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α-(4-Methyl-2-nitrophenylhydrazono)acetanilide, $C_{15}H_{14}N_4O_3$

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Abstract. $M_r = 298{\cdot}3$, monoclinic, $P2_1/a$, $a = 23{\cdot}344\,(15)$, $b = 5{\cdot}905\,(8)$, $c = 12{\cdot}164\,(12)$ Å, $\beta = 121{\cdot}07\,(10)^\circ$, $V = 1436{\cdot}21$ Å^3, $Z = 4$, $D_x = 1{\cdot}380$, $D_m = 1{\cdot}378$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}84$ mm^{-1}, $F(000) = 624$, $T = 293$ K. Final $R = 0{\cdot}045$ for 1183 observed film reflexions. The almost planar molecules exist as hydrogen-bonded dimers with also one internal hydrogen bond per molecule. The C atom of acetanilide to which the azo compound couples is bonded trigonally, transferring its H atom elsewhere; bond lengths indicate this H to be attached to an N of the diazo group.

Introduction. This title compound was obtained as an unwelcome impurity during the coupling of diazotized 2-nitro-*p*-toluidine to acetoacetanilide at 328 K. In this reaction the acetyl group became detached and the product was precipitated as large red crystals. The crystal-structure determination was undertaken in order to characterize this previously unknown substance. A preliminary mention of the crystal data is given by Brown (1967).

Experimental. Sample prepared by J. Mitchell of Imperial Chemical Industries Limited (Organics Division); purified acicular crystals grown from acetone solution, m.p. 476 (5) K; found: C 60·7, H 4·8, N 18·0%; required for $C_{15}H_{14}N_4O_3$: C 60·4, H 4·7, N 18·8%. D_m measured by flotation in aqueous NaI solution. Unit-cell dimensions obtained initially from rotation photographs and more accurately from $\alpha_1\alpha_2$ separations of high-angle reflexions on Weissenberg photographs. Crystal 4·0 × 0·15 × 0·05 mm used for intensities. Stoe integrating Weissenberg camera; multiple-film photographs taken of levels $h0l \rightarrow h3l$ and $hk0$; visual estimations using calibrated scale; interlayer scaling by correlation of common reflexions and comparison of Wilson plots. No corrections for absorption or extinction except for $F(41\bar{3})$. 2090 measured reflexions, 907 with $I < 3\sigma(I)$; index range of observed reflexions: $h = 0$ to 28, $k = 0$ to 7, $l = -14$ to 13. Structure solved by manual enhancement of $\sum_2$ relationships. Least-squares refinement using $\sqrt{w} = 1/F_o$ with B_{iso} initially and B_{ij} finally until shifts $<0{\cdot}3\sigma$. H parameters obtained from difference Fourier sections included with $B_{\text{iso}} = 6{\cdot}0$ Å^2 but not refined. $R = 0{\cdot}045$, $R_w = 0{\cdot}094$. Final $\Delta\rho$ excursions $= \pm 0{\cdot}1$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1962). NRC computer programs used (Ahmed, Hall, Pippy & Huber, 1970) implemented on the ICL 1905E at the London Polytechnics Computer Centre, and on our own DEC-10.

Discussion. The final positional and equivalent isotropic temperature parameters are listed in Table 1.* Numbering of the atoms and the packing arrangement of the molecules in the unit cell are shown in Fig. 1. Bond lengths and interbond angles are given in Table 2.

The molecule is almost planar, the average distance of the 22 non-H atoms out of the mean plane being 0·046 Å (r.m.s. deviation 0·057 Å) with a maximum displacement of 0·111 (4) Å for C(1). Despite this planarity, this substance does not show pigmentary properties such as those possessed by groups of azo dyes which have, for example, an acetyl group substituted on C(8), the atom to which coupling has occurred. C(8) is trigonally bonded, confirming that C(8)—N(3) is formally a double bond [1·284 (5) Å], and N(2)—N(3) is only slightly shorter [1·334 (4) Å] than a single bond. Both of these agree with the corresponding dimensions in the dibromo derivative (Brown, 1967) where the lengths are 1·29 and 1·36 Å

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38816 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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respectively, adopting the hydrazone tautomeric form in preference to the hydroxyazo form (Prendergrass, Paul & Curtin, 1972). It seems that the hydrazone tautomer is the more common arrangement in coupled azo compounds although several stereochemical isomers are known (Fig. 2), exhibiting *cis–trans* differences at appropriate places in the molecules. The other dimensions of the molecule appear to have normal values.

