

The Polymorphs of 2,2'-Dinitroxydiethylnitramine (DINA).^{*} The Structure of DINA (II)

BY A. WILKINS AND R. W. H. SMALL

Chemistry Department, The University, Lancaster LA1 4YA, England

(Received 26 March 1981; accepted 6 July 1981)

Abstract

Preparation of the four polymorphs is discussed. The structure of DINA (II), $C_4H_8N_4O_8$, monoclinic, $P2_1/c$, $a = 9.06$ (1), $b = 9.15$ (1), $c = 12.33$ (2) Å, $\beta = 109.94$ (5)°, $Z = 4$, $D_c = 1.65$ Mg m⁻³, has been determined from 909 diffractometer-measured intensities to $R = 0.039$. The shape of the molecule has been compared with that in DINA (I) by the use of a least-squares molecular-fitting program. The main differences arise from rotations about N–C and C–O bonds in one 'arm' of the molecule.

Introduction

Four polymorphs of the title compound have been described by McCrone (1965) who obtained them by crystallization from a supercooled melt between a microscope slide and a cover slip. The temperature of the melt at the point of crystallization was found to determine which polymorph formed. The melting points were recorded in that investigation as (I) 325 K, (II) 325 K, (III) 311 K, (IV) 303 K. Apart from (I) for which the crystal structure has been determined (Halfpenny & Small, 1978) no other investigations on these polymorphs have been recorded. It was of interest, therefore, to attempt single-crystal preparation and structure determination on other modifications.

It was found possible to grow DINA (III) beneath a cover slip; its presence was confirmed by the melting point. This polymorph was short-lived; several minutes after formation, transformation would commence at some point and propagate in all directions leaving a polycrystalline pseudomorph. Transformation of DINA (III) was initiated whenever any attempt was made to cut sections of crystal from the mass. The original preparation (McCrone, 1965) of DINA (IV) could not be repeated; the ephemeral nature of modifications (III) and (IV) is in accord with McCrone's observations and it appears unlikely that single crystals of either of these could be obtained by

this method. Evaporation of a solution of DINA in ethanol or 1,4-dioxane was found to yield a mixture of polymorphs (I) and (II) with the former greatly in excess. Crystal habits were sufficiently different to distinguish the two types; crystals of DINA (II) were selected from such mixtures. Approximate cell dimensions of DINA (II) were obtained from Weissenberg photographs, using Cu $K\alpha$ radiation, $\lambda = 1.542$ Å, which also indicated Laue symmetry $2/m$ and the systematic absences $h0l$, l odd; $0k0$, k odd. Cell dimensions were determined more accurately from reflexions at high θ values, after setting a crystal about c on the Stoe STADI-2 automatic two-circle diffractometer. This instrument was used for collection of intensity data, using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å); 2θ was limited to 60°. 1361 intensities were measured, of which 452 with $I < 3\sigma(I)$ were omitted from the structure determination and refinement. Data reduction was carried out by the use of the *SHELX* suite of programs (Sheldrick, 1976); an application of *MULTAN* (Germain, Main & Woolfson, 1971) gave the positions of the C, N and O atoms. Refinement of atomic coordinates and anisotropic U_{ij} values was performed using *SHELX*. H-atom positions could be observed on $F_o - F_c$ maps during the later stages of refinement and their positions were fixed with C–H = 1.08 Å using the *AFIX* routine within the *SHELX* program. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final value of R was 0.039; coordinates of non-H atoms are given in Table 1.†

A computer program was written for the comparison of the shapes of similar molecules or fragments of molecules. The program applies rotational and translational transformations to the coordinates of one molecule so as to produce the best fit on the other molecule by least-squares refinement. This routine is based upon a description of a similar program by Nyburg (1974). Using this program the shape of DINA

† Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36235 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Alternative name: *N*-nitrobis(2-nitroxyethyl)amine.

Table 1. Fractional atomic coordinates ($\times 10^4$) and U_{eq} values ($\text{\AA}^2 \times 10^4$) for the C, N and O atoms in DINA (II)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
C(1)	9125 (3)	2100 (4)	968 (3)	329 (20)
C(2)	6810 (4)	3373 (4)	1312 (3)	399 (21)
C(3)	634 (4)	2963 (4)	1464 (4)	464 (23)
C(4)	5363 (4)	2453 (3)	1070 (4)	417 (20)
N(1)	7386 (4)	3672 (3)	9544 (3)	429 (19)
N(2)	7732 (3)	3028 (3)	582 (3)	361 (16)
N(3)	1272 (3)	2828 (4)	3519 (4)	482 (21)
N(4)	4942 (4)	9953 (4)	1474 (3)	468 (19)
O(1)	8261 (3)	3457 (3)	8979 (3)	577 (19)
O(2)	6193 (3)	4444 (3)	9213 (3)	611 (17)
O(3)	709 (3)	3703 (3)	2526 (3)	459 (15)
O(4)	5927 (3)	942 (2)	1225 (2)	484 (15)
O(5)	1586 (3)	1584 (3)	3412 (3)	700 (20)
O(6)	5462 (3)	8728 (3)	1592 (3)	647 (19)
O(7)	1375 (4)	3494 (4)	4382 (3)	692 (22)
O(8)	3746 (3)	383 (3)	1561 (3)	741 (21)

