

## 29. Interactions between Functional Groups

Part III

### The Structure of *N,N*-Dimethyl-8-nitro-1-naphthaleneamine in Seven Crystalline Environments

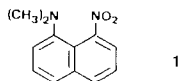
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The *N,N*-dimethyl-8-nitro-1-naphthaleneamine molecule has been observed in seven environments in three crystal modifications. A range of conformations, related by conrotatory motions about the two exocyclic C–N bonds, is observed. In all seven conformations, the lone pair of the amino N-atom is directed approximately towards the nitro N-atom, which is slightly pyramidalized towards the amino group. The NO<sub>2</sub> group appears to be a poorer through-space electron acceptor than the carboxylic ester group, in contrast to their through-bond electron-accepting properties.

It must happen only very rarely that seven conformations of a molecule can be observed by X-ray diffraction. This happens to be possible for *N,N*-dimethyl-8-nitro-naphthaleneamine (**1**), which has been found to occur in three crystal modifications, two of which share the remarkable property of having three molecules in the respective asymmetric crystal units.



We were interested in **1** in connection with our studies of through-space interactions between pairs of proximate functional groups. Our previous work in this area has included crystal structure analyses of 1,2-disubstituted benzenes [1] and 1,8-disubstituted naphthalenes [2] [3] and quinolines [4]. Normally, in this approach, each type of molecule is observed only once, in a single crystalline environment. Since the observed conformation may be distorted from that of the free molecule by the influence of crystal packing forces, general conclusions about favourable interaction geometries usually have to be drawn from series of measurements on families of closely related compounds. Occasionally, among molecular crystals, we can expect to find two or more independent molecules of a given compound in the same crystal structure or two or more polymorphic forms corresponding to different crystal structures of the same compound. Here we describe observations of the conformationally flexible molecule **1** as observed in seven different crystal environments.

Polymorphism among molecular crystals is probably much more widespread than generally believed. Indeed, it may be ubiquitous. Many examples go unnoticed in the

laboratory, because once suitable crystallization conditions for a given compound have been found and a melting point recorded, the matter is usually dropped. Thus, products obtainable by crystallization from other solvents or at different temperatures are rarely examined. Co-occurrence of more than one crystal modification from the same solvent is also a possibility but will usually pass unobserved, unless the colours of the different modifications are quite dissimilar. Yet polymorphism is common among compounds whose physical properties are intensively studied, as pointed out by *McCrone* [5]. Of particular interest is the phenomenon of conformational polymorphism [6] in which a molecule such as **1** adopts significantly different conformations in different crystalline polymorphs. By studying such systems, we may hope to learn something about the influence of crystal environment on molecular conformation, both in its static and dynamic [7] aspects.

**Experimental.** – The three crystalline modifications of **1** were discovered more through chance observations than by systematic study. The compound was prepared from 1-naphthaleneamine according to the published procedures [8]. Slow cooling of a warm hexane soln. sometimes yielded microcrystalline beige product and sometimes larger single crystals of a similar colour (modification **B**). Crystallization from cyclohexane produced usually modification **B**, but on one occasion orange-red flat needles (modification **A**) and on one occasion reddish needles of a third modification **C**. Attempts to find conditions where modifications **A** and **C** could be prepared reproducibly have so far been unsuccessful.

Differential Scanning Calorimetry (DSC) measurements show a melting endotherm of 4.4 kcal/mol at 77.3° for modification **B** and one of 4.0 kcal/mol at 76.0° for modification **C**; thus **B** seems to be slightly more stable close to the m.p. Unfortunately, it was not possible to make DSC measurements for modification **A** since no material was available. There are indications that on cooling, the melt sometimes supercools to yield a solid, which, on reheating, shows a small endotherm at 70–75°, *i.e.* just before the melting endotherm. This may be **A** or it may be yet another undetected modification. Frequently, among polymorphic modifications, the one with the smallest volume is the one that is thermodynamically most stable at low temp. From the molecular volumes at r.t. (**A**: 266.8 Å<sup>3</sup>; **B**: 278.7 Å<sup>3</sup>; **C**: 280.0 Å<sup>3</sup>, see *Table 1*) this would appear to be **A**, the only one of the three with a relatively simple crystal structure containing only a single molecule in the asymmetric crystal unit (as discussed below).

Crystallographic data for the three modifications are given in *Table 1*. All diffraction measurements were made with an *Enraf Nonius CAD4* diffractometer equipped with graphite monochromator (MoK $\alpha$  radiation,  $\lambda = 0.7107$  Å) and cooling device. For modifications **A** and **B**, measurements were made near 100 K, for **C** at r.t. The structures were solved by direct methods [9] and refined by full-matrix (modification **A**) or block-diagonal (**B**)

