packing and the presence or absence of hydrogen bonds.

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Structures of (*E*)-Benzaldehyde Phenylhydrazone, $C_{13}H_{12}N_2$ (1), and (*E*)-Benzaldehyde 4′-Nitrophenylhydrazone, $C_{13}H_{11}N_3O_2$ (2)

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Abstract. (1) $M_r = 196{\cdot}3$, monoclinic, $P2_1/c$, $a = 6{\cdot}053\,(7)$, $b = 17{\cdot}643\,(13)$, $c = 15{\cdot}207\,(15)$ Å, $\beta = 92{\cdot}2\,(1)°$, $V = 1622{\cdot}8$ Å^3, $Z = 6$, $D_m = 1{\cdot}20\,(1)$, $D_x = 1{\cdot}20$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}78$ cm^{-1}, $F(000) = 624$, room temperature, $R = 0{\cdot}077$ for 1069 independent reflections. The structure consists of an ordered molecule in a general position and a molecule disordered around a crystallographic centre of symmetry. Both molecules take up the *E* conformation; in the ordered molecule the angle between the two benzene rings is 8·1 (1)°. (2) $M_r = 241{\cdot}2$, monoclinic, *Cc*, $a = 6{\cdot}049\,(5)$, $b = 23{\cdot}320\,(11)$, $c = 8{\cdot}506\,(11)$ Å, $\beta = 96{\cdot}8\,(1)°$, $V = 1191{\cdot}4$ Å^3, $Z = 4$, $D_m = 1{\cdot}34\,(1)$, $D_x = 1{\cdot}34$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 1{\cdot}15$ cm^{-1}, $F(000) = 504$, room temperature, $R = 0{\cdot}071$ for 789 independent reflections. The molecule takes up the *E* conformation. There is a weak intermolecular hydrogen bond between the NH group and the *p*-nitro group, N···O 3·10 (1) Å.

Introduction. In a series of papers (Willey & Drew, 1985 and references therein), we have studied the structures of various phenylhydrazone derivatives. One of the main points to emerge is that the –NH group will participate in hydrogen bonding whenever possible, either intramolecular (for preference) or intermolecular (Willey & Drew, 1983; Drew, Vickery & Willey, 1984).

We now report the structures of the title compounds (1) and (2), which will provide two different arrangements. (1) can have no hydrogen bonding while (2) only contains a *p*-NO_2 group for possible intermolecular interaction with the NH group. These structures will also confirm the particular structural type (*E v Z*) adopted in such benzaldehyde derivatives.

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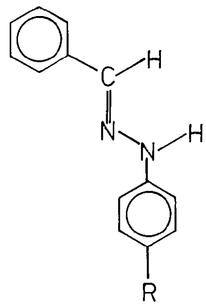

(1) R=H

(2) R = NO$_2$

Experimental. (1) and (2) were prepared by standard procedures (Vogel, 1978) involving the treatment of benzaldehyde with the appropriate phenylhydrazine under strongly acidic conditions. Each gave orange needle crystals following recrystallization from 50/50 (*v*/*v*) ethanol/dichloromethane solutions. Suitable crystals of (1) and (2) placed in Lindemann tubes. D_m by flotation using CCl$_4$/ligroin mixtures. Precession photographs established preliminary cell constants and space groups. Crystals, approximate sizes 0·3 × 0·5 × 0·2 (1), 0·5 × 0·3 × 0·3 (2) mm mounted on Stoe STADI2 diffractometer both to rotate about **a**. Cell dimensions obtained by measurement of *ca* 20 high-angle axial reflections. Intensity data collected *via* variable-width scans, background counts 20s, scan rate 0·033°s^{-1}, scan range $(1{\cdot}5 + \sin\mu/\tan\theta)^\circ$. Absorption and extinction corrections not applied. Standard reflections measured every 20 measurements for each layer; no significant change in intensity. 3132 (1) and 2179 (2) reflections measured, $2\theta_{max}$ 50°. 1069 and 789 independent data with $I > 2\sigma(I)$, index range: *h* 0/6, *k* 0/20, *l* −17/17 (1); *h* 0/6, *k* 0/29, *l* −11/10 (2); refinement to *R* 0·077, 0·071, respectively. Both structures solved by direct methods using *MULTAN*80 (Main *et al.*, 1980). Structure of (1) showed one molecule in a general position and one disordered over a centre of symmetry. The disordered molecule is shown in Fig. 1. The two phenyl rings in the molecule were symmetrically placed with regard to the centre of symmetry and atoms were refined with occupancy 1·0. The three atoms linking the two rings were assigned half occupancy and scattering factors of $\frac{1}{2}$(C+N), N, $\frac{1}{2}$(C+N) respectively. H atoms were only included when bonded to an ordered C atom, *i.e.* on the four carbon atoms in the benzene ring. Structure determination of (2) was straightforward. For ordered molecule in (1) and for (2), H atoms bonded to C were fixed in calculated positions and their thermal parameters refined. H atoms bonded to N(7) were allowed to refine independently. Non-hydrogen atoms were refined anisotropically [apart from those in disordered molecule in (1), which were treated isotropically] by full-matrix least squares. For both crystals, refinement on *F* magnitudes with $w = 1/[\sigma(F) + 0{\cdot}003F^2]$. Scattering factors and dispersion corrections from *International Tables for X-ray Crystallography* (1974). $\Delta\rho$ in final difference-Fourier maps within 0·32 and −0·24 e Å^{-3} in (1), within 0·44 and −0·37 e Å^{-3} in (2). In final cycles of refinement all shifts $\leq 0{\cdot}1\sigma$. Calculations were carried out using *SHELX*76 (Sheldrick, 1976) at the University of Manchester Regional Computer Centre.

