

The Crystal and Molecular Structure of 2,4-Dinitro-5-ethyleneiminobenzamide

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The structure of $C_9H_8N_4O_5$ has been determined by a direct method and refined by least-squares calculations to an R of 0.074 for 1763 counter intensities. The space group is $P\bar{1}$ with $a=9.945$, $b=8.989$, $c=7.633$ Å, $\alpha=116.53$, $\beta=99.64$, $\gamma=110.83^\circ$, $Z=2$.

Introduction

Ross & Mitchley (1950) showed that 2,4-dinitro-1-ethyleneiminobenzene, a compound containing a single alkylating function, effectively inhibited the growth of the Walker rat carcinoma 256. Examination of a series of structurally related compounds gave rise to a derivative carrying an amido substituent, 2,4-dinitro-5-ethyleneiminobenzamide (CB1954) (Fig. 1), which had a higher therapeutic index than any compound tested previously against Walker carcinoma (Cobb *et al.*, 1969). We now report the structure.

Experimental

Crystals of CB1954, in the form of large yellow prisms, were kindly supplied by Professor Ross, Chester Beatty Research Institute. Small pieces of crystal suitable for X-ray work were cut from one large crystal. Photographs showed that they were triclinic and the density indicated $Z=2$. Cell dimensions were measured from Weissenberg photographs taken with Cu $K\alpha$ radiation and confirmed by measurement on a Wooster four-circle diffractometer. Intensities were measured on the diffractometer from three crystals. The data were put on the same scale and converted to structure factors in the usual way.

Crystal data

$C_9H_8N_4O_5$, $M=252.2$, $a=9.945$ (5), $b=8.989$ (5), $c=7.633$ (5) Å, $\alpha=116.53$, $\beta=99.64$, $\gamma=110.83^\circ$, $U=570.5$ Å³, $D_m=1.591$ cm⁻³, $Z=2$, $D_x=1.593$ g cm⁻³, $\lambda=1.5418$ Å, $F(000)=260$. Space group $P\bar{1}$ (from structure determination).

Structure determination

An overall isotropic temperature factor ($U_{iso} 0.049$ Å²) was estimated from a Wilson plot, and normalized structure-factor amplitudes $|E|$ were computed with a program developed in the Oxford Chemical Crystallography Laboratory (Prout, Rollett, Carruthers & Spagna, 1974). The distribution of $|E|$ values indicated

a centrosymmetric space group. The space group was therefore assumed to be $P\bar{1}$.

450 Reflexions with $E > 1.20$ were used with *XTAN*,

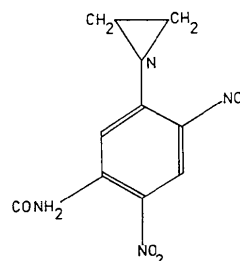


Fig. 1. 2,4-Dinitro-5-ethyleneiminobenzamide (CB1954).

Table 1. Atomic coordinates and thermal parameters

(a) Non-hydrogen atomic coordinates $\times 10^4$; estimated standard deviations are in parentheses

	x/a	y/b	z/c
O(1)	-2294 (5)	4052 (6)	7552 (7)
O(2)	-4193 (6)	1444 (8)	2931 (8)
O(3)	-3249 (6)	2715 (6)	1301 (7)
O(4)	2875 (5)	2371 (8)	2347 (7)
O(5)	932 (5)	1750 (6)	-79 (6)
N(1)	2494 (6)	2305 (6)	5719 (7)
N(2)	1587 (6)	2195 (6)	1725 (7)
N(3)	-3123 (6)	2178 (7)	2518 (8)
N(4)	-2745 (6)	1189 (7)	6973 (7)
C(1)	1205 (6)	2476 (7)	5023 (8)
C(2)	189 (7)	2505 (8)	6102 (8)
C(3)	-1206 (7)	2445 (7)	5368 (8)
C(4)	-1601 (7)	2397 (7)	3475 (9)
C(5)	-646 (7)	2407 (7)	2383 (8)
C(6)	739 (6)	2429 (7)	3133 (8)
C(7)	4123 (7)	3834 (9)	6710 (10)
C(8)	3402 (8)	3276 (10)	8013 (10)
C(9)	-2164 (7)	2628 (8)	6720 (9)

(b) Hydrogen atom coordinates $\times 10^3$; a fixed B of 5.5 Å² was used

	x/a	y/b	z/c
H(5)	-100	231	104
H(2)	58	254	733
H(71)	425	498	688
H(72)	481	360	627
H(81)	313	406	892
H(82)	367	256	852
H(41)	-271	17	633
H(42)	-323	133	775

Table 1 (cont.)