Table 1. *Crystal Data for the Three Crystal Modifications of 1*

Modification		<b>A</b>	<b>B</b>	<b>C</b>
Space group		$P2_1/c$	$C2/c$	$Pn$
Cell constants	$a$ [Å]	8.373(5)	33.15(2)	8.429(3)
	$b$ [Å]	7.268(6)	8.272(3)	21.053(2)
	$c$ [Å]	17.311(6)	26.09(1)	10.199(2)
	$\beta$ [°]	96.75(4)	115.22(5)	111.86(3)
$V$ [Å <sup>3</sup> ]		1046	6471	1680
$\rho_{\text{calc}}$ [g/cm <sup>3</sup> ]		1.37	1.33	1.28
$Z$		4	24	6
$V_m = V/Z$ (100/104 K)		261.5	269.6	–
$V_m$ (RT)		266.8	278.7	279.8
Temp. [K]		100	104	RT
$\theta(\text{max.})$ [°]		29	24	25
Measured reflections		2764	5085	2941
'Observed' reflections ( $I > 3\sigma(I)$ )		1789	2948	1753
$R$ -factor		0.048	0.051	0.049
Average c.s.d. of C–C bond lengths [Å]		0.002	0.01	0.01

Table 2. *Fractional Atomic Coordinates and Displacement Parameters for Modification A* (e.s.d.'s are given in parentheses). The temperature factor has the form of  $\exp\{-T\}$ , where:  $T = 8\pi^2 U(\sin \theta/\lambda)^2$  for isotropic atoms,  $T = 2\pi^2 (a^2 U_{11} h^2 + \dots + 2a^* b^* U_{12} hk + \dots)$  for anisotropic atoms.

Molecule <b>a</b>									
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
C(1a)	-0.2342(2)	-0.2810(2)	-0.95736(8)	0.0122(6)	0.0116(5)	0.0147(6)	0.0007(5)	0.0015(5)	0.0019(5)
C(2a)	0.2074(2)	-0.3281(2)	1.03159(9)	0.0192(7)	0.0154(6)	0.0141(6)	0.0001(5)	0.0011(5)	0.0009(5)
C(3a)	0.0518(2)	-0.3022(2)	1.05368(9)	0.0231(7)	0.0170(6)	0.0167(6)	0.0028(5)	0.0080(5)	0.0021(5)
C(4a)	0.0713(2)	-0.2443(2)	-1.00037(9)	0.0177(6)	0.0142(6)	0.0221(7)	0.0015(5)	0.0080(5)	0.0020(5)
C(5a)	0.1700(2)	-0.1305(2)	-0.8680(1)	0.0135(6)	0.0155(6)	0.0279(8)	0.0004(5)	-0.0005(5)	0.0030(6)
C(6a)	0.1381(2)	-0.0696(2)	-0.7965(1)	0.0179(7)	0.0167(7)	0.0259(7)	-0.0026(5)	-0.0051(6)	0.0029(6)
C(7a)	-0.0215(2)	-0.0565(2)	-0.77869(9)	0.0227(8)	0.0129(6)	0.0154(6)	-0.0027(5)	-0.0014(5)	0.0008(5)
C(8a)	-0.1492(2)	-0.1155(2)	0.83100(8)	0.0168(6)	0.0106(6)	0.0141(6)	0.0005(5)	0.0020(5)	0.0021(4)
C(9a)	-0.1163(2)	-0.1980(2)	-0.90257(8)	0.0141(6)	0.0100(6)	0.0135(6)	0.0011(4)	0.0007(5)	0.0015(4)
C(10a)	0.0433(2)	-0.1915(2)	-0.92381(9)	0.0141(6)	0.0103(6)	0.0201(7)	0.0010(5)	0.0018(5)	0.0023(5)
C(11a)	0.3865(2)	0.0651(2)	-0.8648(1)	0.0195(7)	0.0148(7)	0.0274(7)	0.0040(5)	0.0050(6)	0.0033(6)
C(12a)	-0.3463(2)	-0.0826(2)	-0.73887(9)	0.0298(9)	0.0247(8)	0.0155(6)	-0.0028(6)	0.0097(6)	-0.0049(6)
O(1a)	-0.3804(2)	-0.4631(2)	-0.88221(7)	0.0267(6)	0.0154(5)	0.0182(5)	-0.0050(4)	0.0046(4)	0.0022(4)
O(2a)	0.5139(1)	-0.2902(2)	0.96955(7)	0.0145(5)	0.0279(6)	0.0232(6)	0.0015(4)	-0.0009(4)	-0.0006(4)
N(1a)	-0.3880(2)	-0.3460(2)	-0.93350(8)	0.0152(6)	0.0126(5)	0.0137(5)	-0.0015(4)	0.0020(4)	-0.0018(4)
N(8a)	0.3135(2)	-0.0910(2)	0.81985(7)	0.0170(6)	0.0137(5)	0.0130(5)	0.0001(4)	0.0046(4)	-0.0003(4)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(2a)	0.290(3)	-0.379(3)	-1.066(1)	0.023(6)
H(3a)	-0.036(3)	-0.338(4)	-1.106(2)	0.026(6)
H(4a)	0.183(4)	-0.233(4)	-1.013(2)	0.031(6)
H(5a)	0.275(4)	-0.130(4)	-0.882(2)	0.033(7)
H(6a)	0.225(3)	-0.030(4)	-0.759(2)	0.030(6)
H(7a)	-0.045(3)	0.003(4)	-0.733(2)	0.028(6)
H(11a1)	-0.499(3)	0.075(4)	-0.862(1)	0.024(6)
H(11a2)	-0.372(3)	0.049(4)	-0.920(2)	0.030(7)
H(11a3)	-0.338(4)	0.177(4)	-0.845(2)	0.035(7)
H(12a1)	-0.293(3)	-0.184(3)	-0.708(1)	0.020(6)
H(12a2)	0.460(4)	-0.093(4)	0.739(2)	0.039(8)
H(12a3)	0.308(4)	0.036(4)	-0.712(2)	0.030(6)

