

Structures of Four *o*-Nitrobenzonitriles

DOYLE BRITTON AND CHRISTOPHER J. CRAMER

Department of Chemistry and Supercomputer Institute, University of Minnesota, Minneapolis, MN 55455-0431, USA

(Received 3 June 1994; accepted 25 July 1995)

Abstract

The crystal structures of 6-methyl- (I), 6-chloro- (II) and 5-chloro-2-nitrobenzonitrile (III), as well as 2,6-dinitrobenzonitrile (IV), have been determined. (I), orthorhombic, *Pbca*, $a = 9.969$ (2), $b = 14.728$ (4), $c = 10.179$ (3) Å, $T = 180$ K; (II), orthorhombic, *Pbca*, $a = 9.469$ (5), $b = 14.752$ (7), $c = 10.859$ (5) Å, $T = 297$ K; (III), monoclinic, *P2₁/n*, $a = 7.889$ (2), $b = 15.064$ (12), $c = 7.311$ (4) Å, $\beta = 118.22$ (3)°, $T = 189$ K; (IV), orthorhombic, *Pbcn*, $a = 13.081$ (6), $b = 9.027$ (4), $c = 6.545$ (3) Å, $T = 297$ K. In (I)–(III) there is a short intramolecular distance [I 2.552 (4), II 2.579 (3), III 2.599 (2) Å] between one of the nitro O atoms and the adjacent nitrile C atom. These short distances plus the accompanying molecular distortions are taken as indications of incipient nucleophilic attack of the O atoms on the electrophilic nitrile C atom. Molecular orbital calculations at the Hartree–Fock level using the 6-31G* basis set support this interpretation; natural bond-orbital analysis indicates an $n_{\text{O1}} \rightarrow \pi_{\text{CN}}^*$ delocalization energy of 10–15 kJ mol⁻¹ for (I), (II) and (III). In (III) and (IV) the molecules pack in sheets, apparently driven by two C—H···O hydrogen bonds and a CN···Cl interaction in (III) and two C—H···O and one C—H···N hydrogen bonds in (IV).

1. Introduction

Schweizer, Proctor, Kaftory & Dunitz (1978) determined the crystal structures of seven disubstituted naphthalenes, each of which had a nucleophilic center at the 8 position and an electrophilic center (a carbonyl C atom) at the 1 position. In each case the molecule was distorted in such a way as to suggest an incipient addition of the nucleophile to the carbonyl group. In an extension of this work Proctor, Britton & Dunitz (1981) determined the structures of 8-methoxy- and 8-nitro-1-naphthonitrile. Here the electrophilic center is the nitrile C atom. In the methoxy compound a distortion was found similar to those in the original study (see Fig. 1). In the nitro compound the situation is not analogous since the expected nucleophile is a nitro O atom, rather than the central N atom. This introduces an additional atom into the interaction and prevents any even approximately planar arrangement of the naphthalene plus the

nucleophilic and electrophilic centers. If, however, the nitro group were adjacent to the nitrile group on a benzene ring, as in 2-nitrobenzonitrile, the arrangement of the interacting atoms would be quite similar to that in the 8-methoxy-1-naphthonitrile.

The structures of 6-methyl- (I), 6-chloro- (II) and 5-chloro-2-nitrobenzonitrile (III), as well as 2,6-dinitrobenzonitrile (IV), are reported here.* Four different compounds were studied for two somewhat contradictory-sounding reasons. First, the existence of the effect would be more convincing if essentially the same results were found in different compounds. Second, it is well known that the angles in a benzene ring depend on the substituents on the ring (see, for example, Domenicano, 1992; Domenicano & Murray-Rust, 1979; Norrestam & Schepper, 1981) so that changing the substituents would provide a small but real range of interactions.

2. Experimental

Samples of all four compounds were obtained from Aldrich Chemical Co. All the compounds were recrystallized to provide crystals suitable for data collection; (I) was recrystallized from chloroform, (II) from acetonitrile, (III) from an acetone–carbon tetrachloride mixture and (IV) from an acetone–chloroform mixture. Data were collected on an Enraf–Nonius CAD-4 diffractometer

* It was intended to include 2-nitrobenzonitrile in the list, but repeated attempts, by a variety of methods, have failed to produce crystals suitable for structural studies.

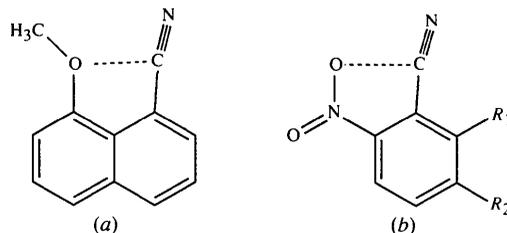


Fig. 1. (a) The interaction in 8-methoxy-1-naphthonitrile. The CN group is bent away from the OCH₃ at the ring and even more at the CN C atom. (b) The analogous interaction in 2-nitrobenzonitriles. (I), $R_1 = \text{CH}_3$, $R_2 = \text{H}$; (II), $R_1 = \text{Cl}$, $R_2 = \text{H}$; (III), $R_1 = \text{H}$, $R_2 = \text{Cl}$; (IV), $R_1 = \text{NO}_2$, $R_2 = \text{H}$.

