

The temperature dependence of conductivity along all three axes is isotropic and varies as $\exp(-E_a/kT)$ where $E_a = 0.27 \pm 0.02$ eV.

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The Crystal and Molecular Structure of 1-Ethyleneimino-2,4,6-trinitrobenzene

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The structure of 1-ethyleneimino-2,4,6-trinitrobenzene (CB1943) has been determined by a direct method. The crystals are monoclinic, $a = 4.715$ (4), $b = 30.48$ (3), $c = 7.119$ (7) Å, $\beta = 97.4^\circ$, space group $P2_1/c$; $R = 0.067$ for 1815 reflexions. The 2-, 4- and 6-substituted nitro groups are inclined to the plane of the benzene ring by 40.4 , 12.5 and 37.3° respectively. The ethyleneimine group is inclined at 127.5° .

Introduction

Several derivatives of trinitrobenzene have been investigated for antitumour activity (Ross & Mitchley, 1950), and the crystal structure of the most active derivative, *i.e.* 2,4-dinitro-5-ethyleneiminobenzamide, has been reported (Iball, Scrimgeour & Williams, 1975). The present compound (Fig. 1) has not shown any antitumour activity (Cobb *et al.*, 1969).

Experimental

Crystals of 1-ethyleneimino-2,4,6-trinitrobenzene (CB1943) in the form of large yellow prisms were supplied by Professor Ross, Chester Beatty Research Institute, and small pieces were cut from these. Different

crystals were mounted about a and b , and data were collected with Cu $K\alpha$ radiation on a Wooster four-circle diffractometer. The cell dimensions were determined from Weissenberg photographs and refined on the diffractometer. No corrections for absorption were made.

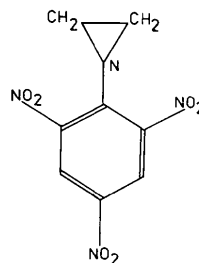


Fig. 1. 1-Ethyleneimino-2,4,6-trinitrobenzene (CB1943).

Crystal data

Structure determination and refinement

$C_8H_6N_4O_6$, $M_r = 254.2$, $a = 4.715$ (4), $b = 30.48$ (3), $c = 7.119$ (7) Å, $\beta = 97.36^\circ$, $U = 1015$ Å³, $D_m = 1.656$, $Z = 4$, $D_x = 1.634$ g cm⁻³; $\lambda = 1.5418$ Å, $F(000) = 520$, $\mu = 11.5$ cm⁻¹. Space group $P2_1/c$ (from systematic absences).

Data from several crystals were placed on a common scale by hand and the structure was determined by direct methods with programs developed by Sheldrick (1975). An E Fourier map gave coordinates for all the non-hydrogen atoms.

Table 1. Final atomic coordinates and thermal parameters

(a) Non-hydrogen atomic coordinates $\times 10^4$; estimated standard deviations are in parentheses. (A) are from block-diagonal and (B) from full-matrix refinements.

	x/a		y/b		z/c	
	(A)	(B)	(A)	(B)	(A)	(B)
C(1)	851 (11)	861 (3)	6044 (2)	6044 (1)	3994 (7)	3993 (2)
C(2)	-348 (11)	-362 (3)	6418 (2)	6419 (1)	3021 (7)	3021 (2)
C(3)	457 (12)	472 (4)	6843 (2)	6844 (1)	3485 (7)	3482 (2)
C(4)	2584 (12)	2587 (4)	6907 (2)	6908 (1)	4963 (7)	4964 (2)
C(5)	3856 (12)	3859 (4)	6564 (2)	6563 (1)	6007 (7)	6012 (2)
C(6)	2932 (11)	2935 (4)	6142 (2)	6143 (1)	5520 (7)	5524 (2)
C(7)	46 (13)	32 (5)	5455 (2)	5456 (1)	1559 (8)	1551 (3)
C(8)	2079 (13)	2082 (5)	5280 (2)	5279 (1)	3141 (9)	3149 (3)
N(1)	23 (10)	24 (3)	5624 (1)	5624 (1)	3481 (6)	3476 (2)
N(2)	-2558 (11)	-2564 (3)	6372 (2)	6370 (1)	1399 (7)	1394 (2)
N(3)	3533 (11)	3536 (4)	7355 (2)	7356 (1)	5459 (7)	5457 (2)
N(4)	4353 (10)	4355 (4)	5793 (2)	5793 (1)	6728 (6)	6724 (2)
O(1)	-2382 (12)	-2371 (6)	6614 (2)	6614 (1)	57 (6)	62 (3)
O(2)	-4458 (9)	-4461 (3)	6102 (2)	6101 (1)	1472 (6)	1463 (2)
O(3)	2079 (11)	2095 (5)	7657 (1)	7656 (1)	4741 (7)	4742 (3)
O(4)	5735 (11)	5752 (5)	7398 (2)	7396 (1)	6558 (7)	6565 (3)
O(5)	2915 (10)	2921 (4)	5480 (1)	5481 (1)	7110 (7)	7114 (3)
O(6)	6874 (9)	6881 (3)	5840 (1)	5838 (1)	7292 (6)	7287 (2)