and **C**, one block per molecule) least-squares analysis [10] [11]. Peaks close to expected positions for most **H**-atoms (for all in **A**) were found in difference *Fourier* maps; the remaining **H** positions were estimated and included (except for the methyl **H**-atoms in modification **C**) with isotropic temperature factors in the least-squares refinement. Final atomic coordinates and displacement parameters for modification **A**, the most accurate measurement, are given in *Table 2*. Data for modifications **B** and **C** have been deposited at the *Cambridge Crystallographic Data Centre*.

**Results.** – We may identify the seven observed conformations of **1** as **a** (modification **A**), **b,c,d** (**B**), **e,f,g** (**C**). As far as corresponding bond distances and angles are concerned, there are no significant differences. *Fig. 1* gives values for conformation **a**, which is the most accurately determined and which may be taken as representative for the series. The naphthalene skeleton is closely similar to that found in other 1,8-disubstituted derivatives [2] [3] and indeed in naphthalene itself [12], apart from the markedly widened angle at **C**(1) induced by the electron-withdrawing **NO**<sub>2</sub> substituent [13]. The slight contraction of the ring angle at **C**(8) is characteristic of the dimethylamino substituent [2] [13] and does not seem to depend much on the degree of pyramidity at the **N**-atom or on the orientation of the lone pair.

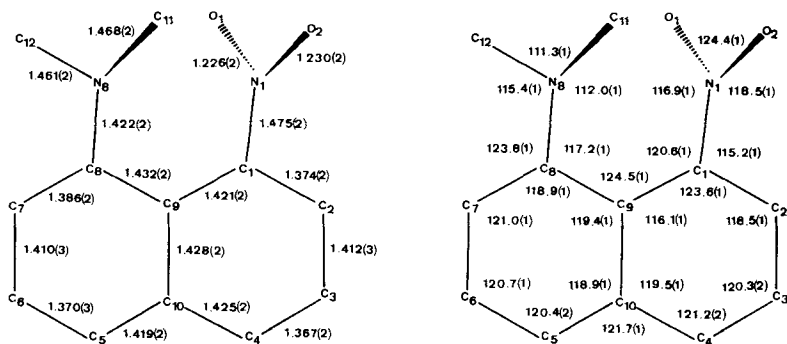


Fig. 1. Bond distances (Å) and angles (°) (with e.s.d.'s in parentheses) for **1a**

Perhaps the most striking feature of *Fig. 1* is the pattern of exocyclic bond angles at the substituted atoms C(1) and C(8). The exocyclic bond to the nitro N-atom is splayed outwards, and the one to the amino N-atom is splayed inwards, the same pattern as observed in other naphthalene derivatives with nucleophilic and electrophilic substituents at the 1- and 8-positions [2] [3]. As we shall see, it is the interaction between the lone pair of the pyramidal dimethylamino group and the  $\pi^*$ -orbital of the NO<sub>2</sub> group which provides a common basis for the discussion of the seven observed conformations.

*Figs. 2, 3, and 4* show stereodiagrams of the seven observed conformations with displacements of the atoms from the mean plane of the naphthalene nucleus, which is seen to be quite closely coplanar in the nearly mirror-symmetric conformations **d–g** and appreciably puckered in conformations **a–c** where the substituents are twisted away from their perpendicular orientations<sup>1</sup>). In **a** (*Fig. 2*), the most twisted conformation, the r.m.s. displacement of the ring atoms amounts to 0.08 Å. As pointed out in [2], the displacements of the individual ring atoms are always such as to tend to preserve  $D_2$  symmetry of the naphthalene nucleus.

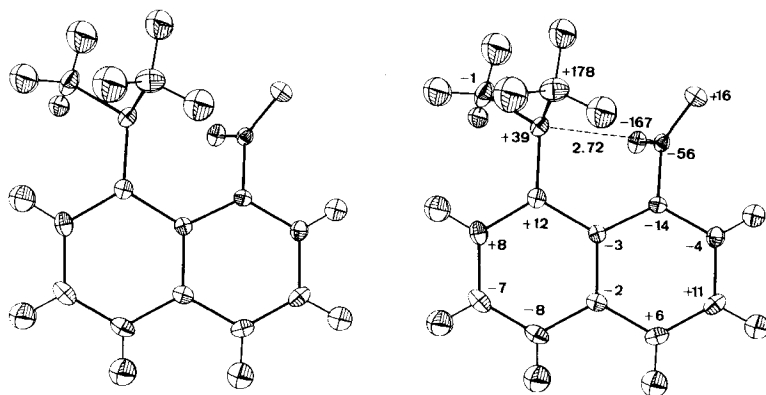


Fig. 2. Stereoview of **1a** showing Gaussian probability ellipsoids at the 50% probability level [30]. The numbers indicate deviations (Å × 10<sup>2</sup>) of atoms from the mean plane of the naphthalene ring.