Table 1. *Experimental details*

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	C ₈ H ₆ N ₂ O ₂	C ₇ H ₃ ClN ₂ O ₂	C ₇ H ₃ ClN ₂ O ₂	C ₇ H ₃ N ₃ O ₄
Chemical formula weight	162.15	182.57	182.57	193.12
Cell setting	Orthorhombic	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>P2₁/n</i>	<i>Pbca</i>
<i>a</i> (Å)	9.969 (2)	9.469 (5)	7.889 (2)	13.081 (6)
<i>b</i> (Å)	14.728 (4)	14.752 (7)	15.064 (12)	9.027 (4)
<i>c</i> (Å)	10.179 (3)	10.859 (5)	7.311 (4)	6.545 (3)
β (°)	90.0	90.0	118.22 (3)	90.0
<i>V</i> (Å ³)	1495 (1)	1517 (2)	766 (1)	773 (1)
<i>Z</i>	8	8	4	4
<i>D_x</i> (Mg m ⁻³)	1.441 (1)	1.599 (2)	1.584 (2)	1.660 (2)
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
No. of reflections for cell parameters	22	24	24	23
θ range (°)	11–17	12–16	11–18	9–15
μ (mm ⁻¹)	0.100	0.453	0.449	0.131
Temperature (K)	180	180	297	297
Crystal form	Plate	Cube	Prism	Prism
Crystal size (mm)	0.35 × 0.22 × 0.10	0.25 × 0.25 × 0.25	0.40 × 0.35 × 0.30	0.24 × 0.17 × 0.16
Crystal color	Yellow	Yellow	Pale yellow	Yellow
Data collection				
Diffractionmeter	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	ω -2 θ	ω -2 θ	ω -2 θ	ω -2 θ
Absorption correction	None	Ψ scans	Ψ scan	None
<i>T</i> _{min}	—	0.97	0.93	—
<i>T</i> _{max}	—	1.00	1.00	—
No. of measured reflections	2304	1922	1925	1001
No. of independent reflections	1427	1350	1706	695
No. of observed reflections	1036	990	1492	533
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
θ_{\max} (°)	30	27	28	26.8
Range of <i>h, k, l</i>	0 → <i>h</i> → 11 0 → <i>k</i> → 20 0 → <i>l</i> → 13	0 → <i>h</i> → 11 0 → <i>k</i> → 18 0 → <i>l</i> → 13	-10 → <i>h</i> → 9 0 → <i>k</i> → 19 0 → <i>l</i> → 8	0 → <i>h</i> → 8 0 → <i>k</i> → 11 0 → <i>l</i> → 16
No. of standard reflections	3	3	3	3
Frequency of standard reflections (s)	5000	5000	5000	5000
Refinement				
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
<i>R</i> (<i>F</i> ² > 0)	0.094	0.074	0.063	0.065
<i>wR</i> (<i>F</i> ²)	0.125	0.082	0.091	0.076
<i>S</i>	1.85	1.46	1.75	1.28
No. of reflections used in refinement	1427	1350	1706	695
No. of parameters used	133	121	122	72
H-atom treatment	All H atoms refined			
Weighting scheme	$w = 1/\sigma^2(F^2)$	$w = 1/\sigma^2(F^2)$	$w = 1/\sigma^2(F^2)$	$w = 1/\sigma^2(F^2)$
(Δ/σ) _{max}	0.02	0.01	0.01	0.01
$\Delta\rho_{\max}$ (e Å ⁻³)	0.55	0.28	0.43	0.20
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.32	-0.34	-0.34	-0.26
Extinction method	None	None	Secondary (Larson, 1967)	None
Extinction coefficient	—	—	7.5×10^{-5}	—
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)

equipped with a graphite monochromator and Mo radiation (*K*α, $\lambda = 0.71073$ Å). Crystal data are given in Table 1. In each case three check reflections measured every 5000 s of exposure time showed no systematic change over the course of the data collection. The structures were solved with the *MULTAN*11/82 program (Main *et al.*, 1982). In each case, refinement was carried out minimizing the function $\sum w(|F_o|^2 - |F_c|^2)^2$ on all reflections with $I > 0$. All non-H atoms were refined

with anisotropic displacement parameters; all H atoms were refined with isotropic displacement parameters. The weights, $w = 1/\sigma^2(F^2)$, were calculated from $\sigma^2(I) = \sigma^2(I)_c + (0.03I)^2$, where $\sigma(I)_c$ is the standard deviation in *I* based on counting statistics alone. The computer programs used were from the Enraf–Nonius Structure Determination Package (Frenz, 1978) and in the later stages from *TEXSAN* (Molecular Structure Corporation, 1985).

3. Discussion

3.1. General

The final positional parameters are given in Table 2.* The displacement ellipsoids and the labeling of the atoms are shown in Fig. 2. Bond lengths and angles are given in Table 3; they are normal within experimental error. The benzene rings are planar within experimental error, except (IV). In (IV), which has a twofold axis passing through C1 and C4, C2 and C3 are 0.011 (2) Å above and below the mean plane. (IV), with its nitro groups oriented symmetrically on both sides of the nitrile, has the longest O1...C7 distance. It has the nitro groups twisted 35.1 (2)° out of the mean plane of the benzene ring. The ring non-planarity could be a consequence of this twisting of the nitro groups.

3.2. The O1...C7 interaction – experimental details

Additional distances and angles relevant to the O1...C7 interaction are given in the first part of Table 4, which is ordered from the shortest to the longest O1...C7 distance. (I), (II) and (III) all have this distance shorter than or comparable to the corresponding distance, 2.594 Å, in 8-methoxy-1-naphthonitrile (Proctor, Britton & Dunitz, 1981). The other parameters in Table 4, the dihedral angle between the planes of the nitro group and the ring, the O1...C7—N1 angle, and the bend of the C1—C7—N1 angle away from linear, all follow the same progression.

The nitro group can twist rather easily out of the plane of the rest of the molecule, which is a degree of freedom not present in the naphthonitrile. This occurs in every case. The primary effect of this twist is to increase the O1...C7 distance, but in spite of this freedom the distances in (I), (II) and (III) are all short.

The bend of the C1—C7—N1 angle away from linearity increases as the O1...C7 distance decreases. The bend of CN is away from the incoming O1, as can be seen from the near planarity of the N1, O1, C1 and C7 atoms. The O1...C7—N1 angle also increases as the O1...C7 distance decreases. This is primarily another manifestation of the bend at C7.†

*Lists of structure factors, anisotropic displacement parameters and least-squares planes data have been deposited with the IUCr (Reference: CR0483). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. †The primary effect of the rotation of the nitro group out of the plane of the ring is to increase the O1...C7 distance and only secondarily to change the O1...C7—N1 (or O1...C7—C1) angle. If we take a molecule with the dimensions of any of the four, except with the dihedral angle 0° and the C1—C7—N1 angle 180°, and ask what happens when the dihedral angle is changed, the answer is the same in each case. For 5, 10 and 15° dihedral angles O1...C7 increases by 0.004, 0.016 and 0.036 Å and the O1...C7—N1 angle increases by 0.07, 0.28 and 0.62°. The bend of the nitrile group is far more important than the dihedral angle in affecting the remaining angles at C7.

