46. Crystal Structures of 8-Methoxy- and 8-Nitronaphthonitrile; Intramolecular Nucleophile-electrophile Interactions

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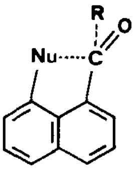
Summary

The crystal structures of 8-methoxy-1-naphthonitrile and 8-nitro-1-naphthonitrile have been determined by X-ray analysis. The methoxynitrile molecule shows a distortion pattern that is essentially similar to that found previously in other 1,8-disubstituted naphthalenes with Nu···C=O interactions; instead of non-planarity at the carbonyl C-atom there is bending at the cyano C-atom. Crystals of the nitronitrile contain two symmetry-independent molecules that differ in structure; both show bent cyano groups, short O···C=N distances, and asymmetric nitro groups, but in different degree. There is no clear correlation between the amount of any given distortion and the strength of the nucleophile-electrophile interaction.

Introduction. - A recent crystallographic study [1] of seven 1,8-disubstituted naphthalenes with various nucleophilic centers at one of the *peri* positions and an electrophilic center (carbonyl C-atom) at the other has shown that these molecules display a characteristic distortion pattern **1**. The main features are that the exocyclic bond to the electrophilic center is splayed outward, the one to the nucleophilic center is splayed inward, and the carbonyl C-atom is displaced from the plane of its three bonded atoms towards the nucleophile. This type of distortion can be regarded as representing an incipient stage of the intramolecular nucleophilic addition to the carbonyl group [1]. In this view, the bond-angle distortion pattern is interpreted as evidence that the preferred Nu···C=O approach angle is greater than 90°. The only



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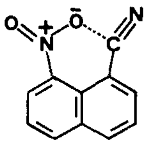

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other compound in this general category whose structure has been reported is 8-benzoyl-5-ethoxy-1-naphthol [2], which shows the same distortion pattern.

We continue our study of this type of interaction with two new examples. In the first example, 8-methoxy-1-naphthonitrile, the electrophilic center is a cyano C-atom. Non-planarity at the carbonyl C-atom should be replaced by a bending at the cyano C-atom, but otherwise the distortion pattern should remain unchanged. In the second example, 8-nitro-1-naphthonitrile, the electrophilic center is again a cyano C-atom, but now the nitro group provides the nucleophilic center, an O-atom once removed from the naphthalene ring rather than directly attached to it. Here we would expect both exocyclic bonds to be splayed outward regardless of whether there is an O···C interaction or not, but the presence of such an interaction **2** could be shown by an appropriate orientation of the nitro group, by a difference between the two N,O-bond distances, and by bending of the cyano group.

Discussion. – A stereoview of the methoxy compound is shown in *Figure 1*, the bond lengths and angles in *Figure 2*, and the packing in *Figure 3*. Stereoviews of the independent molecules of the nitro compound are shown in *Figure 4*, the bond lengths and angles in *Figure 5*, and the packing in *Figure 6*.

The structure of the methoxy compound is as expected by analogy to the carbonyl compounds [1]. The exocyclic C,O bond is bent inward (toward the nitrile