(b) Hydrogen atom coordinates $\times 10^3$; isotropic temperature parameter $U \times 10^3$ (Å²)

	x/a		y/b		z/c		U	
	(A)	(B)	(A)	(B)	(A)	(B)	(A)	(B)
H(1)	537	510 (9)	662	659 (1)	708	689 (6)	56	83 (10)
H(2)	-47	-24 (9)	710	702 (2)	277	272 (6)	56	84 (12)
H(3)	-157	-180 (9)	527	532 (1)	95	116 (5)	56	69 (9)
H(4)	76	76 (9)	565	568 (1)	56	69 (6)	56	65 (10)
H(5)	418	361 (9)	535	535 (1)	323	313 (5)	56	61 (9)
H(6)	185	159 (9)	497	501 (1)	361	367 (5)	56	76 (9)

(c) Anisotropic temperature parameters ($\times 10^4$) from full-matrix refinements; estimated standard deviations are in parentheses.

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)].$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	311 (7)	245 (7)	313 (7)	11 (5)	53 (6)	13 (5)
C(2)	312 (7)	293 (7)	262 (6)	-12 (5)	-7 (5)	31 (5)
C(3)	413 (9)	255 (7)	334 (7)	23 (6)	19 (6)	46 (6)
C(4)	443 (9)	228 (7)	339 (7)	-33 (6)	32 (6)	-30 (6)
C(5)	382 (8)	365 (8)	281 (7)	-28 (6)	-11 (6)	5 (6)
C(6)	350 (8)	293 (7)	297 (6)	33 (5)	15 (5)	33 (5)
C(7)	530 (11)	337 (8)	428 (10)	-121 (7)	70 (8)	-24 (7)
C(8)	519 (12)	271 (7)	538 (11)	-8 (7)	133 (9)	52 (7)
N(1)	394 (7)	245 (6)	376 (7)	-29 (5)	60 (5)	-6 (5)
N(2)	450 (8)	344 (7)	376 (7)	-31 (5)	-105 (6)	50 (6)
N(3)	623 (11)	303 (8)	417 (8)	-82 (6)	55 (7)	-93 (7)
N(4)	438 (9)	371 (7)	293 (6)	44 (5)	33 (6)	102 (6)
O(1)	1253 (18)	562 (10)	465 (9)	132 (7)	-402 (11)	-244 (11)
O(2)	353 (8)	735 (11)	578 (9)	-100 (8)	-30 (6)	-81 (6)
O(3)	851 (13)	260 (6)	780 (12)	-93 (7)	7 (10)	28 (7)
O(4)	834 (13)	510 (10)	666 (11)	-54 (8)	-186 (10)	-259 (9)
O(5)	612 (10)	472 (9)	625 (10)	243 (7)	37 (8)	36 (7)
O(6)	434 (8)	551 (10)	548 (9)	16 (7)	-91 (7)	134 (6)

Two methods of refinement were used: (a) block-diagonal least squares with the program on the Elliott 4130 computer which has been in use in this University for many years and (b) full-matrix least squares with a program supplied by Dr Sheldrick, and adapted to the Elliott Computer by Mr J. N. Low. Unfortunately, on this computer the full-matrix program takes a very long time per cycle and the number of parameters is severely limited. It was of interest therefore to compare the results from the two systems. In each case the refine-

ment began with isotropic temperature parameters and continued with anisotropic parameters. For (a), the H atom coordinates were calculated and were not refined but for (b) the coordinates were obtained from difference syntheses and refined with isotropic temperature parameters. The weighting scheme for (a) was $w^{1/2} = 1/\{1 + [(|F_o| - F^*)/G^*]^2\}^{1/2}$, where $F^* = 25$ and $G^* = 20$; for (b) $w = 1/(\sigma_{F^2} + 0.013079F^2)$.