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j.$$

	x	y	z	B _{eq}
6-Methyl-2-nitrobenzonitrile				
C1	0.4165 (2)	0.3278 (2)	0.1492 (2)	2.1 (1)
C2	0.3325 (3)	0.3012 (2)	0.0468 (2)	2.2 (1)
C3	0.2663 (3)	0.3619 (2)	−0.0335 (3)	2.7 (1)
C4	0.2827 (3)	0.4532 (2)	−0.0091 (3)	2.9 (1)
C5	0.3646 (3)	0.4820 (2)	0.0912 (3)	2.5 (1)
C6	0.4325 (2)	0.4214 (2)	0.1716 (3)	2.5 (1)
C7	0.4871 (3)	0.2660 (2)	0.2336 (3)	2.3 (1)
N1	0.5488 (2)	0.2254 (2)	0.3075 (2)	3.1 (1)
N2	0.3141 (2)	0.2040 (1)	0.0177 (2)	2.7 (1)
O1	0.3715 (3)	0.1490 (1)	0.0876 (2)	5.4 (1)
O2	0.2429 (1)	0.1821 (1)	−0.0743 (2)	3.22 (9)
C8	0.5230 (3)	0.4535 (2)	0.2789 (3)	3.5 (1)
H3	0.206 (3)	0.346 (2)	−0.105 (3)	5.3 (8)
H4	0.227 (3)	0.498 (2)	−0.063 (2)	3.3 (6)
H5	0.375 (2)	0.538 (2)	0.104 (2)	2.0 (5)
H81	0.521 (4)	0.522 (3)	0.282 (3)	7 (1)
H82	0.616 (3)	0.429 (2)	0.268 (3)	4.7 (7)
H83	0.488 (4)	0.429 (2)	0.367 (3)	5.7 (8)
6-Chloro-2-nitrobenzonitrile				
C1	0.52580 (7)	0.46161 (4)	0.28936 (5)	5.62 (3)
C1	0.4175 (2)	0.3281 (1)	0.1477 (2)	3.09 (7)
C2	0.3368 (2)	0.3004 (1)	0.0469 (2)	3.11 (7)
C3	0.2711 (2)	0.3612 (1)	−0.0302 (2)	3.82 (9)
C4	0.2837 (2)	0.4527 (1)	−0.0075 (2)	4.2 (1)
C5	0.3621 (2)	0.4830 (1)	0.0910 (2)	4.1 (1)
C6	0.4282 (2)	0.4217 (1)	0.1675 (2)	3.57 (8)
C7	0.4897 (2)	0.2677 (1)	0.2311 (2)	3.70 (9)
N1	0.5511 (2)	0.2264 (1)	0.3014 (2)	5.2 (1)
N2	0.3217 (2)	0.2033 (1)	0.0191 (2)	3.98 (8)
O1	0.3885 (2)	0.1497 (1)	0.0798 (2)	7.4 (1)
O2	0.2439 (2)	0.1811 (1)	−0.0645 (1)	5.25 (7)
H3	0.221 (2)	0.341 (1)	−0.099 (2)	4.9 (5)
H4	0.240 (2)	0.493 (2)	−0.058 (2)	4.9 (5)
H5	0.369 (2)	0.546 (1)	0.109 (2)	4.9 (5)
5-Chloro-2-nitrobenzonitrile				
C1	0.23796 (6)	0.55824 (3)	0.28334 (7)	2.54 (2)
C1	−0.0885 (2)	0.3496 (1)	0.2429 (2)	1.73 (5)
C2	−0.2524 (2)	0.3914 (1)	0.2288 (2)	1.72 (5)
C3	−0.2687 (2)	0.4830 (1)	0.2256 (2)	1.89 (5)
C4	−0.1174 (2)	0.5344 (1)	0.2402 (3)	1.99 (5)
C5	0.0469 (2)	0.4938 (1)	0.2580 (2)	1.85 (5)
C6	0.0625 (2)	0.4020 (1)	0.2577 (3)	1.96 (5)
C7	−0.0682 (2)	0.2548 (1)	0.2367 (3)	2.29 (6)
N1	−0.0408 (2)	0.1808 (1)	0.2310 (3)	3.41 (7)
N2	−0.4131 (2)	0.3389 (1)	0.2200 (2)	2.29 (5)
O1	−0.3874 (2)	0.26002 (9)	0.2586 (3)	4.70 (7)
O2	−0.5631 (2)	0.37715 (8)	0.1762 (2)	3.05 (5)
H3	−0.387 (3)	0.507 (1)	0.222 (3)	1.9 (4)
H4	−0.127 (3)	0.599 (1)	0.242 (3)	3.0 (4)
H6	0.170 (3)	0.377 (1)	0.262 (3)	1.9 (4)
2,6-Dinitrobenzonitrile				
O1	0.3163 (1)	0.0250 (1)	0.0799 (2)	4.02 (6)
O2	0.2360 (1)	0.1952 (1)	0.2460 (2)	4.94 (7)
N1	1/2	−0.1532 (2)	1/4	3.7 (1)
N2	0.3137 (1)	0.1392 (1)	0.1797 (2)	3.15 (6)
C1	1/2	0.1330 (2)	1/4	2.36 (8)
C2	0.4108 (1)	0.2149 (1)	0.2206 (2)	2.57 (6)
C3	0.4099 (1)	0.3676 (2)	0.2238 (3)	3.29 (7)
C4	1/2	0.4434 (3)	1/4	3.7 (1)
C7	1/2	−0.0277 (2)	1/4	2.60 (9)
H3	0.347 (1)	0.412 (2)	0.203 (3)	5.0 (5)
H4	1/2	0.543 (3)	1/4	4.5 (6)