<sup>1</sup>) In the earlier studies [2] [3] of interactions between peri-substituted dimethylamino and carbonyl-containing groups, only nearly perpendicular conformations corresponding to **1d–g** were observed.

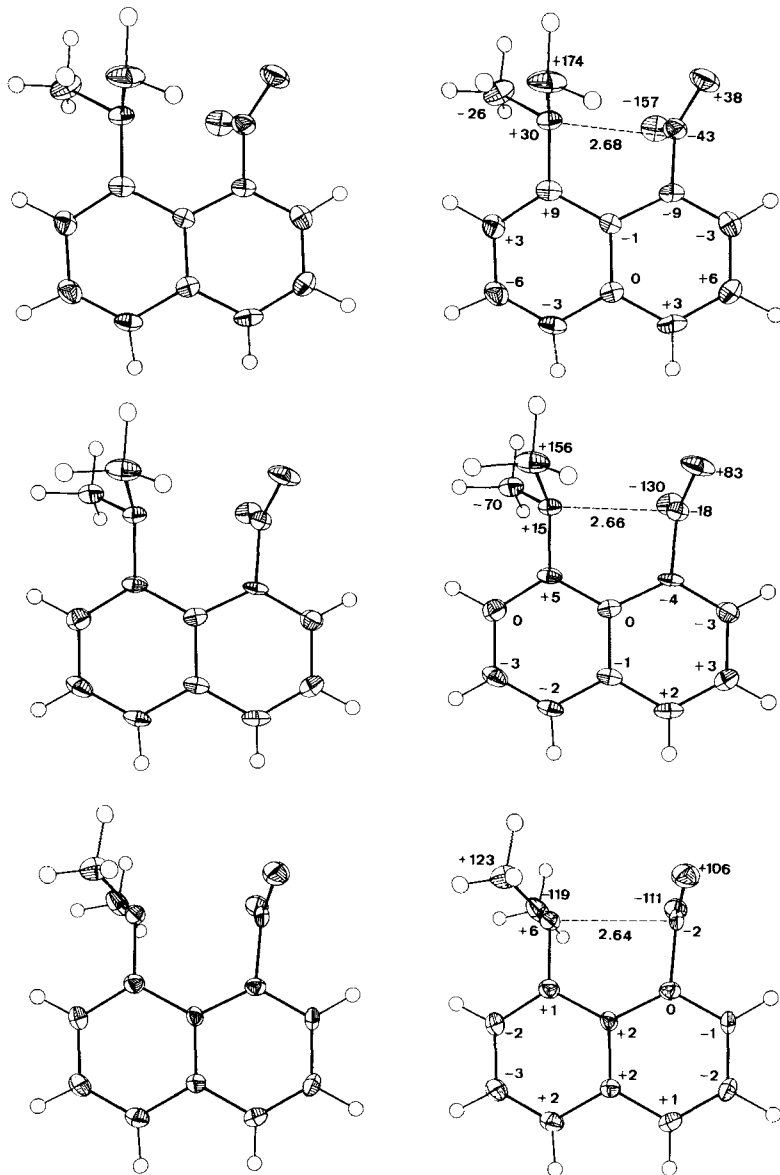


Fig. 3. Stereoviews of **1b d**. See Fig. 2 for explanation.

Conformations **c**, **b**, and **a** are related to the approximately mirror-symmetric conformations by progressively larger conrotatory rotations about the two C–N bonds. In **a**, both rotations amount to more than 40° (see Table 3 for selected parameters of the various observed conformations). Figs. 2, 3, and 4 show that as the functional groups are rotated further from the mirror-symmetric conformation the naphthalene nucleus becomes more puckered and the two N-atoms are increasingly displaced to opposite sides of the naphthalene plane. In conformation **a**, the corresponding displacements amount to

