

	(I)	(II)	(III)
	$C_{10}H_{11}NO_2$	$C_9H_9BrNO$	$C_{10}H_{11}NO$
FW	177.2	226.1	161.2
$T$	130 K	295 K	295 K
$a$ (Å)	8.36 (1)	8.942 (1)	8.771 (1)
$b$ (Å)	12.76 (2)	7.040 (1)	15.124 (3)
$c$ (Å)	9.01 (1)	16.966 (2)	7.070 (1)
$\beta$ ( $^\circ$ )	110.6 (5)	121.16 (1)	105.25 (1)
$U$ (Å <sup>3</sup> )	899	913.9	905.0
$D_x$ (Mg m <sup>-3</sup> )	1.31	1.64	1.18
$D_m$ (Mg m <sup>-3</sup> )	1.26 (at 295 K)	1.62	1.15
$Z$	4	4	4
Crystal size (mm)	$0.3 \times 0.3 \times 0.4$	$0.2 \times 0.3 \times 0.3$	$0.3 \times 0.3 \times 0.3$
Linear absorption coefficient (mm <sup>-1</sup> )	0.877 (Cu $K\alpha$ )	4.856 (Mo $K\alpha$ )	0.091 (Mo $K\alpha$ )
Space group	$P2_1/c$	$P2_1/c$	$C2/c$

the center of mass and the rotation angle about the twofold axis. Although the  $R$  value was 0.059 after the refinement by a conventional least-squares technique, the bond lengths and angles thus obtained were unrealistic. The rigid-body refinement of the structure with space group  $Cc$  was then carried out as for (I). A difference electron density map suggested that one molecule was paired with another, located at the position related, approximately, by a twofold axis parallel to the  $b$  axis. On the assumption that these two positions were crystallographically equivalent, the centrosymmetric structure was refined and the  $R$  value reduced to 0.163 (383 reflexions) with isotropic temperature factors for the non-hydrogen atoms. The refinement of the non-centrosymmetric structure starting from a similar molecular arrangement was also undertaken. The degree of occupancy of the molecule in one of the two independent positions, refined as one of the parameters, was close to 0.5, and a structure very similar to the centrosymmetric one was obtained. However, the  $R$  value had not significantly improved. It therefore appears that the statistically disordered structure with space group  $C2/c$  is preferable. A difference electron density map seemed to support this conclusion.\*

The molecules with half-occupancy, paired about a twofold axis, lie on a plane almost perpendicular to the  $c$  axis. Their centers of mass are very close to each other, and the angle between their long molecular axes is  $9.4^\circ$ . The structure is not discussed in any more detail.

The weighting scheme used for (II) was  $w = 1/\sigma^2(F_o)$  for  $|F_c| \geq \sigma(F_o)$  and  $w = 0$  for  $|F_c| < \sigma(F_o)$  or  $|\Delta F| > 3\sigma(F_o)$ , where  $\sigma(F_o) = [\sigma_1^2(F_o) + 0.0054|F_o|^2]^{1/2}$  and  $\sigma_1(F_o)$  is the estimated standard deviation (e.s.d.) depending on the counting errors (Grant, Killeen & Lawrence, 1969). For (I) and (III),  $w = 1$  for all the

\* See previous footnote.

Table 2. Fractional coordinates ( $\times 10^4$ , for H  $\times 10^3$ ), with e.s.d.'s in parentheses, for (I), (II) and (III)