(II) was compared with that of DINA (I) using the coordinates of Halfpenny & Small (1978). The program *MGTLS* (Schomaker & Trueblood, 1968) was used to calculate torsion angles and distances of atoms from least-squares planes in the molecule.

Discussion

Bond lengths and angles are given in Tables 2 and 3. Corresponding distances and angles in the two halves of the molecule do not differ appreciably and are close to those in DINA (I). In the latter the atoms were found to lie approximately in three planes; those in the nitramine group were planar to within 0.13 Å and the nitroxyethyl groups planar to within 0.2 Å. For DINA (II) the nitramine group O(1)O(2)N(1)N(2)C(1)C(2) is planar to within 0.13 Å, but the nitroxyethyl groups cannot be described as planar; within the group O(6)O(8)N(4)O(4)C(4)C(2), C(2) lies 0.574 Å away from the plane defined by the nitro-group atoms. In the group O(5)O(7)N(3)O(3)C(3)C(1), C(3) lies 0.061 Å away from the nitro-group plane and C(1) lies 1.336 Å to the opposite side of this plane. In an application of the least-squares molecular-fitting program all the atoms except O(7)O(5)N(3)O(3)C(3) were fitted to the corresponding ones in DINA (I). The mean separation of corresponding atom pairs after fitting was 0.281 Å; the group of atoms omitted were clearly in a different conformation. The coordinates of the two molecules after the least-squares-fitting process were used to produce Fig. 1 with the program *ORTEP* (Johnson, 1965). The similarity in shape of the nitramine and one nitroxyethyl groups will be noted; the other nitroxyethyl group in DINA (II) has been twisted compared with that in DINA (I). The pertinent torsion angles,

Table 2. Bond lengths (Å) involving the C, N and O atoms

C(1)—C(3)	1.515 (4)	N(1)—O(1)	1.236 (4)
C(2)—C(4)	1.500 (4)	N(1)—O(2)	1.238 (4)
C(1)—N(2)	1.459 (4)	N(3)—O(3)	1.405 (4)
C(2)—N(2)	1.457 (5)	N(3)—O(5)	1.192 (4)
C(3)—O(3)	1.456 (5)	N(3)—O(7)	1.202 (4)
C(4)—O(4)	1.493 (4)	N(4)—O(4)	1.378 (4)
N(1)—N(2)	1.345 (4)	N(4)—O(6)	1.205 (4)
		N(4)—O(8)	1.191 (4)

Table 3. Bond angles (°) involving the C, N and O atoms

O(1)—N(1)—O(2)	124.1 (4)	O(3)—N(3)—O(5)	118.6 (4)
O(1)—N(1)—N(2)	118.6 (3)	O(3)—N(3)—O(7)	112.2 (3)
O(2)—N(1)—N(2)	117.2 (4)	O(5)—N(3)—O(7)	129.3 (4)
C(1)—N(2)—N(1)	117.4 (3)	N(3)—O(3)—C(3)	114.2 (3)
C(2)—N(2)—N(1)	119.8 (3)	O(4)—N(4)—O(6)	112.4 (3)
C(1)—N(2)—C(2)	122.6 (3)	O(4)—N(4)—O(8)	118.8 (3)
N(2)—C(1)—C(3)	112.9 (3)	O(6)—N(4)—O(8)	128.7 (4)
N(2)—C(2)—C(4)	113.7 (3)	N(4)—O(4)—C(4)	115.2 (3)
C(1)—C(3)—O(3)	111.4 (3)	C(2)—C(4)—O(4)	105.2 (3)

Table 4. Some torsional angles (°) in DINA (I) and (II)

	DINA (I)	DINA (II)
N(1)N(2)C(1)C(3)	-132.0 (5)	80.4 (5)
N(2)C(1)C(3)O(3)	67.8 (5)	66.0 (5)
C(1)C(3)O(3)N(3)	-176.9 (5)	84.4 (5)
N(1)N(2)C(2)C(4)	79.4 (5)	86.5 (5)
N(2)C(2)C(4)O(4)	64.2 (5)	57.3 (5)
C(2)C(4)O(4)N(4)	176.0 (5)	156.7 (5)

