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Benzaldehyde 2-Nitrophenylhydrazone, $C_{13}H_{11}N_3O_2$

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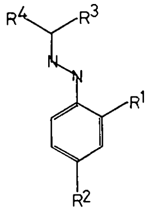
Abstract. $M_r = 241{\cdot}3$, monoclinic, $a = 16{\cdot}71$ (1), $b = 3{\cdot}904$ (4), $c = 17{\cdot}71$ (1) Å, $\beta = 99{\cdot}7$ (1)°, $U = 1138{\cdot}7$ Å^3, $D_m = 1{\cdot}41$, $D_x = 1{\cdot}41$ g cm^{-3}, $F(000) = 504$, $Z = 4$, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}06$ cm^{-1}; space group $P2_1/n$ from systematic absences $h0l$, $h + l = 2n + 1$, $0k0$, $k = 2n + 1$; room temperature, 711 independent reflections, $R = 0{\cdot}082$. The structure consists of centrosymmetric pairs of molecules bridged by two weak N—H···O intermolecular hydrogen bonds.

Introduction. We have studied the structures of a series of substituted phenylhydrazone molecules (Vickery, Willey & Drew, 1981*a*, *b*; Drew, Vickery & Willey, 1982; Drew & Willey, 1983). Among points of interest in this set are the dimensions of the hydrazone moiety and also the pattern of hydrogen bonding.

We have established that the H atom on N(7) is invariably involved in hydrogen bonding, preferably intramolecularly, to an *o*-substituted group on the aromatic ring, *e.g.* $R^1 = NO_2$, and/or to a strategic α-oxo group, *e.g.* $R^4 = {>}C{=}O$. Intermolecular hydrogen bonding between molecules (or with a solvent molecule) is a further possibility but less common. For the chosen molecule (I) we wished to evaluate molecular dimensions and packing in the absence of an α-oxo group and to investigate the possibility of some interaction involving N(7)—H(7) and the 6π electrons of the phenyl ring R^4.



(I) $R^1 = NO_2$, $R^2 = H$, $R^3 = H$, $R^4 = Ph$

(II) $R^1 = NO_2$, $R^2 = NO_2$, $R^3 = H$, $R^4 = Et$

Experimental. Title compound (I) prepared by treating benzaldehyde (1 mol) with an excess (1·5 mol) of *o*-nitrophenylhydrazine in 6M H_2SO_4. Extraction of the resulting solid with a 1:1 mixture of C_2H_5OH:CH_2Cl_2

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (×10³), *with e.s.d.'s in parentheses*

$$\bar{U} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$\bar{U}$(Å^2)
C(1)	2308 (7)	289 (36)	4736 (7)	39 (16)
C(2)	1788 (8)	−1118 (41)	4171 (7)	48 (16)
C(3)	3080 (7)	1193 (34)	4654 (7)	23 (13)
C(4)	3429 (9)	367 (33)	3990 (8)	47 (17)
C(5)	2037 (9)	−1936 (39)	3476 (7)	44 (17)
C(6)	2840 (9)	−1029 (39)	3427 (9)	62 (19)
N(7)	4190 (6)	1116 (32)	3850 (6)	41 (13)
N(8)	4399 (6)	252 (26)	3173 (5)	24 (11)
C(9)	5159 (9)	983 (38)	3142 (8)	61 (18)
C(10	5423 (9)	290 (45)	2408 (9)	75 (21)
C(11)	4994 (8)	−1171 (40)	1757 (7)	36 (17)
C(12)	5371 (10)	−1456 (46)	1135 (9)	71 (22)
C(13)	6162 (9)	−330 (39)	1120 (9)	66 (19)
C(14)	6622 (9)	896 (40)	1785 (8)	62 (17)
C(15)	6228 (9)	1458 (37)	2422 (8)	56 (17)
N(1)	3589 (6)	2840 (26)	5280 (6)	44 (12)
O(3)	4298 (6)	3679 (33)	5226 (6)	68 (15)
O(4)	3301 (6)	3708 (30)	5836 (5)	70 (14)

Table 2. *Interatomic distances* (Å) *and angles* (°)