	x	y	z		x	y	z
Compound (I)							
C(1)	1371 (7)	-756 (5)	1677 (6)	H(C3)	-249	-41	220
C(2)	165 (7)	-339 (5)	2286 (6)	H(C5)	-101	-252	-90
C(3)	-1473 (7)	-754 (5)	1747 (6)	H(C10)	-39	87	381
C(4)	-1899 (7)	-1547 (5)	608 (6)	H'(C10)	110	128	296
C(5)	-699 (7)	-1956 (5)	3 (7)	H''(C10)	149	33	461
C(6)	962 (7)	-1546 (5)	543 (6)	H(C11)	304	-145	-27
C(7)	3055 (7)	-310 (5)	2236 (7)	H'(C11)	164	-227	-137
N(8)	4360 (6)	90 (5)	2789 (6)	H''(C11)	280	-261	55
O(9)	5802 (5)	501 (4)	3383 (5)	H(C13)	-549	-278	-143
C(10)	627 (8)	545 (6)	3489 (6)	H'(C13)	-351	-335	-90
C(11)	2247 (8)	-2004 (6)	-120 (8)	H''(C13)	-397	-233	-228
O(12)	-3546 (5)	-1892 (4)	139 (5)				
C(13)	-4113 (7)	-2640 (6)	-1130 (7)				
Compound (II)							
C(1)	6996 (11)	1459 (10)	2576 (6)	H(C3)	427	125	321
C(2)	6343 (11)	1331 (10)	3173 (5)	H(C5)	317	188	43
C(3)	4532 (11)	1333 (11)	2775 (6)	H(C10)	717	125	464
C(4)	3474 (10)	1380 (10)	1841 (6)	H'(C10)	820	42	434
C(5)	4109 (11)	1484 (11)	1250 (6)	H''(C10)	900	229	457
C(6)	5919 (10)	1540 (12)	1636 (6)	H(C11)	567	192	29
C(7)	8858 (11)	1495 (13)	2974 (7)	H'(C11)	753	283	137
N(8)	10352 (11)	1601 (10)	3387 (6)	H''(C11)	713	83	109
O(9)	11965 (8)	1712 (12)	3824 (5)				
C(10)	7531 (13)	1304 (14)	4200 (6)				
C(11)	6605 (14)	1733 (17)	982 (7)				
Br	1035 (1)	1366 (1)	1344 (1)				
Compound (III)							
C(1)	-32	-474	2505	C(7)	107	-1416	2572
C(2)	-1522	-78	2115	N(8)	218	-2174	2626
C(3)	-1657	845	2050	O(9)	339	-2998	2684
C(4)	-302	1371	2374	C(10)	-3016	-617	1756
C(5)	1188	975	2764	C(11)	2955	-345	3255
C(6)	1323	52	2829	C(12)	-449	2366	2303

observed reflexions. The refinement was carried out to minimize the function  $\sum (w|\Delta F|^2)$ . The scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

### Results and discussion

The positional parameters are listed in Table 2. The coordinates of each atom in (III) were calculated by the use of the positional parameters of the molecular model, which was referred to the molecule of (I), and the internal coordinates of the atom in it. The crystal structures are shown in Figs. 2, 3 and 4.

The molecules of (I) are arranged with their molecular planes parallel to the  $a$  axis, and those of (II) perpendicular to the  $b$  axis. Two molecules of (I) related by the center of symmetry and those of (II) related by a  $2_1$  axis are stacked 3.4 and 3.5 Å apart respectively (Figs. 3 and 5).

Short contacts between C(3) of the benzene ring and O(9) of the  $N$ -oxide group of the neighboring molecule, translated in the direction of the  $a$  axis, are found in (I)

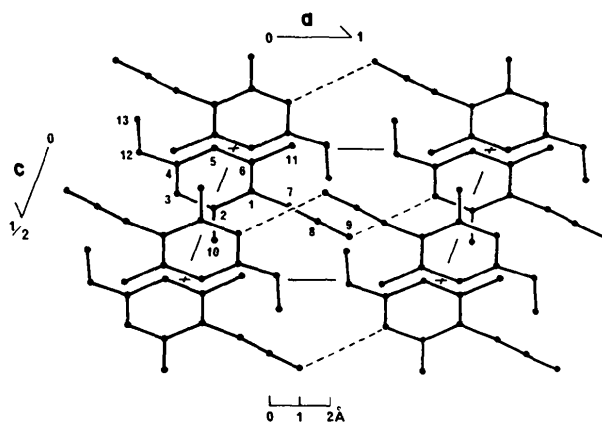


Fig. 2. Crystal structure of (I), viewed down the  $b$  axis.