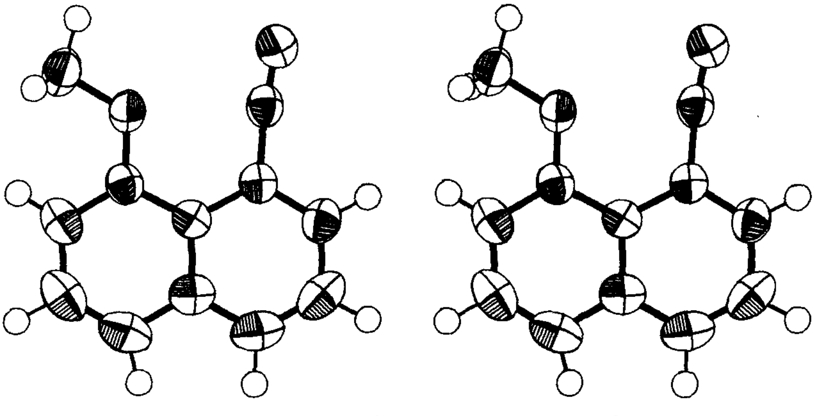

Fig. 1. *Stereoview of 8-methoxy-1-naphthonitrile*

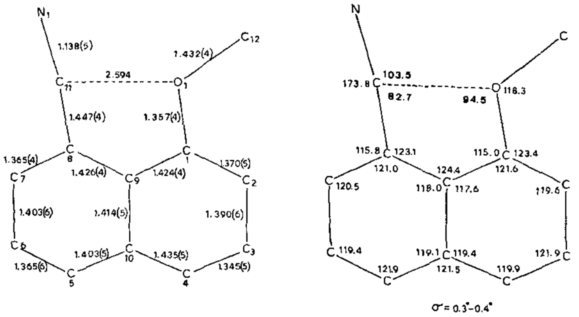

Fig. 2. *Bond lengths and angles in 8-methoxy-1-naphthonitrile*

group), the exocyclic C,C bond is bent outward (away from the methoxy group), and the O···C distance is 2.59 Å, in the middle of the range of distances found previously, 2.56–2.62 Å.

The C–C≡N-bond angle is 174° instead of 180°. Such a deviation from linearity is larger than is commonly found for a cyano group but it is by no means exceptional

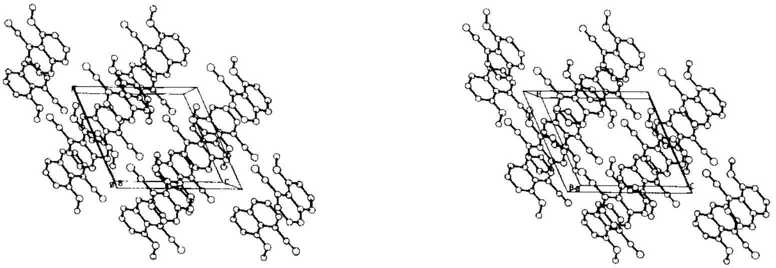

Fig. 3. *Crystal packing of 8-methoxy-1-naphthonitrile*

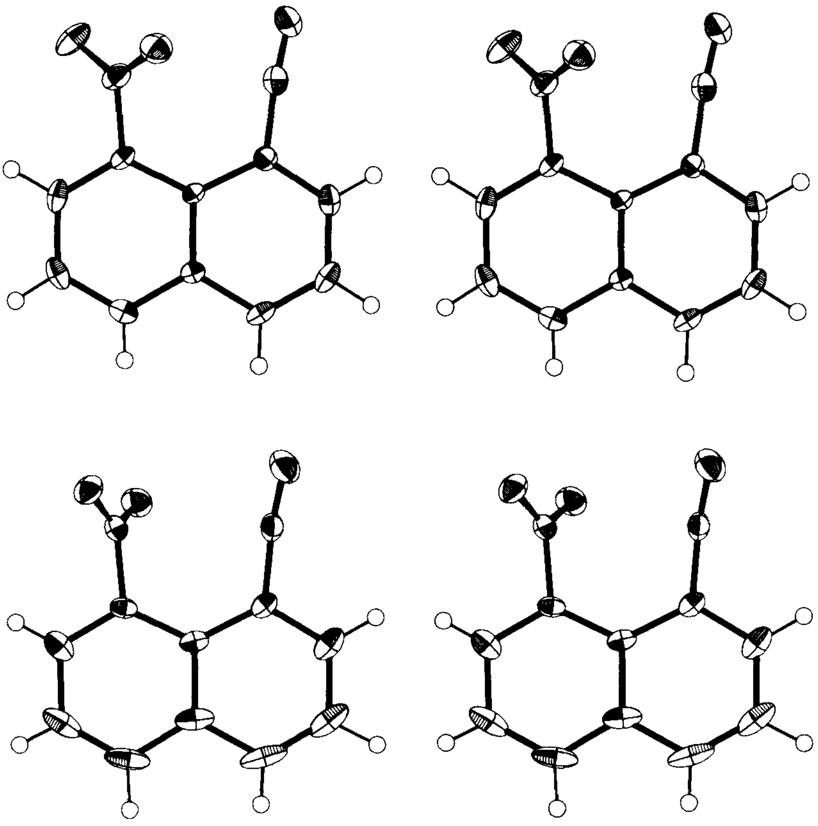

Fig. 4. *Stereoviews of both types of the molecule of 8-nitro-1-naphthonitrile*
Above: molecule **A**. Below: molecule **B**.