(c) Anisotropic temperature parameters ($\times 10^5$); estimated standard deviations in parentheses

$$T = \exp [-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$$

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
O(1)	1854 (56)	2678 (105)	3861 (116)	1890 (71)	3492 (129)	4048 (105)
O(2)	1022 (58)	2054 (134)	2095 (136)	3992 (106)	5757 (152)	4288 (117)
O(3)	1581 (60)	3184 (112)	1935 (128)	3121 (81)	3984 (123)	2699 (93)
O(4)	1236 (50)	3122 (124)	2591 (109)	4321 (112)	4606 (153)	2992 (95)
O(5)	1450 (54)	1857 (102)	2048 (99)	1903 (67)	2610 (99)	2006 (71)
N(1)	877 (54)	1416 (108)	1303 (115)	1578 (73)	2389 (115)	2093 (89)
N(2)	1058 (54)	1532 (112)	1899 (108)	1623 (74)	2469 (114)	2147 (85)
N(3)	1133 (60)	1986 (121)	1702 (128)	2059 (85)	2788 (134)	2420 (107)
N(4)	1249 (58)	1754 (116)	2469 (114)	1748 (76)	3038 (119)	2710 (91)
C(1)	856 (61)	1172 (121)	1361 (125)	1142 (76)	1939 (123)	1948 (97)
C(2)	1029 (66)	1490 (133)	1571 (129)	1547 (84)	2396 (127)	1928 (96)
C(3)	960 (62)	1396 (123)	1562 (125)	1271 (78)	2182 (125)	2000 (97)
C(4)	954 (63)	1475 (127)	1487 (130)	1368 (83)	2121 (133)	2020 (102)
C(5)	1044 (66)	1538 (130)	1536 (132)	1416 (83)	2252 (130)	1998 (100)
C(6)	921 (60)	1275 (124)	1600 (118)	1272 (80)	1973 (123)	1824 (92)
C(7)	810 (68)	1274 (150)	1293 (157)	1981 (107)	2597 (174)	2701 (134)
C(8)	993 (75)	1878 (165)	1174 (167)	2781 (123)	3280 (178)	2390 (128)
C(9)	1085 (65)	1602 (133)	1921 (129)	1576 (87)	2460 (136)	2215 (102)

a program based on a weighted multi-solution tangent refinement (Germain, Main & Woolfson, 1971) and developed by Sheldrick (1974). The reflexions used in the starting set were $\bar{5}24$, $\bar{4}33$ and $\bar{5}65$ to define the origin and $\bar{8}22$, $\bar{4}06$, $\bar{5}74$ as variables. Ten cycles of tangent refinement were computed and the phase set with the lowest $R(\alpha)$, 0.233, was used to calculate an E map which showed the 18 highest peaks in chemically reasonable positions. A structure-factor calculation gave an R of 0.27 for 2242 reflexions.

Refinement, initially with individual isotropic, and later anisotropic temperature parameters for non-hydrogen atoms, was by block-diagonal least-squares calculations. H atoms located from a difference map computed in the latter stages of anisotropic refinement

Table 2. Bond lengths (Å) and angles (°)

Estimated standard deviations are in parentheses.

O(1)-C(9)	1.216 (9)	N(4)-C(9)	1.332 (10)
O(2)-N(3)	1.211 (9)	C(1)-C(2)	1.407 (10)
O(3)-N(3)	1.231 (10)	C(1)-C(6)	1.416 (10)
O(4)-N(2)	1.215 (8)	C(2)-C(3)	1.378 (10)
O(5)-N(2)	1.226 (7)	C(3)-C(4)	1.409 (10)
N(1)-C(1)	1.391 (9)	C(3)-C(9)	1.513 (10)
N(1)-C(7)	1.470 (7)	C(4)-C(5)	1.365 (10)
N(1)-C(8)	1.479 (8)	C(5)-C(6)	1.390 (10)
N(2)-C(6)	1.463 (9)	C(7)-C(8)	1.477 (13)
N(3)-C(4)	1.467 (9)		
C(1)-N(1)-C(7)	124.1 (6)	C(2)-C(3)-C(9)	119.1 (6)
C(1)-N(1)-C(8)	121.1 (6)	C(4)-C(3)-C(9)	122.7 (6)
C(7)-N(1)-C(8)	60.1 (5)	N(3)-C(4)-C(3)	120.6 (6)
O(4)-N(2)-O(5)	122.7 (6)	N(3)-C(4)-C(5)	117.4 (6)
O(4)-N(2)-C(6)	119.3 (6)	C(3)-C(4)-C(5)	121.8 (7)
O(5)-N(2)-C(6)	118.0 (6)	C(4)-C(5)-C(6)	119.2 (7)
O(2)-N(3)-O(3)	123.6 (7)	N(2)-C(6)-C(1)	122.4 (6)
O(2)-N(3)-C(4)	118.3 (7)	N(2)-C(6)-C(5)	115.3 (6)
O(3)-N(3)-C(4)	118.1 (6)	C(1)-C(6)-C(5)	121.9 (6)
N(1)-C(1)-C(2)	119.6 (6)	N(1)-C(7)-C(8)	60.2 (5)
N(1)-C(1)-C(6)	123.9 (6)	N(1)-C(8)-C(7)	59.7 (5)
C(2)-C(1)-C(6)	116.2 (6)	O(1)-C(9)-N(4)	125.1 (7)
C(1)-C(2)-C(3)	123.0 (6)	O(1)-C(9)-C(3)	119.9 (7)
C(2)-C(3)-C(4)	117.9 (6)	N(4)-C(9)-C(3)	114.8 (6)