The final values for R were (a) 0.0610 for 1858 reflexions and (b) 0.067 for 1815 reflexions. In each

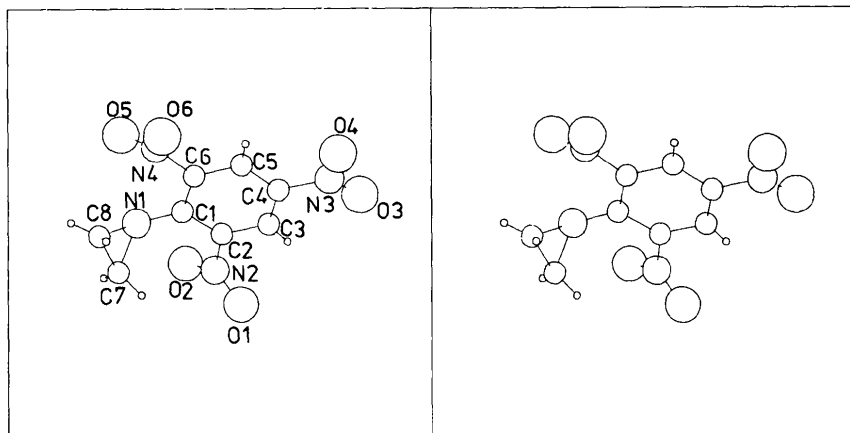


Fig. 2. Stereo diagram of the structure viewed down a.

Table 2. Bond lengths (Å) and angles (°) in 1-ethyleneimino-2,4,6-trinitrobenzene

Estimated standard deviations from full-matrix refinement are in parentheses.

C(1)—C(2)	1.418 (2)	N(2)—C(2)	1.461 (2)
C(2)—C(3)	1.381 (2)	N(2)—O(1)	1.218 (3)
C(3)—C(4)	1.370 (2)	N(2)—O(2)	1.219 (2)
C(4)—C(5)	1.381 (2)	N(3)—C(4)	1.464 (2)
C(5)—C(6)	1.383 (2)	N(3)—O(3)	1.214 (3)
C(6)—C(1)	1.401 (2)	N(3)—O(4)	1.233 (3)
C(1)—N(1)	1.377 (2)	N(4)—C(6)	1.473 (2)
N(1)—C(7)	1.463 (3)	N(4)—O(5)	1.218 (3)
C(7)—C(8)	1.469 (3)	N(4)—O(6)	1.216 (3)
C(8)—N(1)	1.469 (3)		
C(1)—C(2)—C(3)	123.6 (1)	C(5)—C(6)—N(2)	115.8 (1)
C(2)—C(3)—C(4)	118.3 (1)	C(2)—N(2)—O(1)	116.0 (2)
C(3)—C(4)—C(5)	122.0 (1)	C(2)—N(2)—O(2)	119.2 (2)
C(4)—C(5)—C(6)	118.0 (1)	O(1)—N(2)—O(2)	124.8 (2)
C(5)—C(6)—C(1)	124.0 (1)	C(5)—C(4)—N(3)	118.8 (1)
C(6)—C(1)—C(2)	114.0 (1)	C(3)—C(4)—N(3)	119.2 (1)
C(2)—C(1)—N(1)	123.7 (1)	C(4)—N(3)—O(3)	117.7 (2)
C(6)—C(1)—N(1)	122.2 (1)	C(4)—N(3)—O(4)	117.1 (2)
C(1)—N(1)—C(7)	122.7 (2)	O(3)—N(3)—O(4)	125.2 (2)
C(1)—N(1)—C(8)	122.3 (2)	C(1)—C(6)—N(4)	121.1 (1)
N(1)—C(7)—C(8)	59.5 (1)	C(3)—C(6)—N(4)	114.8 (1)
N(1)—C(8)—C(7)	59.1 (1)	C(6)—N(4)—O(5)	118.1 (2)
C(7)—N(1)—C(8)	61.3 (1)	C(6)—N(4)—O(6)	117.5 (2)
C(1)—C(2)—N(2)	120.6 (1)	O(5)—N(4)—O(6)	124.3 (2)

Table 3. Mean planes of constituent groups and angles between the benzene-ring plane and those of the substituent groups

Equations of mean planes have X parallel to a , Y to b , Z to c^* .