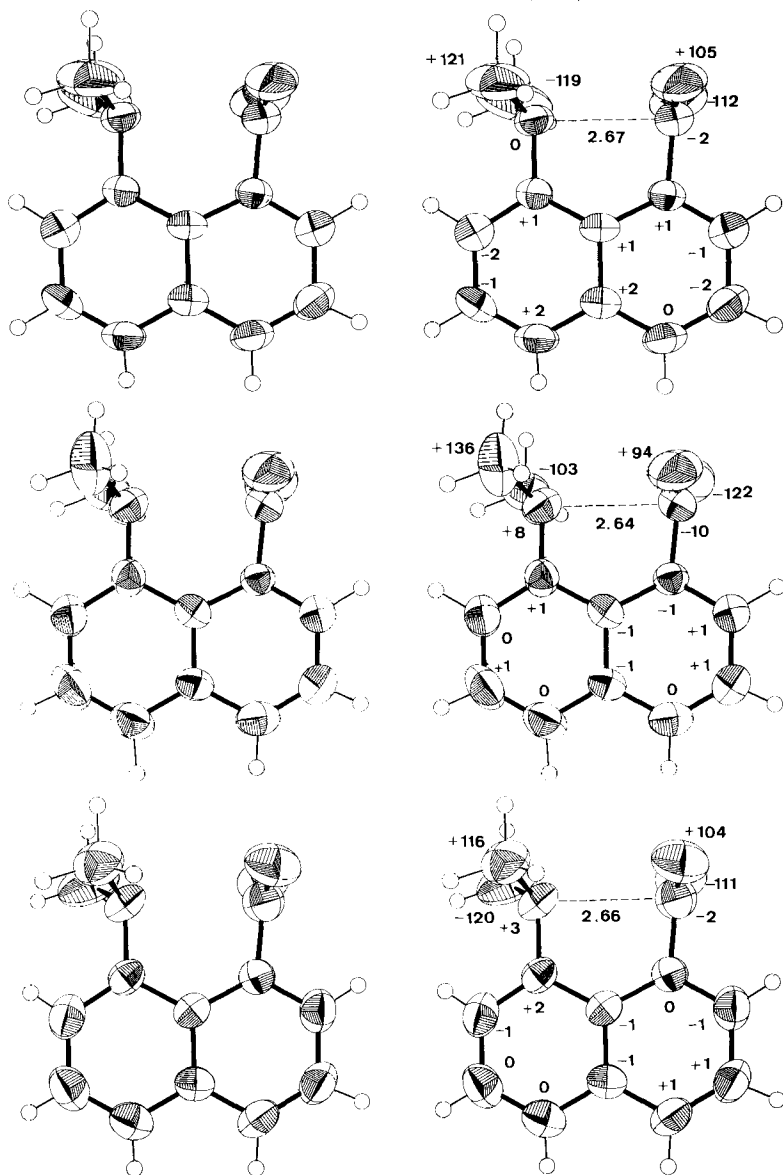


Fig. 4. Stereoviews of **1e-g**. See Fig. 2 for explanation.

+ 0.39 Å for the amino N(8) and -0.56 Å for the nitro N(1), thus producing an out-of-plane separation that is even larger than in the symmetrically disubstituted molecules, 1,8-dinitronaphthalene (**2**; 0.79 Å) [14] or 1,8-bis(dimethylamino)naphthalene (**3**; 0.81 Å) [15]. These displacements have only a minor effect on the N...N distance, which is increased from 2.64–2.67 Å in the mirror-symmetric conformations to 2.72 Å in **a**. In spite of the larger out-of-plane displacement in **a** compared with the symmetrically disubstituted molecules **2** and **3**, the N...N distance in **a** is shorter (*cf.* 2.95 Å in **2** and

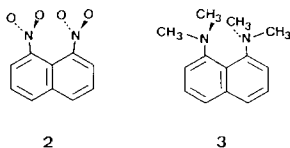


Table 3. Selected Structural Parameters for **1** in Seven Observed Conformations<sup>a)</sup>

Molecule	a	b	c	d	e	f	g
$\rho 1$	+40.8	+37.3	+12.2	+3.0	+ 11.6	+8.8	- 5.7
$\rho 8$	+41.2	+35.3	+22.8	+4.2	+0.8	+5.6	+6.1
$\Delta 1$	- 0.04	- 0.05	- 0.04	- 0.02	- 0.03	- 0.03	- 0.03
$\Delta 8$	+0.40	+0.43	+0.43	+0.40	+0.37	+0.40	+0.42
$d(\text{N} \cdots \text{N})$	2.72	2.68	2.66	2.64	2.67	2.64	2.66
$\alpha 1$	13.7	12.1	8.4	6.0	6.7	7.2	6.2
$\alpha 8$	26.7	24.0	21.2	16.9	15.1	16.2	18.7

<sup>a)</sup>  $\rho 1$  = Rotational angle of nitro-group (in degrees, 0° for [N(1) O(1) O(2)] plane-normal in aromatic plane).  
 $\rho 8$  = Rotational angle of dimethylamino-group (in degrees, 0° for [N(8) C(11) C(12)] plane-normal in aromatic plane).  
 $\Delta 1$  = Distance of N(1) to plane [C(1) O(1) O(2)] (in Å).  
 $\Delta 8$  = Distance of N(8) to plane [C(8) C(11) C(12)] (in Å).  
 $d(\text{N} \cdots \text{N})$  = Distance between N(1) and N(8) (in Å).  
 $\alpha 1$  = Angle between N(1)–N(8) and [C(1) O(1) O(2)] normal (in degrees).  
 $\alpha 8$  = Angle between N(1)–N(8) and [C(8) C(11) C(12)] normal (in degrees).