The hydrogen-bond system is shown in Fig. 1. Molecules are linked in pairs through H(14), and there is one internal hydrogen bond in each molecule through H(13). The dimeric molecular pairs are coplanar, lying approximately in $(41\bar{3})$.

Table 1. *Final atomic parameters with e.s.d.'s*

	x	y	z	B_{eq}(Å^2)*
C(1)	0·1345 (2)	−0·2418 (7)	0·5630 (3)	4·95 (8)
C(2)	0·2025 (2)	−0·1281 (6)	0·6262 (3)	3·68 (6)
C(3)	0·2568 (2)	−0·2272 (6)	0·7297 (3)	4·06 (6)
C(4)	0·3201 (2)	−0·1250 (7)	0·7874 (3)	3·70 (6)
C(5)	0·3303 (2)	0·0778 (6)	0·7416 (3)	2·95 (6)
C(6)	0·2731 (2)	0·1814 (6)	0·6365 (3)	3·45 (6)
C(7)	0·2119 (2)	0·0761 (6)	0·5814 (3)	3·56 (6)
C(8)	0·4597 (2)	0·4496 (6)	0·7978 (3)	3·67 (6)
C(9)	0·4749 (2)	0·6576 (6)	0·7549 (3)	3·47 (6)
C(10)	0·5762 (2)	0·8910 (6)	0·8131 (3)	3·36 (6)
C(11)	0·6446 (2)	0·9049 (7)	0·9049 (4)	4·04 (7)
C(12)	0·6832 (2)	1·0776 (8)	0·8987 (4)	5·28 (8)
C(13)	0·6548 (2)	1·2399 (7)	0·8046 (4)	5·90 (9)
C(14)	0·5865 (2)	1·2248 (8)	0·7117 (4)	5·76 (10)
C(15)	0·5478 (2)	1·0508 (7)	0·7163 (4)	4·68 (8)
N(1)	0·3744 (1)	−0·2410 (5)	0·8970 (2)	3·93 (6)
N(2)	0·3920 (1)	0·1840 (5)	0·7940 (2)	3·59 (5)
N(3)	0·3994 (1)	0·3769 (5)	0·7456 (2)	3·62 (5)
N(4)	0·5422 (1)	0·7094 (5)	0·8262 (3)	3·94 (5)
O(1)	0·3620 (1)	−0·4153 (5)	0·9353 (2)	4·94 (5)
O(2)	0·4316 (1)	−0·1581 (5)	0·9492 (2)	4·45 (5)
O(3)	0·4338 (1)	0·7760 (5)	0·6672 (3)	5·28 (5)

$$* B_{eq} = \tfrac{4}{3}(\beta_{11}/a^{*2} + \beta_{22}/b^{*2} + \beta_{33}/c^{*2}).$$