Group	Angle to benzene ring (°)	Mean plane
Benzene ring	—	$-0.78171X + 0.05642Y + 0.62108Z = 2.7734$
1-Ethyleneimine	127.5	$0.69266X + 0.70071Y - 0.17094Z = 11.3799$
2-Nitro	40.4	$-0.60355X + 0.68746Y + 0.40389Z = 14.5537$
4-Nitro	12.5	$-0.63664X - 0.00485Y + 0.77114Z = 2.1186$
6-Nitro	37.3	$-0.34357X + 0.48490Y + 0.80426Z = 11.8868$

Table 4. Intermolecular contacts (O...H) < 2.75 Å

	Distance (Å)	Symmetry of H atom		
O(1)...H(1)	2.242	$1 + x,$	$y,$	$1 + z$
O(2)...H(4)	2.661	$1 + x,$	$y,$	z
O(3)...H(2)	2.706	$-x,$	$y,$	$1 + z$
O(4)...H(2)	2.433	$x,$	$\frac{1}{2} - y,$	$\frac{1}{2} + z$
O(5)...H(6)	2.633	$-x,$	$-y,$	$-z$
O(6)...H(6)	2.644	$-x,$	$-y,$	$-z$

case some reflexions, which had large $F_o - F_c$ differences or were suspect for other reasons, were left out of the refinements. The tables of F_o and F_c include all observed reflexions.*

Results and discussion

The coordinates from both refinements are listed in Table 1: the agreement is excellent, in most cases well within a single standard deviation (as computed by the block-diagonal least-squares program). Bond lengths and angles are given in Table 2. Several mean planes with the interplanar angles are listed in Table 3. The mean bond length in the benzene ring is 1.389 Å and the C—H lengths given by the full-matrix refinement lie between 0.75 and 1.01 Å. One might have expected mirror symmetry in the molecule through N(1), C(1), C(4) and N(3), but the two nitro groups [N(2), N(4)] are rotated about their respective C—N bonds to dif-

ferent extents (Fig. 2). However, the shortest contacts between the *ortho* nitro groups and the ethyleneimine are the same: O(2)—N(1) = 2.807, O(5)—N(1) = 2.803 Å. Each O atom has one intermolecular contact to a H atom of less than 2.71 Å (Table 4).

There are no significant differences in bond lengths or angles between this compound and the corresponding values in 2,4-dinitro-5-ethyleneiminobenzamide (Iball, Scrimgeour & Williams, 1975), so the difference in biological activity is probably dependent on the presence of the CONH₂ group in the latter compound.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32118 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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The Crystal Structure of *syn*-5,7-Diformyltricyclo[9.4.1.1^{3,9}]heptadeca-2,4,7,9,11,13,15-heptaene

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The title compound, C₁₉H₁₆O₂ (DIAL), an open 18π-electron system, is an intermediate in the synthesis of *syn,syn*-trismethano[18]annulene and of its homologues. DIAL crystallizes in the monoclinic space group *P*2₁/*n*, with $a = 13.305$ (3), $b = 9.254$ (2), $c = 11.371$ (2) Å, $\beta = 95.89^\circ$, $Z = 4$, $D_o = 1.318$, $D_x = 1.318$ g cm⁻³. Intensities were collected on a four-circle diffractometer. The structure was solved by direct methods and refined by full-matrix least squares. The final *R* was 0.055 and the weighted *R* 0.041. The distance between H(16') and H(17'') is 1.83 Å. Steric hindrance between the methano bridges is reflected in a large deviation from planarity of the perimetral ring.

Introduction

The synthesis of polymethano-bridged annulenes is difficult because of the steric hindrance between the H atoms at the bridges. Knowledge of the geometry of these molecules is useful in understanding H · · · H non-

bonded interaction at short distances. This work is part of a project aimed at studying the relation between geometry and steric hindrance in annulenes. Geometrical analogies between DIAL and other similar compounds are evident and will be discussed. In particular we will compare the geometry of DIAL with SYNDIM