Final coordinates are given in Tables 1 and 2.* Molecular dimensions are in Tables 3 and 4.

Discussion. In (1) the absence of —NO$_2$ substituents automatically nullifies the normal hydrogen-bonding requirements (inter–intra) and allows a reference set of parameters for a 'naked' NH environment (N—H···N hydrogen bonding is geometrically impossible in this case). However, the very absence of hydrogen bonding is no doubt the cause of the disordered structure that occurs (see below). Steric access to solvent molecules is unhindered and the frequency difference in ν(NH) between 3301 cm^{-1} (Me$_2$SO) and 3313 cm^{-1} (Nujol) indicates the formation of some weak Me$_2$SO···HN hydrogen bonding in solution. Solvent participation is also reflected by ^{1}H NMR measurements where there is a discernible low-field shift δ_{NH} 7·51→7·99 on changing from a non-polar to a polar medium. The unique methine singlet at δ_H 1·56 remains effectively unchanged, however.

Much the same spectral pattern is observed for (2) but with less conspicuous shifts of $\nu(NH)_{mull}$ 3265→ $\nu(NH)_{Me_2SO}$ 3258 cm^{-1} and δ_{NH} 8·06→8·19 on changing from CDCl$_3$ to Me$_2$SO-d^6 solutions. Compared with the N—H···O$_2$N bifurcated bonds of the *o*-NO$_2$ derivative, benzaldehyde 2-nitrophenylhydrazone (Drew, Vickery & Willey, 1984), with δ_{NH} 11·05 (CDCl$_3$), these solvent interactions are predictably much weaker.

The structural and conformational features of disordered (1), ordered (1) and (2) are shown in Figs. 1,2 and 3 respectively. None contains any solvent of crystallization and in each case the *E* isomer is confirmed; presumably steric requirements are minimized with the bulkier phenyl and anilino groups lying across the C=N double bond.

For the ordered molecule of (1) (Fig. 2), the two benzene rings intersect at an angle of 8·1 (1)°. In the disordered molecule these two rings are perforce parallel owing to the crystallographic symmetry. It can be no coincidence that of the *ca* 25 structures of various derivatives of phenylhydrazones we have investigated this structure is the only one disordered and also the only one without any hydrogen bonding.

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* 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 42113 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure of (2) is shown in Fig. 3. This has the potential for intermolecular hydrogen bonding and there is a weak interaction between N(7) and O(1) ($-1+x$, $-y$, $0{\cdot}5+z$) of 3·10 (1) Å [H(7)···O(1) 2·40 (14) Å, N(7)—H(7)···O(1) 157 (5)°]. The existence of hydrogen bonding confirms the view that the participation of the —NH group in hydrogen bonding is the predominant force in determining the configuration in the solid state and in solution. In general the —NH group is preferentially involved in intramolecular hydrogen bonding. However, in the absence of suitably electronegative atoms in adjacent sites, the —NH group will hydrogen bond with neighbouring molecules or with included solvent molecules.