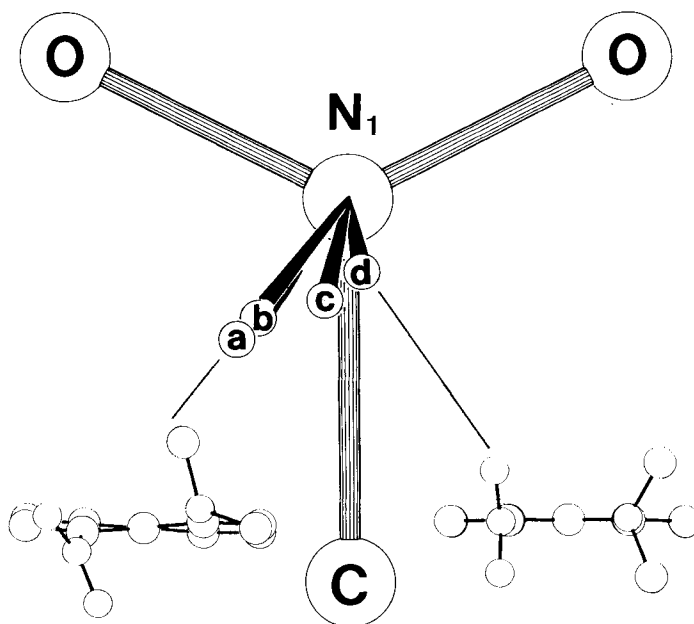


Fig. 5. Diagram [31] showing the positions of the amino N-atoms in **1a** and **1d** relative to the  $\text{NO}_2$  group. The views of **1a** and **1d** show the difference in the puckering of their naphthalene rings.

2.79 Å in **3**). Furthermore, in all observed conformations of **1** the nitro N(1) is slightly displaced (0.03–0.05 Å) from the plane of its three bonded neighbours, always towards the dimethylamino group (see *Table 3*). Although small, these pyramidalities are among the largest known for NO<sub>2</sub> groups<sup>2)</sup>. Together with the short N···N contacts, these small but consistent pyramidalities suggest that there is an attraction between the two groups.

It is interesting that as the two groups are rotated out of their mirror-symmetric orientations, the accompanying out-of-plane displacements bring the angle between the amino group lone pair axis and the N···N direction back towards its initial value. This angle is about 17° in the approximately mirror-symmetric conformation **d**, and it increases only by about 10° on going to **a**, despite the amino group rotation of 37° about the C–N bond. *Fig. 5* shows the relative displacement of the amino N(8)-atom with respect to the NO<sub>2</sub> group on passing from the mirror-symmetric conformations to the most strongly rotated one **a**.

All these features can be interpreted in terms of an attractive interaction between the lone pair of the dimethylamino group and the π\*-orbital of the NO<sub>2</sub> group, localized mainly on N(1). This through-space interaction is presumably most favourable in the mirror-symmetric conformation, but, on the other hand, the through-bond interaction of the lone pair with the aromatic π-system vanishes in this conformation. Rotation of the functional groups away from the mirror-symmetric conformation could make one interaction better, the other worse, leaving the overall conformational energy approximately constant. Unfortunately, the data are not accurate enough to quantify the small changes in bond length and bond angle at the dimethylamino group that would be expected to occur as its orientation varies.

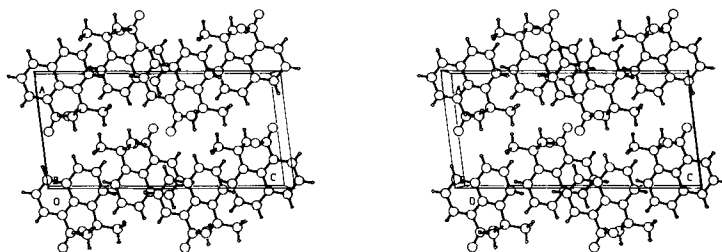
The observed structures can thus be considered as examples of incipient nucleophilic attack of the dimethylamino N-atom on the NO<sub>2</sub> group. Nucleophilic attack on a NO<sub>2</sub> group can hardly be described as a common chemical reaction. One reason is that the strong electron-attracting effect of the NO<sub>2</sub> group often activates another part of the molecule to nucleophilic attack (*e.g.* *Michael* reaction of nitroalkenes) or to deprotonation<sup>3)</sup>. In any case, it is apparent from the structural data that the NO<sub>2</sub> group is a weaker electrophile than the carbonyl groups of ketones or of carboxylic acids and esters. In the analogous 1,8-disubstituted naphthalene derivatives [2] the relevant N···C distances are in the range 2.56–2.61 Å, *i.e.* shorter than the N···N distance in **1**, despite the larger *van der Waals* radius of the C-atom compared with the N-atom. The carboxylic ester group is a better through-space acceptor of electron density than the NO<sub>2</sub> group, but the NO<sub>2</sub> group is a better through-bond acceptor. The structural evidence for the latter is to be found in the bond angle pattern in substituted benzene derivatives; the better the electron-withdrawing power of substituent, the wider the bond angle at the substituted C-atom [13].

<sup>2)</sup> A search of the *Cambridge Crystallographic Database* yielded reasonably precise structural data (C–C bond e.s.d.'s reported as < 0.005 Å, *R* < 0.08) for over 500 NO<sub>2</sub> groups. The average pyramidalities were less than 0.01 Å (discounting a few large pyramidalities calculated for orientationally disordered NO<sub>2</sub> groups). Only in three structures was the pyramidalities of a nitro N-atom greater than 0.03 Å, and in each case an O-atom from another part of the molecule was contiguous to the nitro N-atom [16–18].