and (II) (broken lines in Figs. 2, 3 and 5), where C(3)—H(C3) bonds point approximately to the O atoms, and C...O distances are 3.507 and 3.569 Å respectively. After H(C3) is set at the normal position of the H atom in benzene, the O...H distance is 2.44 Å in (I) and 2.52 Å in (II), and the angle C—H...O is 169° in (I)

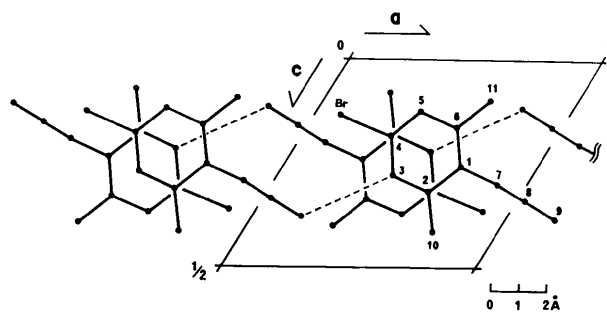
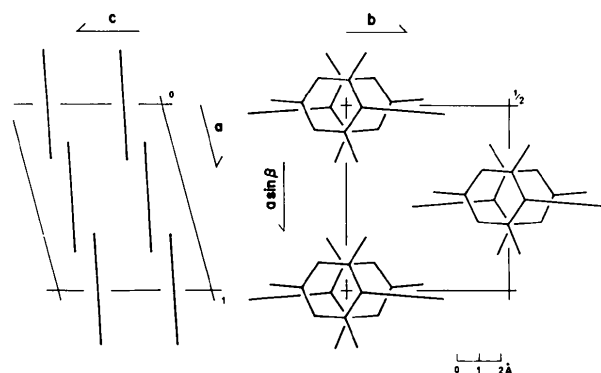
Fig. 3. Crystal structure of (II), viewed down the *b* axis.

Fig. 4. Crystal structure of (III). The other molecule in a pair of molecules disordered about the twofold axis is not shown for clarity.

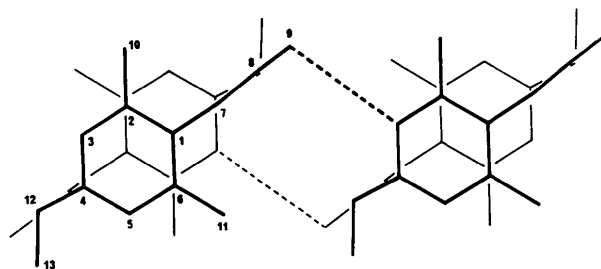


Fig. 5. Projection vertical to the molecular plane for (I).

and  $164^\circ$  in (II). Short approaches of the same type have been observed in crystals of pyridine *N*-oxide derivatives:  $\text{>N}\rightarrow\text{O}\cdots\text{C}(2)$  is 3.259 Å in 3-methyl-4-nitropyridine *N*-oxide, 3.322 Å in 3,5-dimethyl-4-nitropyridine *N*-oxide (Shiro, Yamakawa & Kubota, 1977), and 3.262 Å in the 2:1 molecular complex between 4-nitropyridine *N*-oxide and hydroquinone (Shiro & Kubota, 1972).

These intermolecular contacts may be due to  $\text{>C}-\text{H}\cdots\text{O}$  hydrogen bonding. The hydrogen-bond lengths in (I) and (II) are longer than those found in the crystals of pyridine *N*-oxides. This seems to support the argument that the *n*-type electron-donating ability of the O atom of the *N*-oxide group in benzonitrile *N*-oxides is less than that in pyridine *N*-oxides (Kubota *et al.*, 1967).