As shown in Fig. 3 there is also a C(3)—H(3)···O(2) contact alongside the N(7)—H(7)···O(1) interaction, C(3)···O(2) 3·40 (1) Å, H(3)···O(2) 2·65 (12) Å, C(3)—H(3)···O(2) 153 (3)°.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for* (1) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}†
C(1)	−1185 (15)	8797 (5)	4708 (7)	93 (12)
C(2)	546 (16)	8780 (5)	5317 (6)	88 (12)
C(3)	2335 (15)	8312 (4)	5172 (6)	72 (10)
C(4)	2378 (14)	7857 (4)	4438 (5)	72 (10)
C(5)	606 (14)	7880 (5)	3828 (6)	65 (11)
C(6)	−1127 (14)	8363 (5)	3967 (6)	84 (11)
N(7)	4230 (12)	7358 (4)	4348 (5)	87 (10)
N(8)	4335 (12)	6897 (4)	3659 (5)	73 (9)
C(9)	6170 (13)	6504 (4)	3625 (5)	60 (9)
C(10)	6454 (13)	5973 (4)	2940 (5)	74 (10)
C(11)	8461 (13)	5578 (5)	2925 (6)	77 (11)
C(12)	8748 (16)	5043 (5)	2293 (7)	96 (12)
C(13)	7123 (16)	4863 (5)	1671 (6)	94 (12)
C(14)	5180 (14)	5270 (5)	1687 (6)	79 (11)
C(15)	4840 (13)	5809 (4)	2314 (5)	71 (10)
C(41)	2802 (14)	4285 (5)	4127 (5)	79 (2)‡
C(42)	1029 (14)	3780 (5)	4223 (5)	79 (2)‡
C(43)	1150 (16)	3071 (5)	3861 (6)	93 (3)‡
C(44)	2937 (17)	2843 (6)	3390 (6)	99 (3)‡
C(45)	4637 (16)	3342 (5)	3296 (6)	91 (3)‡
C(46)	4603 (15)	4045 (5)	3653 (6)	93 (3)‡
CN(47)	2515 (24)	4974 (8)	4481 (9)	74 (4)‡
N(48)	625 (20)	5198 (7)	4929 (9)	76 (4)‡
CN(49)	−575 (21)	4086 (7)	4778 (8)	64 (4)‡

† $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j$.

‡ Refined isotropic temperature factor for atom of disordered molecule.

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *for* (2) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}†
C(1)	676 (15)	300 (3)	383 (12)	70 (7)
C(2)	230 (15)	879 (3)	168 (11)	84 (8)
C(3)	−1437 (14)	1139 (3)	825 (11)	79 (7)
C(4)	−2742 (14)	815 (3)	1763 (11)	68 (7)
C(5)	−2279 (15)	235 (3)	2014 (12)	85 (8)
C(6)	−622 (15)	−23 (3)	1323 (12)	80 (8)
N(1)	2383 (14)	34 (3)	−353 (10)	90 (8)
O(1)	2654 (15)	−490 (3)	−209 (11)	128 (8)
O(2)	3535 (14)	327 (3)	−1128 (12)	112 (7)
N(7)	−4427	1060 (3)	2463	90 (7)
N(8)	−4965 (13)	1617 (2)	2153 (10)	80 (6)
C(9)	−6666 (15)	1817 (3)	2726 (12)	87 (8)
C(10)	−7393 (14)	2403 (3)	2409 (11)	75 (7)
C(11)	−6066 (16)	2792 (4)	1658 (13)	102 (9)
C(12)	−6765 (20)	3341 (4)	1296 (16)	122 (12)
C(13)	−8726 (20)	3528 (5)	1727 (16)	105 (12)
C(14)	−10012 (19)	3179 (5)	2463 (16)	117 (14)
C(15)	−9353 (17)	2599 (4)	2843 (16)	107 (11)

† $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j$.

Table 3. *Molecular dimensions of* (1) (Å, °)