In the naphthonitrile the entire nitrile group was bent away from the methoxy, while the methoxy was bent towards the nitrile. The data in Table 3 show that in (I),

Table 3. Bond lengths (Å) and angles (°)

	(I)	(II)	(III)	(IV)
N1—C7	1.141 (3)	1.137 (2)	1.140 (2)	1.133 (3)
C1—C7	1.436 (4)	1.443 (3)	1.440 (2)	1.451 (3)
N2—O1	1.221 (3)	1.209 (2)	1.216 (2)	1.222 (2)
N2—O2	1.218 (3)	1.214 (2)	1.216 (2)	1.215 (2)
C2—N2	1.475 (3)	1.470 (2)	1.469 (2)	1.466 (2)
C1—C2	1.393 (4)	1.396 (3)	1.398 (2)	1.394 (2)
C2—C3	1.379 (4)	1.376 (3)	1.384 (2)	1.379 (2)
C3—C4	1.376 (4)	1.378 (3)	1.384 (2)	1.373 (2)
C4—C5, C3'	1.374 (4)	1.376 (3)	1.383 (2)	1.373 (2)
C5—C6, C3'—C2'	1.388 (4)	1.379 (3)	1.389 (2)	1.379 (2)
C6—C1, C2'—C1	1.407 (3)	1.400 (3)	1.389 (2)	1.394 (2)
C3—H3	0.97 (3)	0.94 (2)	0.99 (2)	0.92 (2)
C4—H4	1.03 (3)	0.91 (2)	0.97 (2)	0.90 (3)
C5—H5, Cl	0.85 (2)	0.95 (2)	1.727 (2)	
C6—Cl, C8, H6	1.493 (4)	1.718 (2)	0.92 (2)	
C8—H81	1.00 (4)			
C8—H82	1.00 (3)			
C8—H83	1.02 (3)			
C1—C7—N1	172.3 (3)	174.3 (2)	175.3 (2)	180.0
C2—C1—C7	124.4 (2)	124.8 (2)	123.8 (1)	122.0 (1)
C6—C1—C7	117.9 (2)	118.5 (2)	117.5 (1)	122.0 (1)
C1—C2—N2	119.9 (2)	120.0 (2)	120.6 (1)	120.2 (1)
C3—C2—N2	116.8 (2)	117.8 (2)	117.7 (1)	117.5 (1)
C2—N2—O1	118.0 (2)	118.3 (2)	118.1 (1)	117.8 (1)
C2—N2—O2	119.0 (2)	118.4 (2)	117.9 (1)	117.8 (1)
O1—N2—O2	123.0 (2)	123.2 (2)	124.0 (1)	124.4 (2)
C2—C1—C6, C2'	117.7 (2)	116.7 (2)	118.7 (1)	116.0 (2)
C1—C2—C3	123.3 (2)	122.2 (2)	121.6 (1)	122.3 (2)
C2—C3—C4	118.0 (3)	119.4 (2)	119.2 (1)	119.5 (2)
C3—C4—C5, C3'	120.5 (3)	120.2 (2)	119.7 (1)	120.3 (2)
C4—C5—C6	121.9 (2)	120.0 (2)	121.4 (1)	
C5—C6—C1	118.7 (2)	121.4 (2)	119.4 (1)	
C1—C6—Cl, C8	119.8 (2)	119.7 (2)		
C5—C6—Cl, C8	121.5 (2)	118.9 (2)		
C4—C5—Cl			119.5 (1)	
C6—C5—Cl			119.1 (1)	

(II) and (III) the nitrile groups are also bent away from the nitro group; the C2—C1—C7 angles are all *ca* 6° larger than the corresponding C6—C1—C7 angles. On the other hand in all four compounds the nitro group is bent away from the nitrile group; the C1—C2—N2 angles are all 2–3° larger than the corresponding C3—C2—N2 angles. The angle that corresponds to the bend of the methoxy group in the naphthonitrile, C2—N2—O1, is not significantly different from the C2—N2—O2 angle in any of the cases, nor do the N2—O1 and N2—O2 distances differ significantly in any case.

3.3. The O1...C7 interaction – considered as nucleophilic attack

The short O1...C7 distances and the correlated bending at C7 described in the preceding section support the idea that there is incipient nucleophilic attack of O1 on C7. This suggested interaction can also be considered as part of a larger picture. In a discussion of the elimination of X from RCXO to give RCO⁺, which is analogous to the reverse of the incipient reaction in the nitronitriles, Ferretti, Dubler-Stuedle & Bürgi (1992) consider the reaction in terms of four variables. In our system these are the O1...C7 and C7—N1 distances and

Table 4. Parameters involved in the O1...C7 contact

	(I)	(II)	(III)	(IV)
	6-CH ₃	6-Cl	5-Cl	6-NO ₂
Experimental values				
O1...C7 (Å)	2.552 (4)	2.579 (3)	2.599 (2)	2.690 (2)
Dihedral angle between CNO ₂ and C ₆ planes (°)	1.4 (2)	5.3 (2)	11.9 (2)	35.1 (2)
Distances of N1 from O1, C1, C7 plane (Å)				
O1...C7—C1 (°) = α	81.8 (2)	80.8 (2)	81.0 (2)	79.8 (2)
O1...C7—N1 (°) = γ	105.9 (2)	104.8 (2)	103.8 (1)	100.2 (2)
C1—C7—N1 (°) = β	172.3 (3)	174.3 (2)	175.3 (2)	180
Calculated values from empirical relationships				
α (°)	81.5	80.6	80.1	78.0
γ (°)	106.2	105.1	104.6	102.0
Δr(C7—N1) (Å)	0.0019	0.0013	0.0011	–
r(O1...C7) (Å)	2.57	2.65	2.70	2.92
n (from Δr)	0.019	0.013	0.011	–
n (from r)	0.017	0.013	0.011	0.005
Calculated values from MO calculations				
O1...C7 (Å)	2.682	2.700	2.669	2.718
Dihedral angle between CNO ₂ and C ₆ planes (°)	26.5	29.6	17.0	34.1
C1—C7—N1 (°)	173.8	176.1	173.4	180
Mulliken overlap population (e)	0.0067	0.0065	0.0063	0.0057
NBO n _{O1} → π _{CN} [*] (kJ mol ⁻¹)	11.7	9.6	14.2	5.4