and can hardly be regarded in itself as evidence for a specific interaction with the methoxy group. More significant than the magnitude of the bending from linearity is its direction: the bend is away from the methoxy group and lies exactly (within 1σ) in the O···C(11)–C(8) plane. Also the angles O···C(11)–C(8) (82.7°) and C(11)···O–C(1) (94.5°) are close to the corresponding angles in the carbonyl compounds (compare with the angles γ and δ in Table 2 of [1]). Hence, not only

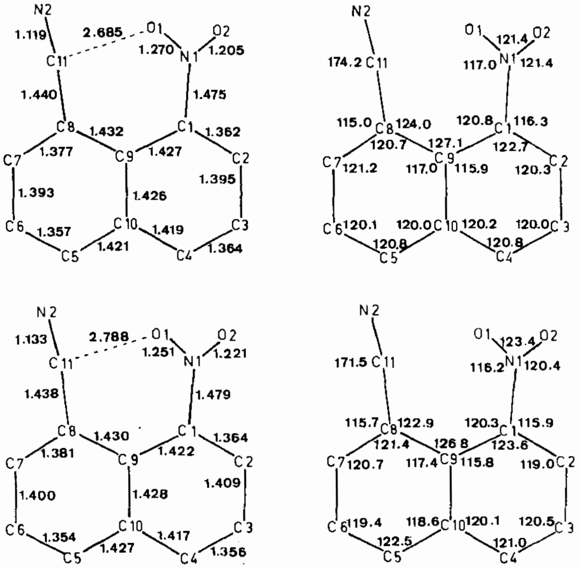

Fig. 5. *Bond lengths and angles in 8-nitro-1-naphthonitrile.* Above: molecule **A**. Below: molecule **B**. The calculated esd. are about 0.004 Å for the distances and 0.3° for the angles. In view of the disorder present (see text) these should be viewed as underestimates.

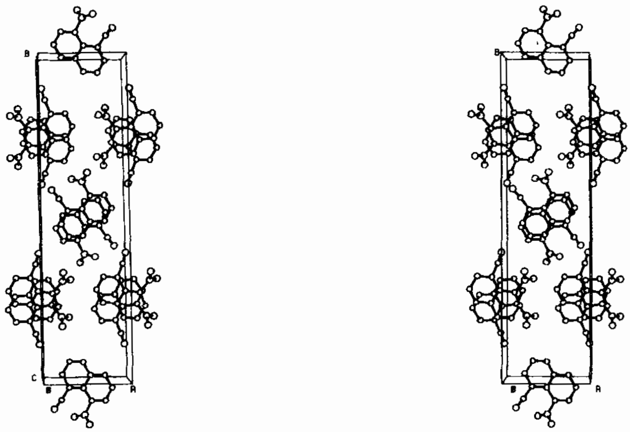

Fig. 6. *Crystal packing of 8-nitro-1-naphthonitrile*

does the nitrile group appear to be comparable in strength to the carbonyl group as an electrophile in these compounds, but also the preferred approach angle Nu···C–X must be very similar in the two classes of molecules.

The situation with the nitro compound is not so clear. The two non-equivalent molecules differ beyond any question of experimental error. First, the rotation angle of the nitro group about the C–N bond is different, with the result that in the one molecule (**A**) the O(1)···C(11) distance is 2.69 Å whereas in the other (**B**) it is 2.79 Å. This would suggest a stronger interaction in molecule **A** than in molecule **B**. On the other hand, the bending of the cyano group is 5.8° in molecule **A** and 8.5° in molecule **B**, suggesting the opposite; in both molecules the bend is away from the O-atom, the O···C–N angle is about 95° and the N-atom lies nearly in the O···C(11)–C(8) plane - but not as nearly as in the methoxy compound, only within 0.04 Å.

At first sight, a decision would seem to be provided by the asymmetric pattern of bond distances in the nitro group. The N–O(1) distance is longer than the N–O(2) distance, by 0.065 Å in molecule **A** but only by 0.030 Å in molecule **B**. The molecule with the stronger interaction between O(1) and the electrophile C-atom C(11) should show more pronounced charge localization in the nitro group (formula **2**), and hence must be molecule **A**. Unfortunately for this argument, nitro groups in other molecules with non-bonded O···C=O distances in the range 2.58–2.60 Å, considerably shorter than those observed here, show virtually symmetrical nitro groups [3] [4]. Perhaps the cyano group can induce abnormally large asymmetry in the nitro group, or perhaps unrecognized factors are at work, or perhaps the disorder in the crystal structure (see Experimental Part) has a more adverse effect on the accuracy of the parameters than we would like to believe.