C(1)—C(2)	1·372 (12)	C(12)—C(13)	1·376 (12)
C(1)—C(6)	1·363 (11)	C(13)—C(14)	1·379 (10)
C(2)—C(3)	1·386 (11)	C(14)—C(15)	1·367 (10)
C(3)—C(4)	1·376 (10)	C(41)—C(42)	1·407 (11)
C(4)—C(5)	1·392 (11)	C(41)—C(46)	1·395 (11)
C(4)—N(7)	1·435 (10)	C(41)—CN(47)	1·344 (15)
C(5)—C(6)	1·374 (10)	C(42)—C(43)	1·370 (11)
N(7)—N(8)	1·330 (8)	C(42)—CN(49)	1·418 (13)
N(8)—C(9)	1·312 (9)	C(43)—C(44)	1·380 (11)
C(9)—C(10)	1·416 (10)	C(44)—C(45)	1·366 (11)
C(10)—C(11)	1·401 (10)	C(45)—C(46)	1·354 (10)
C(10)—C(15)	1·369 (10)	CN(47)—N(48)	1·410 (16)
C(11)—C(12)	1·362 (11)		
C(2)—C(1)—C(6)	120·1 (8)	C(11)—C(12)—C(13)	122·5 (9)
C(1)—C(2)—C(3)	119·1 (8)	C(12)—C(13)—C(14)	117·1 (9)
C(2)—C(3)—C(4)	121·0 (8)	C(13)—C(14)—C(15)	121·7 (8)
C(3)—C(4)—C(5)	119·1 (8)	C(10)—C(15)—C(14)	120·6 (7)
C(3)—C(4)—N(7)	118·4 (8)	C(42)—C(41)—C(46)	118·4 (8)
C(5)—C(4)—N(7)	122·6 (8)	C(42)—C(41)—CN(47)	114·9 (10)
C(4)—C(5)—C(6)	119·2 (8)	C(46)—C(41)—CN(47)	126·7 (10)
C(1)—C(6)—C(5)	121·3 (8)	C(41)—C(42)—C(43)	118·9 (8)
C(4)—N(7)—N(8)	120·8 (7)	C(41)—C(42)—CN(49)	111·3 (9)
N(7)—N(8)—C(9)	114·9 (7)	C(43)—C(42)—CN(49)	129·5 (9)
N(8)—C(9)—C(10)	120·4 (7)	C(42)—C(43)—C(44)	122·0 (9)
C(9)—C(10)—C(11)	118·1 (8)	C(43)—C(44)—C(45)	118·4 (9)
C(9)—C(10)—C(15)	123·2 (7)	C(44)—C(45)—C(46)	121·7 (9)
C(11)—C(10)—C(15)	118·6 (8)	C(41)—C(46)—C(45)	120·6 (9)
C(10)—C(11)—C(12)	119·4 (8)	C(41)—CN(47)—N(48)	124·5 (12)

Table 4. *Molecular dimensions of* (2) (Å, °)

C(1)—C(2)	1·385 (10)	N(7)—N(8)	1·358 (8)
C(1)—C(6)	1·405 (10)	N(8)—C(9)	1·278 (8)
C(1)—N(1)	1·412 (10)	C(9)—C(10)	1·450 (11)
C(2)—C(3)	1·352 (9)	C(10)—C(11)	1·414 (11)
C(3)—C(4)	1·407 (10)	C(10)—C(15)	1·362 (10)
C(4)—C(5)	1·393 (10)	C(11)—C(12)	1·372 (13)
C(4)—N(7)	1·364 (8)	C(12)—C(13)	1·355 (16)
C(5)—C(6)	1·361 (10)	C(13)—C(14)	1·333 (16)
N(1)—O(1)	1·237 (8)	C(14)—C(15)	1·436 (16)
N(1)—O(2)	1·224 (9)		
C(2)—C(1)—C(6)	119·0 (6)	O(1)—N(1)—O(2)	121·8 (6)
C(2)—C(1)—N(1)	120·7 (6)	C(4)—N(7)—N(8)	119·3 (6)
C(6)—C(1)—N(1)	120·2 (6)	N(7)—N(8)—C(9)	117·5 (5)
C(1)—C(2)—C(3)	121·7 (6)	N(8)—C(9)—C(10)	120·9 (6)
C(2)—C(3)—C(4)	119·4 (6)	C(9)—C(10)—C(11)	120·9 (6)
C(3)—C(4)—C(5)	119·4 (5)	C(9)—C(10)—C(15)	121·4 (7)
C(3)—C(4)—N(7)	121·5 (6)	C(11)—C(10)—C(15)	117·8 (7)
C(5)—C(4)—N(7)	119·1 (6)	C(10)—C(11)—C(12)	121·6 (7)
C(4)—C(5)—C(6)	120·6 (6)	C(11)—C(12)—C(13)	119·8 (10)
C(1)—C(6)—C(5)	119·9 (6)	C(12)—C(13)—C(14)	120·6 (9)
C(1)—N(1)—O(1)	119·1 (7)	C(13)—C(14)—C(15)	121·3 (8)
C(1)—N(1)—O(2)	119·1 (6)	C(10)—C(15)—C(14)	118·9 (9)