any two of the three angles around C7, O1...C7—C1 = α, C1—C7—N1 = β, O1...C7—N1 = γ. They give the following relationships*

$$(\alpha \cdot \beta)^{1/2} = 118.5^\circ \quad (1)$$

$$\Delta r(C7—N1) = 0.0031[\exp\{0.0625(180 - \beta)\} - 1] \quad (2a)$$

$$r(O1 \cdots C7) = 1.10 + 0.0031[\exp\{0.0625(180 - \alpha)\}] \quad (2b)$$

$$\Delta r(C7—N1) = 0.300 \ln\{3/(3 - n)\} \quad (3a)$$

$$r(O1 \cdots C7) = 1.334 - 0.300 \ln(n). \quad (3b)$$

In the second part of Table 4 the values calculated from these equations are given. Since α is partly constrained by being in a cyclic system, β is taken as the reference angle, α is calculated from (1), and γ is calculated from the observed β and the calculated α. Δr(C7—N1), the lengthening expected in the triple bond, is calculated from (2a) and is too small to be observable in every case. The interaction distances, r(O1)···C7, are calculated from (2b) using the same parameters as in (2a) and agree roughly with the experimental values, although the calculated values differ from each other considerably more than the experimental values. The two sets of distances can be used to calculate n, the bond order of the

* These equations are stated here in a slightly different form than in the original, but the only change of significance is the use of Pauling's (1947) original value of 0.300 in (3a) and (3b) rather than the 0.2164 that Ferretti *et al.* use.

O1...C7 interaction, and again the agreement is reasonable. Clearly there are weak points in the argument, for example, the strictly linear nitrile in (IV) would require the O1...C7 distance to be infinite, but this set of fairly simple relationships summarizes the observed parameters remarkably well.

3.4. Electronic structure calculations

To provide further insight into interactions between the adjacent nitro and nitrile groups in (I)–(IV), molecular orbital calculations (Glendening, Carpenter & Weinhold, 1995; Frisch *et al.*, 1995) were carried out at the Hartree–Fock (HF) level (Hehre, Radom, Schleyer & Pople, 1986) using the 6-31G* basis set (Ditchfield, Hehre & Pople, 1971; Hehre, Ditchfield & Pople, 1972; Hariharan & Pople, 1973; contracted Gaussian basis functions: I, 192; II and III, 190; IV 216). All structures were fully optimized (IV within the constraints of C_2 symmetry) and verified as local minima by analytical calculation of molecular force constants (Hehre, Radom, Schleyer & Pople, 1986). Comparison between several calculated and experimental geometrical parameters is provided in Table 4. Additionally, the molecular wave

functions were analyzed to assess interactions between O1 and C7. A crude measure of that interaction may be gained from the Mulliken overlap population (Mulliken, 1955*a,b*) between the two atoms. In essence, this value measures the extent to which occupied molecular orbitals simultaneously incorporate atomic basis functions from both these two atoms, *i.e.* how many electrons are 'shared' between the two atoms. Although computationally appealing because it is simple, Mulliken population analysis is known to be quite dependent on the basis set and its shortcomings have been extensively discussed (Singh & Kollman, 1984; Reed, Weinstock & Weinhold, 1985; Hehre, Radom, Schleyer & Pople, 1986; Cioslowski, 1989; Besler, Merz & Kollman, 1990; Davidson & Chakravorty, 1992; Ghanty & Ghosh, 1992; Merz, 1992; Bachrach, 1993; Chipot, Angyán, Ferenczy & Scheraga, 1993; Park, No, Jhon & Scheraga, 1993; Wiberg & Rablen, 1993; Wang & Ford, 1994; Storer, Giesen, Cramer & Truhlar, 1995). An alternative analysis method is to examine the importance of the energetic stabilization associated with the $n_{O1} \rightarrow \pi_{CN}^*$ interaction. Natural bond-orbital (NBO) analysis, as described by Reed and Weinhold (Reed, Weinhold, Curtiss & Pochatko, 1986), uses second-order perturba-