Table 1. *8-Methoxy-1-naphthonitrile, positional and vibrational parameters* × *10*^{4} (standard deviations in parentheses). The temperature factor expression is $\exp[-2\pi^2(U_{11}h^2a^{*2}+\ldots 2U_{12}hka^*b^*\ldots)]$ for non-hydrogen atoms, $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$ for hydrogen atoms.

	x	y	z	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	559 (4)	8005 (2)	4412 (3)	652 (19)	540(18)	447(17)	-20(14)	213(15)	-17(14)
C2	367 (4)	7323 (2)	5420 (4)	927 (24)	641(21)	611(21)	-87(17)	364(19)	28(17)
C3	-1037 (5)	7416 (3)	5837 (4)	1066 (27)	745(24)	708(24)	-241(21)	395(22)	6(21)
C4	-2219 (4)	8164 (3)	5289 (4)	735 (22)	969(26)	685(23)	-253(20)	370(19)	-147(21)
C5	-3288 (4)	9666 (3)	3607 (4)	591 (19)	1003(26)	708(23)	-16(19)	281(17)	-200(22)
C6	-3153 (4)	10355 (3)	2589 (4)	689 (23)	878(27)	766(26)	229(19)	144(20)	-113(22)
C7	-1731 (4)	10301 (2)	2169 (3)	697 (19)	626(19)	567(20)	92(16)	207(16)	21(17)
C8	-495 (3)	9563 (2)	2763 (3)	580 (18)	492(17)	436(17)	-28(13)	166(14)	-51(14)
C9	-633 (3)	8821 (2)	3797 (3)	520 (16)	524(17)	407(17)	-72(13)	157(14)	-92(13)
C10	-2054 (3)	8892 (2)	4235 (3)	555 (19)	733(21)	552(21)	-80(16)	187(17)	-135(17)
C(N)	946 (4)	9599 (2)	2293 (3)	688 (19)	493(18)	526(19)	36(15)	234(16)	6(15)
N(N)	2014 (4)	9707 (2)	1854 (3)	914 (20)	744(19)	922(21)	139(16)	525(18)	199(17)
O(M)	1867 (3)	7956 (1)	3917 (2)	820 (14)	627(13)	686(14)	193(11)	388(12)	174(11)
C(M)	3182 (4)	7195 (2)	4563 (4)	909 (24)	701(21)	838(24)	251(19)	364(19)	172(19)
H2	1203(32)	6758(20)	5744(30)	963 (88)					
H3	-1142(34)	6889(21)	6574(32)	1149(105)					
H4	-3299(30)	8347(19)	5387(28)	886 (84)					
H5	-4283(30)	9665(18)	3930(28)	904 (89)					
H6	-4005(35)	10904(21)	2128(33)	1177(103)					
H7	-1648(30)	10824(18)	1474(28)	852 (83)					
H1(CM)	4038(35)	7312(21)	4037(33)	1127(101)					
H2(CM)	2511(34)	6496(23)	4277(31)	1096 (96)					
H3(CM)	3699(34)	7292(21)	5715(34)	1087(100)					

Table 2. *8-Nitro-1-naphthonitrile* (low-temperature structure), *positional and vibrational parameters* × 10^4 for molecules **A** and **B** and for six possible additional atom-sites E(1)–E(6) with estimated population parameters (P.P.). See *Table 1* for other details.