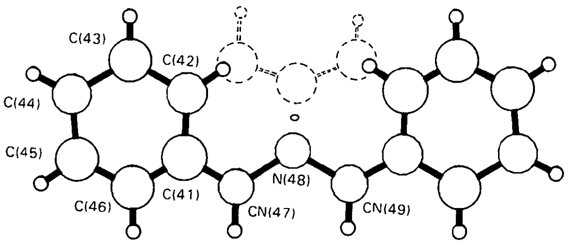

Fig. 1. The disordered molecule in (1) with isotropic thermal parameters drawn at the 50% probability level. Full lines and circles represent atoms of one distinct molecule. Dotted lines and circles complete the disordered model that was refined around the centre of symmetry indicated by a small circle.

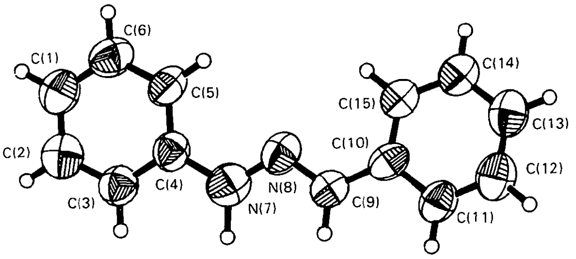

Fig. 2. The ordered molecule of (1) showing the atomic numbering scheme.

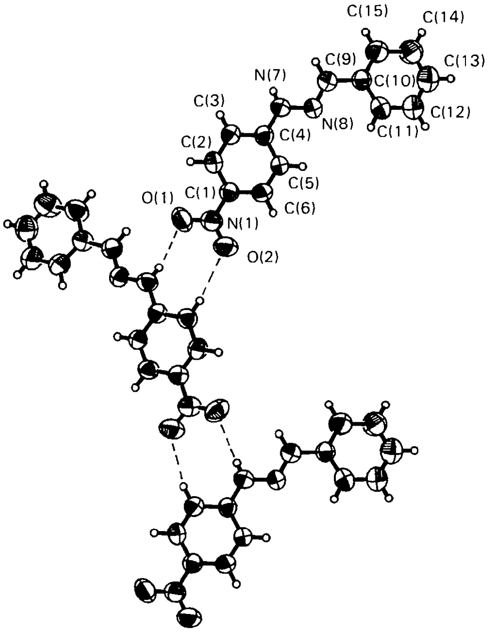

Fig. 3. The structure of (2). Three molecules are shown illustrating the weak intermolecular hydrogen bonding between molecules x, y, z and $-1+x$, $-y$, $0{\cdot}5+z$. Thermal ellipsoids are at the 50% probability level.

An interesting comparison can be made with the structures of (*E*,*E*)-2,3-butanedione bis(4′-nitrophenylhydrazone) (3) and (*E*)-2,3-butanedione 4′-nitrophenylhydrazone (4) (Willey & Drew, 1983), both of which contain *p*-NO_2 groups similar to (2). Conspicuously neither (3) nor (4) forms *p*-$NO_2\cdots HN$ hydrogen bonds; *viz.* in (3) a solvent molecule (dimethylformamide) is hydrogen bonded to each NH group and in (4) the NH group forms a weak intramolecular hydrogen bond to a dione group. This indicates that interaction with the *p*-NO_2 group is the least desirable hydrogen bond and is observed only when no other interaction is possible. A similar interaction is observed in acetone *p*-nitrophenylhydrazone (Menczel, Samay & Simon, 1972).

In previous work we have established that the dimensions of the phenylhydrazone skeleton are very dependent upon the presence of intramolecular hydrogen bonding between a carbonyl oxygen and N(7). With such a bond, the C(4)—N(7), N(7)—N(8) and N(8)—C(9) bond lengths average 1·400, 1·307, 1·313 Å and without such a bond 1·36, 1·39, 1·28 Å. (These are taken from 18 and nine structures, respectively.) In (1) the bond lengths are 1·435 (10), 1·330 (8), 1·312 (9) Å (ignoring the disordered molecule) and in (2) 1·364 (8), 1·358 (8), 1·278 (8) Å. The dimensions in (1) do not fit in with this pattern. However, in all these examples the N—H group participated in some kind of hydrogen bonding and it may be that the values in (1) represent a third category. The values in (2) are more representative of the second category, that is molecules with no C=O to H—N hydrogen bonding.

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