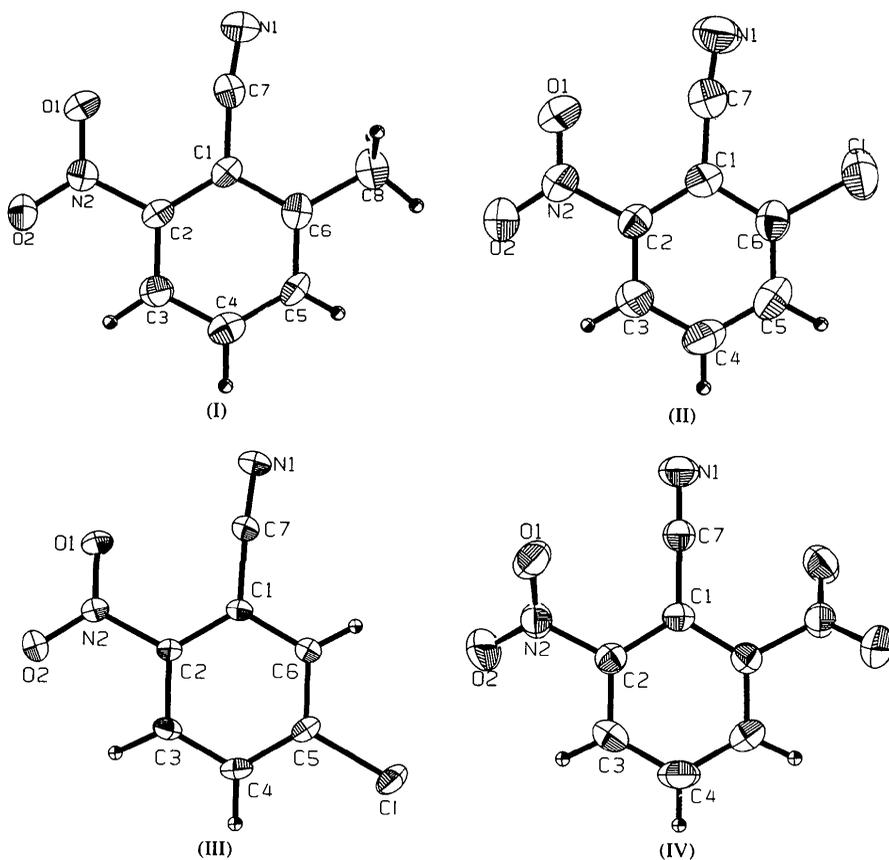


Fig. 2. 6-Methyl- (I), 6-chloro- (II), 5-chloro-2-nitro- (III) and 2,6-nitrobenzonitrile (IV). Displacement ellipsoids are shown at the 50% probability level. H atoms have been given an arbitrary radius.

tion theory to deduce the magnitude of filled/empty orbital interactions in stabilizing an electronic structure relative to a 'pure' Lewis structure (in particular, the Lewis structure associated with the most reasonable resonance contributor). Table 4 lists both the Mulliken overlap populations and the $n_{O1} \rightarrow \pi_{CN}^*$ delocalization energies for (I)–(IV).

The first point to be made in comparing the calculated and experimental structures is that agreement for the dihedral angle between the CNO_2 and C_6 planes is good for (IV), fair for (III) and off by $\sim 25^\circ$ for (I) and (II). Such a significant disagreement in structure is unusual at the HF/6-31G* level. Moreover, including electron correlation at the MP2 level (Moller & Plesset, 1934; Pople, Seeger & Krishnan, 1977) does not significantly change the value of this dihedral angle – for (II) it is 29.7° for the MP2/6-31G* optimized structure, a change of only 0.1° . This appears instead to be a manifestation of crystal packing forces. The force constant calculations at the HF/6-31G* level indicate the lowest vibrational frequency in each of (I)–(IV) to be associated with the torsional motion of the nitro group and the frequencies are very small [$\nu(\text{cm}^{-1})$: I, 49; II, 53; III, 35; IV, 49 (asym) 65 (sym)]. Such a flat torsional potential permits large deviations from the equilibrium structure at very little energetic cost. This analysis is possibly consistent with the observation that (I) and (II) manifest the largest discrepancies in nitro-group torsion angles and that these two molecules pack very similarly (*vide infra*). This analysis also implies that it is *not* worthwhile to attempt to correlate the observed X-ray structures with the usual physical organic constants associated with aromatic ring substituents (*e.g.* Hammett correlation), because there are other influences on the solid-state structures of similar energetic magnitude.

Although it is not particularly fruitful to compare calculated and experimental structures directly, it is quite instructive to compare *trends* in both sets of structures as a function of the nitro-group torsion angle. For the calculated structures, the $O1 \cdots C7$ distance increases monotonically by a total of 0.05 \AA as the nitro-group torsion angle increases from 17 to 34° . In the experi-

mental structures a similar monotonic increase is observed (0.14 \AA) as the torsion angle increases from 1 to 35° . Similar behavior is observed for the $C1-C7-N1$ bond angle. In the calculated structures (I)–(III), the bond angle increases by 2.7° as the nitro-group torsion increases by 12.6° . In the experimental structures (I)–(III), the bond angle increases by 3.0° as the nitro-group torsion increases by 10.5° . In (IV) symmetry requires linearity of this bond angle.

Analysis of the molecular wave functions provides additional support for the suggested nucleophilic $O1 \cdots C7$ interaction. Mulliken overlap populations between the two atoms are similar for (I), (II) and (III), and somewhat reduced for (IV), as might be expected based on the nitro group torsion angles. NBO analysis provides a more definite trend. The stabilization energy associated with the $n_{O1} \rightarrow \pi_{CN}^*$ interaction increases monotonically with decreasing nitro group torsion angle (and hence decreasing $O1 \cdots C7$ distance). It is noteworthy that NBO analysis predicts no stabilization for a $n_{O2} \rightarrow \pi_{CN}^*$ interaction (which is intuitively obvious), nor is there any stabilization from a $n_{O1} \rightarrow \sigma_{CN}^*$ interaction, which is consistent with the usual molecular orbital arguments rationalizing nucleophilic addition to multiple bonds.

Finally, although it was computationally impractical to optimize any structures other than (II) at the MP2/6-31G* level, we note that at this level the

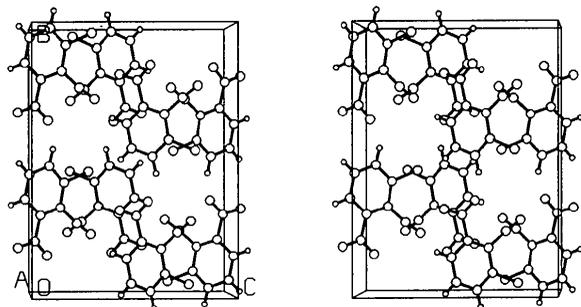


Fig. 3. The packing of 6-chloro-2-nitrobenzonitrile, viewed along the a axis. The packing of the 6-methyl compound is essentially the same.

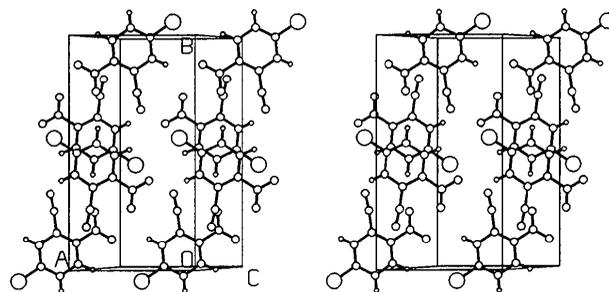


Fig. 4. The packing of 5-chloro-2-nitrobenzonitrile. The view is almost perpendicular to the xy plane.