	x	y	z	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1(A)	11221(3)	2295(1)	-8823(3)	129(10)	250(12)	116(10)	24 (9)	-3 (8)	-23 (9)
C2(A)	11884(3)	2707(1)	-9086(4)	186(12)	356(15)	165(11)	-85(11)	21 (9)	25(11)
C3(A)	10911(4)	3085(1)	-8781(4)	342(15)	205(13)	215(12)	-95(11)	-12(11)	46(10)
C4(A)	9305(4)	3044(1)	-8167(4)	283(13)	188(12)	177(12)	21(10)	-33(10)	-6 (9)
C5(A)	6899(3)	2583(1)	-7264(3)	152(11)	305(14)	157(11)	67(10)	-7 (9)	-36(10)
C6(A)	6166(3)	2180(1)	-7036(4)	143(11)	398(16)	174(12)	-16(11)	25 (9)	-34(11)
C7(A)	7034(4)	1794(1)	-7490(4)	253(13)	262(13)	202(12)	-99(11)	19(10)	-17(10)
C8(A)	8668(3)	1810(1)	-8096(3)	220(12)	191(12)	158(11)	-5 (9)	36 (9)	-3 (9)
C9(A)	9529(3)	2226(1)	-8255(3)	138(10)	177(11)	103 (9)	15 (8)	6 (8)	-6 (8)
C10(A)	8581(3)	2618(1)	-7890(3)	168(11)	184(11)	109(10)	17 (9)	-13 (8)	-20 (8)
C11(A)	9332(4)	1392(1)	-8721(4)	288(15)	259(14)	345(16)	-32(12)	85(12)	39(12)
N1(A)	12396(3)	1918(1)	-8990(3)	176(10)	320(13)	296(12)	10 (9)	-5 (9)	-108(10)
N2(A)	9720(3)	1061(1)	-9270(4)	324(14)	242(12)	466(16)	-60(11)	-1(12)	-1(11)
O1(A)	12446(3)	1642(1)	-7679(3)	345(12)	312(11)	342(12)	40 (9)	-7 (9)	54 (9)
O2(A)	13343(3)	1888(1)	-10258(3)	233(10)	572(15)	208(10)	77(10)	63 (8)	-47(10)
C1(B)	5684(3)	-686(1)	-7496(3)	226(12)	199(12)	142(10)	-55(10)	14 (9)	15 (9)
C2(B)	7328(4)	-701(1)	-8015(4)	227(13)	385(16)	182(12)	-58(12)	17(10)	-55(11)
C3(B)	8156(4)	-301(1)	-8443(4)	304(15)	550(21)	221(14)	-233(15)	67(12)	-94(14)
C4(B)	7330(4)	93(1)	-8346(4)	512(20)	391(17)	157(12)	-307(16)	-6(12)	-5(12)
C5(B)	4764(5)	527(1)	-7650(4)	708(24)	181(13)	212(13)	-173(14)	-194(15)	62(11)
C6(B)	3153(5)	557(1)	-7076(4)	605(22)	175(13)	335(16)	43(13)	-240(15)	-20(12)
C7(B)	2298(4)	170(1)	-6568(4)	384(16)	212(13)	254(13)	67(12)	-130(12)	-53(11)
C8(B)	3068(3)	-240(1)	-6683(3)	270(13)	163(11)	152(11)	9(10)	-49 (9)	-22 (9)
C9(B)	4754(3)	-285(1)	-7319(3)	280(13)	161(11)	101(10)	-47(10)	-35 (9)	8 (8)
C10(B)	5631(4)	113(1)	-7781(4)	455(17)	228(13)	129(11)	-150(12)	-68(11)	19(10)
C11(B)	2099(3)	-610(1)	-6032(4)	211(12)	238(13)	277(13)	57(10)	21(10)	0(11)
N1(B)	4837(3)	-1121(1)	-7299(3)	245(12)	227(12)	299(12)	8 (9)	119(10)	-4 (9)
N2(B)	1279(4)	-868(1)	-5348(4)	323(14)	439(17)	387(15)	-14(12)	116(12)	-21(13)
O1(B)	3663(3)	-1200(1)	-8406(3)	273(11)	314(11)	356(12)	-62 (9)	-4 (9)	-63 (9)
O2(B)	5313(3)	-1385(1)	-6135(3)	362(12)	237(10)	292(11)	55 (9)	5 (9)	61 (8)
H2(A)	13031(42)	2734(11)	-9461(46)	317(93)					
H3(A)	11285(41)	3363(11)	-9029(45)	301(90)					
H4(A)	8672(39)	3279(10)	-7951(43)	255(83)					
H5(A)	6292(41)	2849(11)	-7014(45)	301(88)					
H6(A)	5049(41)	2163(11)	-6665(44)	295(88)					
H7(A)	6540(41)	1518(11)	-7422(44)	302(88)					
H2(B)	7839(40)	-963(11)	-8162(44)	274(85)					
H3(B)	9207(41)	-328(11)	-8744(45)	319(89)					
H4(B)	7873(44)	360(11)	-8620(47)	349(97)					
H5(B)	5332(45)	759(12)	-8008(49)	403(104)					
H6(B)	2543(49)	837(13)	-6895(54)	544(118)					
H7(B)	1138(46)	186(12)	-6119(50)	406(104)	P. P.				
E(1)	1245(21)	1428 (6)	-7195(23)	300	0. 138(5)				
E(2)	2087(21)	-923 (6)	-7631(23)	300	0. 134(5)				
E(3)	10107(39)	1426(10)	-7952(42)	300	0. 076(5)				
E(3)	1157(37)	-630(10)	-4949(40)	300	0. 077(5)				
E(4)	5547(81)	-1082(22)	-6273(88)	300	0. 032(5)				
E(5)	9068(62)	1121(16)	-8717(67)	300	0. 044(5)				
E(6)	13671(308)	1470(82)	-10614(339)	400	0. 015(7)				