C(1)—C(2)	1·327 (17)	C(2)—C(1)—C(3)	122·1 (13)
C(1)—C(3)	1·372 (17)	C(1)—C(2)—C(5)	120·3 (13)
C(2)—C(5)	1·401 (20)	C(1)—C(3)—C(4)	123·6 (11)
C(3)—C(4)	1·430 (20)	C(1)—C(3)—N(1)	118·3 (11)
C(3)—N(1)	1·433 (15)	C(4)—C(3)—N(1)	117·9 (11)
C(4)—C(6)	1·389 (20)	C(3)—C(4)—C(6)	109·9 (13)
C(4)—N(7)	1·368 (19)	C(3)—C(4)—N(7)	128·3 (12)
C(5)—C(6)	1·405 (22)	C(6)—C(4)—N(7)	121·4 (14)
N(7)—N(8)	1·347 (15)	C(2)—C(5)—C(6)	115·1 (12)
N(8)—C(9)	1·312 (18)	C(4)—C(6)—C(5)	128·5 (15)
C(9)—C(10)	1·467 (22)	C(4)—N(7)—N(8)	119·8 (11)
C(10)—C(11)	1·375 (19)	N(7)—N(8)—C(9)	112·4 (10)
C(10)—C(15)	1·417 (22)	N(8)—C(9)—C(10)	115·8 (12)
C(11)—C(12)	1·363 (22)	C(9)—C(10)—C(11)	128·9 (14)
C(12)—C(13)	1·398 (23)	C(9)—C(10)—C(15)	110·6 (13)
C(13)—C(14)	1·379 (19)	C(11)—C(10)—C(15)	120·5 (14)
C(14)—C(15)	1·416 (21)	C(10)—C(11)—C(12)	117·7 (14)
N(1)—O(3)	1·248 (15)	C(11)—C(12)—C(13)	123·9 (15)
N(1)—O(4)	1·215 (15)	C(12)—C(13)—C(14)	119·0 (13)
		C(13—C(14)—C(15)	117·9 (13)
		C(10)—C(15)—C(14)	120·3 (15)
		C(3)—N(1)—O(3)	120·3 (10)
		C(3)—N(1)—O(4)	119·4 (10)
		O(3)—N(1)—O(4)	120·0 (11)

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* Deceased.

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gave a yellow solution from which fine yellow needle crystals separated out on standing over a period of several hours. Composition: calculated for $C_{13}H_{11}N_3O_2$: C 64·7, H 4·6, N 17·4%; found: C 64·6, H 4·7, N 17·4%. Density measured by the method of flotation. Crystal: approximate size 0·1 × 0·5 × 0·1 mm, mounted on a Stoe STADI2 diffractometer to rotate around the b axis. Cell dimensions obtained by measurement of high-angle axial reflections. Intensity data collected *via* variable-width ω scan; background counts 20s; step-scan rate of $0{\cdot}033^\circ s^{-1}$ applied to a width of $(1{\cdot}5 + \sin\mu/\tan\theta)^\circ$; $2\theta_{\max} = 45^\circ$. Absorption and extinction corrections not applied. Standard reflections measured every 20 measurements for each layer: no significant change in intensity. 1543 independent reflections measured; 711 with $I > 2\sigma(I)$ used in subsequent calculations. The crystal was twinned with $hk0$ common. A separate scale factor was used for this zone and it subsequently refined to 0·62 (1). Several reflections in other zones had $F_o >> F_c$ because of overlap from reflections of the weaker twin and were removed from the refinement. Structure determined by direct methods using *MULTAN*80 (Main *et al.*, 1980). H atoms bonded to C were positioned in trigonal sites at 0·95 Å from the atoms to which they are bonded. H on N(7) was refined independently with no constraints. The thermal parameter refined to 0·047 (11) Å^2. Non-hydrogen atoms were refined anisotropically. Final $R = 0{\cdot}082$ ($R_w = 0{\cdot}085$). Calculations carried out using *SHELX*76 (Sheldrick, 1976) at the University of Manchester Regional Computing Centre. Scattering factors from *International Tables for X-ray Crystallography* (1974). Weighting scheme chosen to give similar values of $w\Delta^2$ over ranges of $\sin\theta/\lambda$ and F_o; $w = 1/[\sigma^2(F) + 0{\cdot}002F^2]$; $\sigma(F)$ from counting statistics. $(\Delta/\sigma)_{\max} = 0{\cdot}2$. Difference Fourier maps showed no significant peaks.

Discussion. Atomic coordinates for (I) are given in Table 1 and molecular dimensions in Table 2.*

Spectral characterization of (I) follows from δ_{NH} 11·05p.p.m. ($CDCl_3$) and ν(NH) 3290 cm^{-1} (Nujol mull) with the unique methine proton located at δ 1·54 p.p.m. ($CDCl_3$) as a sharp singlet. Aromatic-ring protons appear as a complex multiplet in the region δ 8·29 to 6·83 p.p.m. These values lie within the spectral pattern now firmly established by us for intramolecular o-$NO_2\cdots H$—N hydrogen bonding. Significantly, both the chemical shift δ_{NH} and the ν(NH) stretching mode are insensitive to solvent participation, *e.g.* δ_{NH} 11·10 p.p.m. (Me_2SO-d^6); ν(NH) 3293 cm^{-1} ($CHCl_3$) and 3289 cm^{-1} (Me_2SO) which implies an exclusive commitment to such hydrogen bonding even in the presence of strong donors.

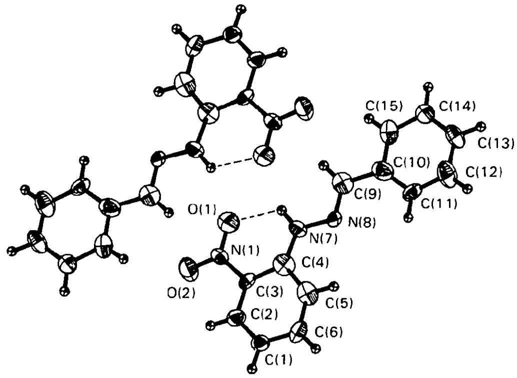

Fig. 1. The structure of (I); 50% probability ellipsoids are shown. For clarity H atoms are given a fixed radius.