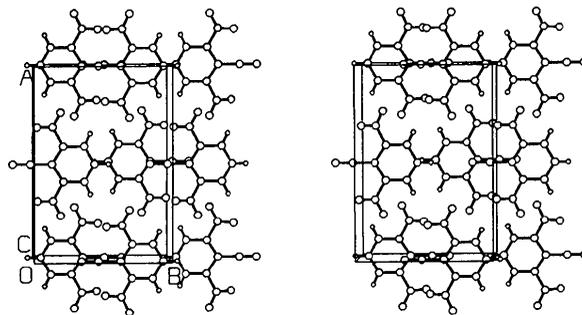


Fig. 5. The packing of 2,6-dinitrobenzonitrile. The view is almost perpendicular to the xy plane.

O1...C7 distance decreases to 2.681 Å. The C1—C7—N1 angle also decreases to 175.3°. This suggests that accounting for electron correlation further advances the nucleophilic addition character of the structure.

3.5. Related work

In addition to the work described in the *Introduction* the structure of 2,2'-bipyridine-3,3'-dicyanitrile (Baxter, Connor, Povey & Wallis, 1991) shows a similar interaction to a nitrile, in this case from the ring nitrogen. The two N...C distances are 2.695 and 2.740 Å, both longer than the O1...C7 distances reported here, but the bends away from linearity at the C atoms, 8.4 and 8.7°, are both larger than the largest reported here. A similar situation, with a longer distance of 2.704 Å and a larger bend of 9.1°, occurs in 8-dimethylamino-1-naphthonitrile (Parvez & Schuster, 1990).

Short distances between nitro O atoms and other electrophilic atoms have also been found: O...B in 4-carboxy-2-nitrobenzeneboronic acid (Soundararajan, Duesler & Hageman, 1993); O...S in *cis*-3-nitro-2-thiocyanato-2-butene (Carpenter & Park, 1987); O...Se in 7-nitrobenzo-2,1-thiaselenole-3-one (Dupont, Dideberg, Sbit & Lambert, 1989).

If one considers the isosteric replacements of CN with N₂⁺ and NO₂ with CO₂⁻, the same interaction would be expected in *ortho*-diazonium carboxylate zwitterions. Gougoutas (1982) has reported the structure of naphthalene-2-diazonium-3-carboxylate monohydrate, where an O...N distance of 2.517 Å is found. In naphthalene-2-diazonium-3-carboxylic acid salts (Gougoutas, 1978, 1979; Gougoutas & Johnson, 1978) similar but longer distances are found. Similar results have been found by Horan, Barnes & Glaser (1993) in 2-carboxybenzenediazonium chloride monohydrate, and by Horan, Haney, Barnes & Glaser (1993) in the 1:1 complex between 2-carboxybenzenediazonium chloride and benzenediazonium-2-carboxylate, but the suggested interpretation (Glaser, Horan, Nelson & Hall, 1992) is quite different. They present arguments for a repulsive interaction between the O and the central N and attractive interactions between the O and both the terminal N and the attached ring C. The geometries are similar in the diazonium carboxylates and the nitronitriles, however, and it is not obvious that their arguments would transfer from the diazonium group to the nitrile group. In a diazonium compound analogous to the methoxy naphthonitrile, Wallis & Dunitz (1984) found an O...N distance of 2.443 Å in the quinoline-8-diazonium-1-oxide ion.

3.6. Packing

The packing of (II) is shown in Fig. 3. The packing of (I) (not shown) is essentially the same. Molecules lie in ribbons parallel to the *b* axis; the ribbons are packed in a

herringbone fashion. There are no intermolecular distances in either structure shorter than the usual van der Waals distances.

The packing of (III) is shown in Fig. 4. The molecules pack in sheets parallel to the *xy* plane. The ring plane in each molecule makes an angle of 4.8(1)° with the plane of the sheet. In the plane of the sheet there are three short intermolecular distances. N1...C1 is 3.060(2) Å, with C7—N1...C1 139.1(1) and C5—C1...N1 172.3(2)°. H4...O1 is 2.43(2) Å, with C4—H4...O1 172(2) and N2—O1...H4 168(2)°. H6...O2 is 2.46(2) Å, with C6—H6...O2 152(2) and N2—O2...H6 141(1)°. The latter two distances are at the limit for C—H...O bonds, as discussed by Taylor & Kennard (1982), but in both cases the C—H...O angles are reasonably close to linear and the three interactions taken together provide an explanation for the formation of the two-dimensional sheets.

The packing of (IV) is shown in Fig. 5. The molecules form sheets parallel to the *xy* plane with the plane of the molecular rings making an angle of 8.8(1)° with the plane of the sheet. There are two short intermolecular distances. H3...O1 is 2.50(2) Å, with C3—H3...O1 170(2)° and N2—O1...H3 99(1)°. H4...N1 is 2.74(3) Å in an exactly linear C4—H4...N1—C7 arrangement. Again these are at the limits for C—H...O and C—H...N bonds, but again the C—H...X angles are close to ideal and taken together the interactions provide an explanation for the sheets. In this picture the 8.8° tilt of the molecules out of the sheets would be a consequence of the twist of the nitro groups of the plane of the rings, since the tilt leads to a shorter H3...O1 distance and a more closely linear C3—H3...O1 angle.

References

- Bachrach, S. M. (1993). *Reviews in Computational Chemistry*, edited by K. B. Lipkowitz & D. B. Boyd, Vol. 5, pp. 171–227. New York: VCH.
- Baxter, P. N. W., Connor, J. A., Povey, D. C. & Wallis, J. D. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1135–1137.
- Besler, B. H., Merz, K. M. & Kollman, P. A. (1990). *J. Comput. Chem.* **11**, 431–439.
- Carpenter, G. B. & Park, K. P. (1987). *Acta Cryst.* **C43**, 1821–1822.
- Chipot, C., Angyán, J. G., Ferenczy, G. G. & Scheraga, H. A. (1993). *J. Phys. Chem.* **97**, 6628–6636.
- Ciosłowski, J. (1989). *J. Am. Chem. Soc.* **111**, 8333–8336.
- Davidson, E. R. & Chakravorty, S. (1992). *Theoret. Chim. Acta*, **83**, 319–330.
- Ditchfield, R., Hehre, W. J. & Pople, J. A. (1971). *J. Chem. Phys.* **54**, 724–728.
- Domenicano, A. (1992). *Accurate Molecular Structures*, edited by A. Domenicano & I. Hargittai, pp. 437–468. Oxford University Press.
- Domenicano, A. & Murray-Rust, P. (1979). *Tetrahedron Lett.* **24**, 2283–2286.
- Dupont, L., Dideberg, O., Sbit, M. & Lambert, C. (1989). *Acta Cryst.* **C45**, 489–491.