were included in the last three cycles of refinement; a fixed isotropic B of 5.5 \AA^2 was used, but their positions were not refined. The weighting scheme was

$$w = 1 / \{1 + (|F_o| - F^*) / G^*\}^{1/2}$$

with values of 10 and 15 for F^* and G^* respectively. The final R was 0.074 for 1763 reflexions.† Scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Results

The final positional and thermal parameters are given in Table 1 and bond lengths and angles in Table 2. In the benzene ring average C-C distance is 1.394 Å. The C-H bonds range from 0.862 to 0.979 Å and the N-H bonds were 0.819 and 0.844 Å. The equation of the plane of the benzene ring is

$$0.29048X + 0.79685Y + 0.52977Z = 1.6849$$

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30808 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

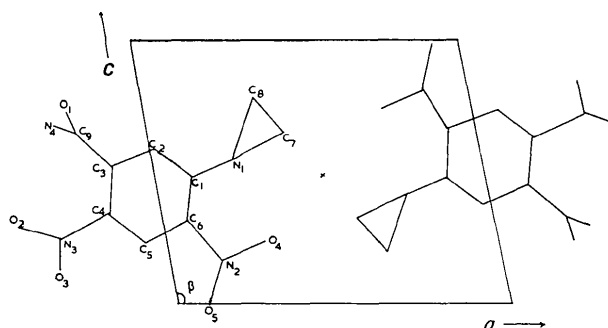


Fig. 2. Contents of unit cell showing the numbering system.

Table 3. *Angles between the benzene ring plane and the planes of the substituent groups*

Group	Angle (°)	Mean plane of group
Amide	64.7	$0.58928X - 0.19889Y + 0.78306Z = 0.902$
2-Nitro	26.3	$-0.06329X + 0.63758Y + 0.76678Z = 2.8468$
4-Nitro	13.6	$0.32142X + 0.89287Y + 0.31540Z = 1.4039$
Ethyleneimine	133.4	$0.42857X - 0.87896Y - 0.20918Z = 0.2564$

where X is parallel to \mathbf{a} , Y to \mathbf{b} and Z to \mathbf{c}^* . The four atoms attached to the ring are coplanar with the ring.

The angles between the plane of the benzene ring and the four substituent groups are given in Table 3 with the equation of the mean plane of each substituent.

The ethyleneimine ring is, within experimental error, an equilateral triangle with C–N lengths of 1.479 and 1.470 Å and C–C of 1.477 Å. The C–C bond is significantly shorter than a C–C single bond. A similar shortening has been observed in *meso*-1,4-diaziridinyl-2,3-butanediol (Gould & Pasternak, 1961) and in aziridine borane (Ringertz, 1969). The group is trigonal pyramidal at the nitrogen atom.

The average N–O distance and ONO angle are 1.221 Å and 123.2°. The average N–C(ring) distance is 1.465 Å and the average O···O distance 2.147 Å. As in many similar compounds containing nitro groups the twists (26.3 and 13.6°) are probably due to steric hindrance.

Comparison of the *o*-nitrobenzamide portion of the molecule with *o*-nitrobenzamide (Fujimori, Tsukihara, Katsube & Yamamoto, 1972) shows good agreement: ONO 124° N–O 1.226, N–C (ring) 1.465 Å. Similar good agreement is found for the *m*-dinitrobenzene portion with *m*-dinitrobenzene (Trotter, 1961, 1966) where C–N, N–O and O–N–O distances and angles are 1.47, 1.20 Å and 125° respectively.

The contents of the cell are shown in Fig. 2. The shortest intramolecular contact, 2.687 Å, is between N(1) of the ethyleneimine ring and one of the oxygens, O(4), of the nitro group adjacent to it. The shortest intermolecular distances across centres of symmetry

are C(8)···C(8), 3.206 and O(5)···O(5), 3.101 Å. Other short intermolecular distances are between O(1) in the molecule at x, y, z and O(5) and N(2) in the molecule at $\bar{x}, 1-y, 1-z$ [O(1)···O(5) = 2.963, O(1)···N(2) = 2.949 Å].

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