Table 3. Bond lengths (Å) for (I) and (II)

	(I)	(II)		(I)	(II)
C(1)–C(2)	1.410	1.410	C(7)–N(8)	1.148	1.146
C(2)–C(3)	1.386	1.395	N(8)–O(9)	1.249	1.237
C(3)–C(4)	1.395	1.363	C(2)–C(10)	1.517	1.500
C(4)–C(5)	1.400	1.386	C(6)–C(11)	1.518	1.526
C(5)–C(6)	1.401	1.398	C(4)–O(12)	1.364	–
C(6)–C(1)	1.390	1.373	O(12)–C(13)	1.436	–
C(1)–C(7)	1.435	1.437	C(4)–Br	–	1.888

Table 4. Bond angles ( $^\circ$ ) for (I) and (II)

	(I)	(II)
C(2)–C(1)–C(6)	122.3	122.4
C(1)–C(2)–C(3)	118.3	117.4
C(2)–C(3)–C(4)	119.9	119.8
C(3)–C(4)–C(5)	121.6	123.0
C(4)–C(5)–C(6)	119.0	118.1
C(5)–C(6)–C(1)	118.9	119.3
C(2)–C(1)–C(7)	117.5	118.2
C(6)–C(1)–C(7)	120.1	119.4
C(1)–C(7)–N(8)	173.8	171.7
C(7)–N(8)–O(9)	178.3	179.3
C(1)–C(2)–C(10)	121.4	121.9
C(3)–C(2)–C(10)	120.4	120.6
C(1)–C(6)–C(11)	123.0	123.0
C(5)–C(6)–C(11)	118.2	117.8
C(3)–C(4)–O(12)	115.5	–
C(5)–C(4)–O(12)	122.9	–
C(4)–O(12)–C(13)	118.3	–
C(3)–C(4)–Br	–	117.7
C(5)–C(4)–Br	–	119.3

Various ring-substituted benzonitrile *N*-oxides form a hydrogen bond with phenol in tetrachloroethylene (Battaglia, Dondoni, Galloni & Ghersetti, 1970). The frequency shifts of the hydroxylic stretching vibration of phenol are linearly correlated with the Hammett  $\sigma$  constants of the substituents: the larger the  $\sigma$ , the smaller the shift. Such a relationship suggests that the hydrogen-bond length in (I) is shorter than that in (II), and this is in good agreement with the results obtained here.

The molecules of (I) and (II) are almost planar, but C(13) of (I) and O(9) of (II) are out of the mean planes of the rest of the atoms by 0.14 and 0.13 Å respectively. Bond lengths and angles are listed in Tables 3 and 4. Their mean e.s.d. values are 0.008 Å and  $0.6^\circ$  for (I), and 0.013 Å and  $0.9^\circ$  for (II).

The fulminate groups are bent slightly in (I) and (II), but they may be considered to be linear, in the free state, as are those of fulminic acid (Winnewisser, Winnewisser & Winther, 1974), acetonitrile *N*-oxide (Bodenseh & Morgenstern, 1970; Blackburn, Brown, Burden, Crofts & Gillard, 1970) and silver fulminate (Britton & Dunitz, 1965).

The N–O dative bonds of (I) and (II) are longer than those of fulminic acid (1.1994 Å) and acetonitrile *N*-oxide (1.218 Å) not attached to the conjugated

systems, but shorter than those of pyridine *N*-oxide derivatives (1.28–1.30 Å) having double-bond character. Also, the N→O length in (I) is a little longer than that in (II), though the difference is comparable to the e.s.d. value. These bond lengths correspond reversely to the hydrogen-bond lengths in (I) and (II), as described above. This trend is mainly a result of the decrease in the intramolecular charge transfer from the O atom of the *N*-oxide group to the  $\pi$  systems with increasing electron-donating ability of the *p*-substituent ( $OCH_3 > Br$ ).

The C≡N bonds in hydrogen cyanide [1.1532 Å (Winnewisser, Maki & Johnson, 1971); 1.158 Å (Karakida, Fukuyama & Kuchitsu, 1974)] and acetonitrile [1.159 Å (Karakida, Fukuyama & Kuchitsu, 1974)] are elongated in the corresponding *N*-oxides. As those of benzonitrile derivatives range from 1.14 to 1.16 Å, it is not evident whether the bonds in (I) and (II) are lengthened by the formation of the N→O bond.

The bond lengths of (I) are in good agreement with the bond orders calculated by the MO method (Shiro, Yamakawa & Kubota, 1968), and the results obtained here seem to support the electron structure of benzonitrile *N*-oxides proposed previously.

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