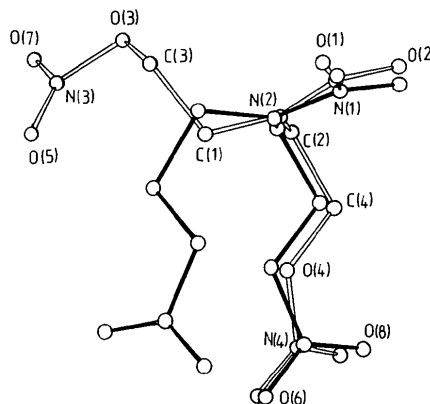


Fig. 1. *ORTEP* drawing (see text) of molecules of DINA (I) and (II) with the atom-numbering scheme.

Table 4, show that rotation has occurred about the bonds C(1)—N(2) and C(3)—O(3); the torsion angles show also that the conformation about the bond C(1)—C(3) is unchanged, the attached groups remaining in the *gauche* conformation. This result is not unexpected since the barrier to rotation about C(1)—C(3) will be of the familiar threefold ethane type

with three pairs of atoms simultaneously eclipsed whereas rotational barriers about C(1)–N(2) and C(3)–O(3) will involve the eclipsing of one pair of atoms at a time and are therefore likely to be lower. The question of whether these two forms of DINA are polymorphs or rotational isomers depends upon whether the difference in conformation is brought about by packing or intramolecular effects. The coexistence of the two forms during crystallization from solution indicates a similar degree of thermodynamic stability. Solid–solid transitions between DINA (II) and DINA (I) have not been observed; the spatial requirements involved in the change of conformation imply a severe mechanistic barrier to transformation in the solid state. Crystals of DINA (II) become opaque and slightly discoloured over a period of one year or more but an oscillation photograph shows them to be structurally unchanged.

The shortest intermolecular contacts in DINA (II) are 3.12 Å between O(6) and N(3) of 2₁-related molecules; none of the other O...N intermolecular contacts are significantly less than the sum of the van der Waals radii across π -bonding electrons (Bondi, 1964). Closer interactions (2.9 Å) have been found in DINA (I) (Halfpenny & Small, 1978) and in other nitramines (Cobbedick & Small, 1973).

We thank the Science Research Council for the award of a research studentship to one of us (AW).

References

- BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
 COBBLEDICK, R. E. & SMALL, R. W. H. (1973). *Acta Cryst.* **B29**, 1659–1666.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 HALFPENNY, J. & SMALL, R. W. H. (1978). *Acta Cryst.* **B34**, 3452–3454.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 MCCRONE, W. C. (1965). *Physics and Chemistry of the Organic Solid State*. Vol. II, edited by D. FOX, M. M. LABES & A. WEISSBERGER, pp. 725–768. New York: Wiley–Interscience.
 NYBURG, S. C. (1974). *Acta Cryst.* **B30**, 251–253.
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
 SHELDRIK, G. M. (1976). *SHELX 76*. A program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1982). **B38**, 490–494

6,9-Dimethoxy-2,13-diaza[4]paracyclo[4](3,5)pyridinophane-1,14-dione, C₁₉H₂₁N₃O₄, and 19-Benzyl-16,19-dihydro-2,13-diaza[4]paracyclo[4](3,5)pyridinophane-1,4-dione, C₂₄H₂₅N₃O₂

BY A. M. VAN HERK, K. GOUBITZ, A. R. OVERBEEK AND C. H. STAM*

Laboratory for Crystallography, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

(Received 27 April 1981; accepted 30 June 1981)

Abstract

C₁₉H₂₁N₃O₄: *P*2₁/*n*, with *a* = 10.2801 (4), *b* = 9.4333 (4), *c* = 18.7174 (7) Å, β = 101.42 (1)°, *Z* = 4. Final *R* = 0.041 for 2519 observed reflexions. The pyridine ring is above and roughly perpendicular to the benzene ring with the H atom at the 4 position of the

pyridine ring close to the benzene ring (shortest H–C distance 2.80 Å). The molecules are interconnected by means of N...O hydrogen bonds to form sheets parallel to (001). C₂₄H₂₅N₃O₂: *P*2₁/*c*, with *a* = 12.980 (2), *b* = 5.719 (2), *c* = 26.721 (2) Å, β = 99.26 (2)°, *Z* = 4. Final *R* = 0.048 for 2704 observed reflexions. The 1,4-dihydropyridine ring is in a boat conformation. One of the H atoms of its CH₂ group is roughly above the centre of the benzene ring with shortest H–C distance of 2.94 Å.

* To whom correspondence should be addressed.