<sup>3)</sup> Nevertheless, in some reactions formation of a bond to a nitro N-atom is reported: *Grignard* reagents can add to NO<sub>2</sub> groups [19] [20], and products containing N–N bonds have been isolated from the reactions of NO<sub>2</sub> compounds with hydroxylamines [21], sodium amide [22] and amines [23]. However, in the absence of mechanistic studies, radical mechanisms involving electron transfer to the NO<sub>2</sub> group cannot be excluded.

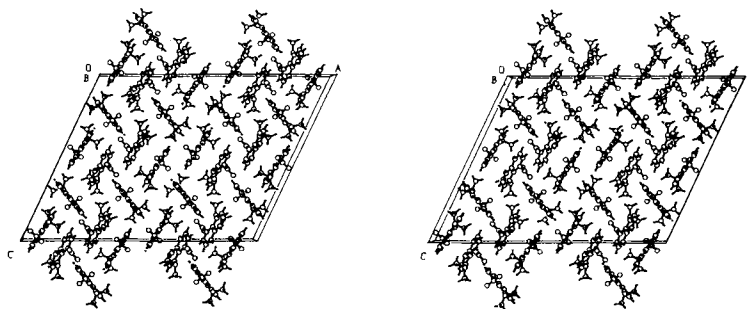


**Packing.** – Obviously, modification **A** with just a single molecule in the asymmetric crystal unit is the only one of the three to have a relatively simple type of packing. This is illustrated in *Fig. 6*. The molecules are arranged in corrugated stacks running along the *b* direction of the crystal with their aromatic planes inclined at about 20° to the stacking



*Fig. 6. Stereoview of the packing of modification A, viewed down the [010] axis [31]*

direction. Adjacent molecules within a given stack are related by non-equivalent inversion centres at  $y = 0$  and  $y = 0.5$ , but the tendency towards dimer formation across one of these sets is only slight. The shortest C...C distance between a pair of molecules related by the inversion centre at  $y = 0.5$  is 3.44 Å (between C(3) and C(4)), while the shortest between a pair related by the other set of inversion centres is 3.61 Å (between C(3) and C(10)). Thus the main interactions between adjacent molecules within a stack involve the naphthalene rings that hold the NO<sub>2</sub> groups. Individual stacks are related along the [100] direction by translation and along the [001] direction by glide-reflection.



*Fig. 7. Stereoview of the packing of modification B, viewed down the [010] axis [31]. The mean plane of molecule **d** lies approximately perpendicular to the planes of the other two. The planes of molecules **c** and **d** are viewed almost edgewise.*

In contrast, the packing arrangements in the two other crystal modifications are extremely intricate. In modification **B** (*Fig. 7*), one can distinguish a trimeric unit in which molecule **d** sits with its aromatic plane nearly perpendicular to the aromatic planes of molecules **b** and **c**, such that each of its NO<sub>2</sub> group O-atoms points roughly towards the space between the two CH<sub>3</sub> groups of a **b** or **c** molecule. Repeated by the symmetry operations of the *C2/c* space group, this produces dimeric pairs of parallel **b** and **c** molecules related by an approximate non-crystallographic twofold rotation axis parallel

to the actual twofold axes of the space group but displaced from them by roughly one-eighth along the *a* and *c* axes. One can also recognize dimeric pairs of non-equivalent molecules in the structure of modification C (molecules *e* and *f* in Fig. 8) but they are only very roughly parallel. Similarly, the aromatic plane of the third type of molecule in modification C is roughly perpendicular to the planes of the other two. Altogether, the packing in modification C is the least dense, and the displacement parameters of some of the atoms are so large that the structure should probably be considered as disordered to some extent.

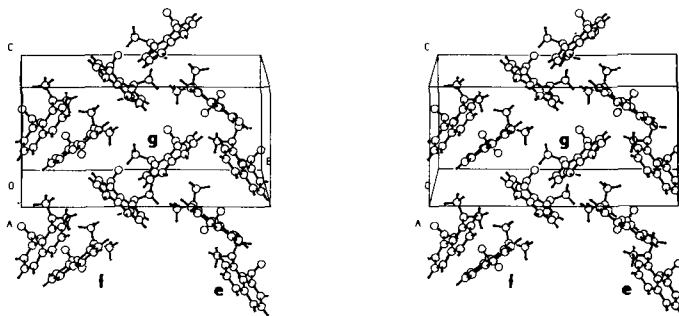


Fig. 8. Stereoview of the packing of modification C, viewed almost down the  $[100]$  axis [31]. Molecules *e, f, g* are indicated by lettering.

Although the preference for one or other of the conformations shown in Figs. 2, 3, and 4 must depend on the environment of the molecules in the crystal, there does not seem to be any very obvious relationship. The problem could certainly be investigated by force-field calculations using a program such as *Busing's* WMIN [24], but we have no immediate plans for such a study.