Further work is required to decide among these possibilities. At any rate, although the reason for the differences between the two types of molecules is not obvious it probably has to do with differences in packing *(Fig. 6)*. The two types **A** and **B** of this molecule occur in separate stacks with quite different stacking arrangements. Neighbouring **A** molecules are related to one another by a center of symmetry within the stack, neighbouring **B** molecules by a glide reflection.

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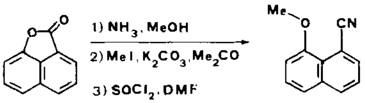
Experimental Part

8-Methoxy-1-naphthonitrile, $C_{12}H_9NO$, was prepared as outlined below. Intensity data at RT. were collected on an automated *Enraf-Nonius* CAD-4 diffractometer with graphite-monochromatized MoKα radiation ($\lambda = 0.7107$ Å). The crystals are monoclinic, $a = 8.366$ Å, $b = 13.263$ Å, $c = 9.460$ Å, $\beta = 114.28°$, space group $P2_1/n$, $Z = 4$, $D_x = 1.271$ gcm^{-3}. Of the 1500 symmetry-independent reflections measured ($\theta \leq 25°$), 769 had $I \geq 3\sigma(I)$ and were used in the calculations. A trial structure was obtained using MULTAN [5] and refined by least-squares analysis with anisotropic thermal parameters for the non-hydrogen atoms. Refinement converged at $R = 0.033$. The final parameters are given in *Table 1*.



8-Nitro-1-naphthonitrile, $C_{11}H_6N_2O_2$, was kindly supplied by Professor *J.D. Roberts* and recrystallized from $CCl_4/HCCl_3$. Intensity data were first collected at RT. The structure analysis presented some difficulties that have been described [6]. In order to improve the accuracy a new data set was collected at 96 ± 3 K. The crystals are monoclinic, space group $P2_1/c$, $Z = 8$; at 96 K, $a = 7.939$, $b = 30.080$, $c = 7.325$ Å, $\beta = 90.73°$, $D_x = 1.505$ gcm^{-3} (at 295 K, $a = 8.035$, $b = 30.221$, $c = 7.508$ Å, $\beta = 90.18°$, $D_x = 1.444$ gcm^{-3}). Of the 5080 symmetry-independent reflections measured ($\theta \leq 30°$), 3179 had $I > 2\sigma(I)$ and were used in the subsequent least-squares refinement. With two molecules in the asymmetric unit the number of parameters was large enough that block refinement had to be used. Refinement with anisotropic thermal parameters for non-hydrogen atoms converged at $R = 077$. This seemed too large for a properly refined structure considering the apparent quality of the data. Also the vibrational parameters for some atoms seemed unusually large. The presence of orientational disorder was suspected and confirmed by a difference *Fourier* map which showed peaks in the neighbourhood of the nitro and cyano groups of both molecules. The pattern of subsidiary peaks is compatible with a disorder model in which the nitro and cyano positions are reversed in a few per cent of the molecules. Further refinement appeared to be pointless with respect to improving the positional parameters (listed in *Table 2*) so the analysis was not pursued.

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