The structure (Fig. 1) shows this strong intramolecular hydrogen bond with dimensions N(7)—H(7) 1·07 (7), N(7)···O(3) 2·61 (2), H(7)···O(3) 1·76 (8) Å, N(7)—H(7)···O(3) 132 (8)°. The angles C(4)—N(7)—H(7), N(8)—N(7)—H(7) are 110 (5), 130 (5)° respectively.

In addition, as shown in the figure, two such molecules form weak intermolecular hydrogen bonds around a centre of symmetry. Dimensions are H(7)···O(3') 2·52 (8), N(7)···O(3') 3·43 (1) Å, N(7)—H(7)···O(3') 143 (6)°. These dimensions suggest that the interaction can only be very weak. A consequence, however, is that the O(3)···O(3') distance is only 2·80 (2) Å, a surprisingly short distance for an O···O contact without an intervening H atom.

It is interesting that this mode of packing is also observed in (II) which is the only other derivative possessing a similar structural combination of an o-NO_2 group on the aromatic ring and an H atom rather than a carbonyl group at C(9) (Vickery, Willey & Drew, 1981). Indeed, the dimensions of the intermolecular interaction are the same in (I) and (II), within experimental error.

There are no other short distances of note in the molecule.

The dimensions of the phenylhydrazone skeleton fall into the pattern that we have established in previous structures – namely that the absence of a carbonyl group at C(9) directly hydrogen bonded to H(7) gives relatively long C(4)—N(7), short N(7)—N(8) and long N(8)—C(9) distances. Thus, average dimensions are 1·400, 1·307, 1·313 Å with such a bond and 1·36, 1·39, 1·28 Å without. [These are averaged from 18 and 9 structures respectively (Drew & Willey, 1983).] In the present instance these dimensions are 1·368 (19), 1·347 (15) and 1·312 (18) Å respectively. All values are thus within 3σ of the expected values.

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* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38943 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

As can be seen from the figure the molecule adopts the *E* configuration in which the bulkier phenyl and *o*-nitroanilino groups lie on opposite sides of the C—N double bond. This is almost certainly a consequence of steric effects and emphasizes the size aspect of the particular substituents at C(9), *e.g.* whenever these differ in steric bulk (and in the absence of any intramolecular hydrogen-bonding dictates to the contrary), it seems that the *Z* isomer is normally formed. This immediately precludes any hydrogen-bonding interactions between R^4 and H(7). Such investigations will need to be performed for compounds with $R^3 = R^4 = \text{Ph}$.

Least-squares planes show that the two phenyl rings intersect at an angle of 3·2 (1)°. The *o*-nitro group intersects the hydrazine ring at an angle of 7·7 (1)°. This relatively small angle is similar to that found in (II) and therefore must be part of the general dimer geometry. In other phenylhydrazine structures the angle of rotation of attached nitro groups can be up to 15°.

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Refinement of the Structure of *N*-Phenyl-*N'*-sulfinylhydrazine, $C_6H_6N_2OS$, at 120 (1) K with Neutron Data

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Abstract. $M_r = 154·19$, monoclinic, $P2_1/a$, $a = 10·451\ (10)$, $b = 15·561\ (18)$, $c = 8·346\ (10)$ Å, $\beta = 95·44\ (4)°$, $V = 1351·2$ Å^3, $Z = 8$, $D_x = 1·516$ Mg m^{-3}, $R = 0·056$, $R_w = 0·055$, 1789 unique reflections, $\sin\theta/\lambda \leq 0·56$ Å^{-1}. The asymmetric unit contains two identical molecules which form a dimer. They are linked by two (N)—H···O=(S) hydrogen bonds. The hydrogen bonds are bifurcated, forming a five-membered chelate ring with the intramolecular branch. The intermolecular H···O distances are 1·99 (1) and 1·95 (1) Å, respectively; the intramolecular H···O distances are 2·380 (8) Å.

Introduction. This work is part of a series of structural investigations of a compound class containing formal S^{IV}=N bond systems (Gieren, Lamm, Haddon & Kaplan, 1979; Gieren & Dederer, 1980; Dederer & Gieren, 1979). A better characterization of the S—N bonding is possible with a charge density analysis. For this purpose we undertook as a first step a neutron diffraction experiment to determine unbiased (by bonding effects) atomic positional and thermal parameters of the title compound. An advantage is the fact that the crystal structure contains two chemically identical molecules, which are crystallographically independent. An internal check of the results is provided in this way.

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Experimental. Crystal obtained from ethanolic solution, dimensions 2·78 × 2·71 × 1·00 mm. Diffractometer D10 at the Institut Laue–Langevin (Grenoble), vertically focusing Cu monochromator (200, $\lambda = 1·262$ Å), maximum flux at the sample $6·8 \times 10^6$ n cm^{-2} s^{-1}. Lattice parameters and orientation from the