**Analysis of Atomic Displacement Parameters.** – The first conclusion that may be reached by analysis of the atomic *Gaussian* displacement parameters or AGDP's (listed in Table 2 for modification A along with the positional parameters) is that the molecules do not behave as rigid bodies in the crystals but show appreciable internal motion (or possibly static disorder). As a criterion of molecular rigidity, and also to assess the quality of the AGDP's we use *Hirshfeld's* 'rigid bond' test [25] and its generalization to detect internal motion of molecules in crystals [26]. These tests are based on examination of the mean-square displacement amplitudes (MSDA's) of the atoms along interatomic vectors. For a rigid body, by definition, MSDA's of all atom pairs must be equal along the interatomic vectors. The rigid-bond test assumes that this equality holds at least for any pair of bonded atoms of roughly similar mass. Thus, the quantities of interest in this connection are the differences  $\Delta(A,B)$  between MSDA's of atoms A and B along the interatomic vectors, which are readily calculated (in dyadic notation) as

$$\Delta(A,B) = \mathbf{n} \cdot \mathbf{U}(A) \cdot \mathbf{n} - \mathbf{n} \cdot \mathbf{U}(B) \cdot \mathbf{n}$$

where  $\mathbf{n}$  is the unit vector in the A,B direction. For bonded pairs of atoms, these differences give an idea of the quality of the data; for non-bonded pairs, they may provide indications of non-rigid-body behaviour, *i.e.*, of internal motion. We illustrate this for the best and for the worst defined of the seven molecules. For molecule *a*, with standard

deviations in MSDA's of about  $0.0006 \text{ \AA}^2$ , the r.m.s. value of  $\Delta$  over the 11 bonds of the naphthalene skeleton is  $0.0010 \text{ \AA}^2$ , larger by a factor of about  $\sqrt{2}$ , as expected for the rigid-bond model. On the other hand, some of the  $\Delta$  values involving the methyl C-atoms C(11) and C(12) and the nitro O-atoms O(1) and O(2) are many times larger, indicating that these atoms are carrying out motions relative to the rest of the molecule. For molecule **e** (room-temperature data) the standard deviations in MSDA are about  $0.0048 \text{ \AA}^2$ , the r.m.s. value of  $\Delta$  over the 11 naphthalene bonds is  $0.0076 \text{ \AA}^2$ , and some of the  $\Delta$  values involving the substituent atoms amount to more than  $0.0500 \text{ \AA}^2$ . Very similar patterns are found for the five other molecules.

Table 4. *Results of Thermal Motion Analysis.* All results were obtained with program THMB, using unit weights. Overall and internal librations around defined axes were estimated without regard to their mutual correlations. The eigenvalues of the libration tensors **L** and the translation tensors **T** refer to the individual inertial systems of molecules **a–g**. The quantities  $\Omega 1$  and  $\Omega 8$  are mean-square internal libration amplitudes around the axes C(1)–N(1) and C(8)–N(8), respectively. The *R*-factor is defined as  $(\Sigma[U_{\text{obs.}} - U_{\text{calc.}}]^2 / \Sigma[U_{\text{obs.}}]^2)^{1/2}$ .

Molecule	L1 [deg <sup>2</sup> ]	L2 [deg <sup>2</sup> ]	L3 [deg <sup>2</sup> ]	T1 [Å <sup>2</sup> ]	T2 [Å <sup>2</sup> ]	T3 [Å <sup>2</sup> ]	$\Omega 1$ [deg <sup>2</sup> ]	$\Omega 8$ [deg <sup>2</sup> ]	<i>R</i> [%]
<b>a</b>	5.91	4.24	2.40	0.014	0.014	0.007	15.7	12.9	0.09
<b>b</b>	10.55	5.85	4.16	0.025	0.015	0.006	7.7	16.4	0.16
<b>c</b>	10.31	3.97	2.94	0.027	0.013	0.005	30.9	0.0	0.15
<b>d</b>	5.69	5.44	2.37	0.020	0.017	0.012	26.0	19.5	0.16
<b>e</b>	55.10	26.51	0.00	0.055	0.045	0.022	206.0	350.0	0.16
<b>f</b>	51.02	19.84	6.31	0.058	0.051	0.028	112.0	17.3	0.18
<b>g</b>	28.08	17.49	14.00	0.060	0.047	0.029	50.7	52.9	0.11

Results of more detailed calculations with the computer program THMB [27] are summarized in *Table 4*. The indication is that in the crystals the internal rotations about the C(1)–N(1) and C(8)–N(2) bonds are of considerable amplitude. In these calculations, correlations among the internal rotations and the overall molecular motions [28] have been neglected; when such correlation terms are included as parameters in the least-squares calculation, we obtain a nearly singular normal-equations-matrix, leading to enormous standard deviations in the internal rotation mean-square amplitudes, although to quite similar values. In any case, as *Trueblood* and *Schomaker* [29] have pointed out, even when correlation terms are included, neither the mean-square torsional amplitude  $\langle \phi \cdot \phi \rangle$  about a given axis nor the mean correlation  $\langle \phi \cdot \lambda \rangle$  between this motion and the component of overall libration parallel to the axis in question can be determined from the AGDP's, only the sum of these averages. For our molecules, the internal rotation axes are nearly parallel to one of the inertial axes. As shown in *Table 4*, the values of  $\langle \phi \cdot \phi \rangle$  calculated without correlation are mostly considerably larger than the components of the overall librational motion. Thus, the qualitative conclusions about the internal motion should not depend too much on whether the correlation terms are included or not.

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