- Ferretti, V., Dubler-Stuedle, K. C. & Bürgi, H.-B. (1992). *Accurate Molecular Structures*, edited by A. Domenicano & I. Hargittai, pp. 412–436. Oxford University Press.
- Frenz, B. A. (1978). *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.
- Frisch, M. J., Trucks, G. W., Schlegel, H. B., Gill, P. M. W., Johnson, B. G., Robb, M. A., Cheeseman, J. R., Keith, T., Petersson, G. A., Montgomery, J. A., Raghavachari, K., Al-Laham, M. A., Zakrzewski, V. G., Ortiz, J. V., Foresman, J. B., Cioslowski, J., Stefanov, B. B., Nanayakkara, A., Challacombe, M., Peng, C. Y., Ayala, P. Y., Chen, W., Wong, M. W., Andres, J. L., Replogle, E. S., Gomperts, R., Martin, R. L., Fox, D. J., Binkley, J. S., Defrees, D. J., Baker, J., Stewart, J. P., Head-Gordon, M., Gonzalez, C. & Pople, J. A. (1995). *Gaussian94 RevA.1*. Pittsburgh, PA: Gaussian Inc.
- Ghanty, T. K. & Ghosh, S. K. (1992). *J. Mol. Struct. (Theochem.)* **226**, 83–96.
- Glaser, R., Horan, C. J., Nelson, E. D. & Hall, M. K. (1992). *J. Org. Chem.* **57**, 215–228.
- Glendingen, E. D., Carpenter, J. E. & Weinhold, F. (1995). *NBO*, Version 3.1.
- Gougoutas, J. Z. (1978). *Cryst. Struct. Commun.* **7**, 183–186.
- Gougoutas, J. Z. (1979). *J. Am. Chem. Soc.* **101**, 5672–5675.
- Gougoutas, J. Z. (1982). *Cryst. Struct. Commun.* **11**, 1305–1310.
- Gougoutas, J. Z. & Johnson, J. (1978). *J. Am. Chem. Soc.* **100**, 5816–5820.
- Hariharan, P. C. & Pople, J. A. (1973). *Theoret. Chim. Acta*, **28**, 213–222.
- Hehre, W. J., Ditchfield, R. & Pople, J. A. (1972). *J. Chem. Phys.* **56**, 2257–2261.
- Hehre, W. J., Radom, L., Schleyer, P. v. R. & Pople, J. A. (1986). *Ab Initio Molecular Orbital Theory*. New York: Wiley.
- Horan, C. J., Barnes, C. L. & Glaser, R. (1993). *Acta Cryst.* **C49**, 507–509.
- Horan, C. J., Haney, P. E., Barnes, C. L. & Glaser, R. (1993). *Acta Cryst.* **C49**, 1525–1528.
- Larson, A. C. (1967). *Acta Cryst.* **23**, 664–665.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Universities of York, England, and Louvain, Belgium.
- Merz, K. M. (1992). *J. Comput. Chem.* **13**, 749–767.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
- Moller, C. & Plesset, M. S. (1934). *Phys. Rev.* **46**, 618–622.
- Mulliken, R. S. (1955a). *J. Chem. Phys.* **23**, 1833–1840.
- Mulliken, R. S. (1955b). *J. Chem. Phys.* **23**, 1841–1846.
- Norrestam, R. & Schepper, L. (1981). *Acta Chem. Scand. A*, **35**, 91–103.
- Park, J. M., No, K. T., Jhon, M. S. & Scheraga, H. A. (1993). *J. Comput. Chem.* **14**, 1482–1490.
- Parvez, M. & Schuster, I. I. (1990). *Acta Cryst.* **C46**, 947–948.
- Pauling, L. (1947). *J. Am. Chem. Soc.* **69**, 542–553.
- Pople, J. A., Seeger, R. & Krishnan, R. (1977). *Int. J. Quant. Chem., Quant. Chem. Symp.* **11**, 149–163.
- Proctor, G., Britton, D. & Dunitz, J. D. (1981). *Helv. Chim. Acta*, **64**, 471–477.
- Reed, A. E., Weinhold, F., Curtiss, L. A. & Pochatko, D. J. (1986). *J. Chem. Phys.* **84**, 5687–5705.
- Reed, A. E., Weinstock, R. B. & Weinhold, F. (1985). *J. Chem. Phys.* **83**, 735–746.
- Schweizer, W. B., Proctor, G., Kaftory, M. & Dunitz, J. D. (1978). *Helv. Chim. Acta*, **61**, 2783–2808.
- Singh, U. C. & Kollman, P. A. (1984). *J. Comput. Chem.* **5**, 129–145.
- Soundararajan, S., Duesler, E. N. & Hageman, J. H. (1993). *Acta Cryst.* **C49**, 690–693.
- Storer, J. W., Giesen, D. J., Cramer, C. J. & Truhlar, D. G. (1995). *J. Comput.-Aided Mol. Des.* **9**, 87–110.
- Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
- Wallis, J. D. & Dunitz, J. D. (1984). *J. Chem. Soc. Chem. Commun.* pp. 734–735.
- Wang, B. & Ford, G. P. (1994). *J. Comput. Chem.* **15**, 200–207.
- Wiberg, K. B. & Rablen, P. R. (1993). *J. Comput. Chem.* **14**, 1504–1518.