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

C(1)–C(2)	1·517 (6)	C(8)–C(9)	1·448 (5)
C(2)–C(3)	1·374 (5)	C(9)–O(3)	1·221 (4)
C(2)–C(7)	1·386 (5)	C(9)–N(4)	1·380 (5)
C(3)–C(4)	1·402 (6)	N(4)–C(10)	1·392 (5)
C(4)–C(5)	1·392 (5)	C(10)–C(11)	1·402 (6)
C(4)–N(1)	1·452 (4)	C(10)–C(15)	1·382 (5)
N(1)–O(1)	1·225 (4)	C(11)–C(12)	1·389 (7)
N(1)–O(2)	1·246 (4)	C(12)–C(13)	1·373 (6)
C(5)–C(6)	1·425 (5)	C(13)–C(14)	1·403 (8)
C(6)–C(7)	1·374 (5)	C(14)–C(15)	1·389 (7)
C(5)–N(2)	1·388 (5)	N(2)[H(13)]···O(2)	2·909 (3)
N(2)–N(3)	1·334 (4)	N(4)[H(14)]···O(1^{i})	3·119 (4)
N(3)–C(8)	1·284 (5)		
C(1)–C(2)–C(3)	120·3 (3)	N(4)–C(9)–O(3)	123·3 (3)
C(1)–C(2)–C(7)	121·5 (3)	C(11)–C(10)–C(15)	119·2 (4)
C(3)–C(2)–C(7)	118·2 (3)	C(11)–C(10)–N(4)	115·9 (3)
C(2)–C(3)–C(4)	120·7 (4)	C(15)–C(10)–N(4)	124·9 (3)
C(3)–C(4)–C(5)	121·5 (3)	C(10)–C(11)–C(12)	120·3 (4)
C(4)–C(5)–C(6)	117·0 (3)	C(11)–C(12)–C(13)	120·6 (4)
C(3)–C(4)–N(1)	116·8 (3)	C(12)–C(13)–C(14)	119·1 (4)
C(5)–C(4)–N(1)	121·6 (3)	C(13)–C(14)–C(15)	120·5 (4)
C(4)–C(5)–N(2)	123·8 (3)	C(10)–C(15)–C(14)	120·2 (4)
C(6)–C(5)–N(2)	119·2 (3)	C(4)–N(1)–O(1)	118·7 (3)
C(5)–C(6)–C(7)	120·0 (3)	C(4)–N(1)–O(2)	118·8 (3)
C(2)–C(7)–C(6)	122·5 (3)	O(1)–N(1)–O(2)	122·6 (3)
C(9)–C(8)–N(3)	121·1 (3)	C(5)–N(2)–N(3)	121·5 (3)
C(8)–C(9)–N(4)	111·9 (3)	C(8)–N(3)–N(2)	115·2 (3)
C(8)–C(9)–O(3)	124·8 (3)	C(9)–N(4)–C(10)	129·0 (3)

Symmetry code: (i) $1-x, -y, 2-z$.

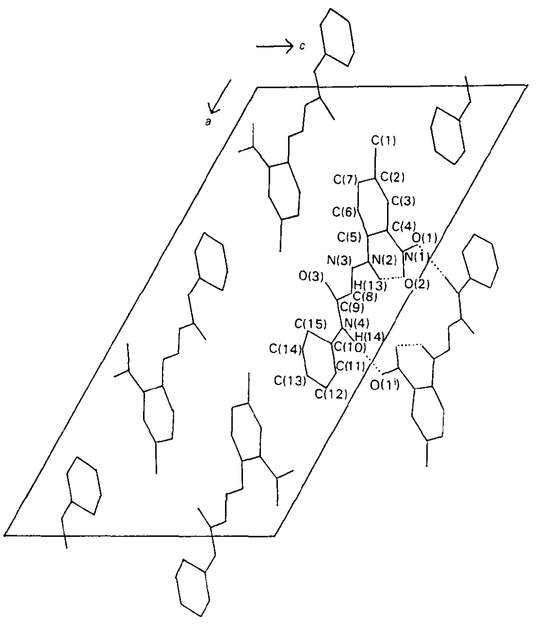

Fig. 1. Projection of the unit cell on (010) showing numbering of atoms, packing of molecules and hydrogen-bond system.

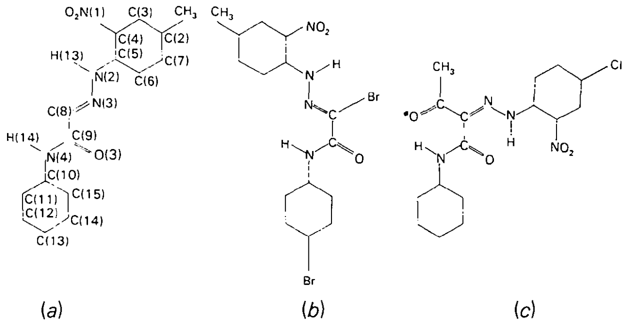

Fig. 2. Stereochemical relationship of the title compound to that of two analogous molecules: (*a*) Title compound. (*b*) Dibromo derivative (Brown, 1967). (*c*) Chloro- and acetyl-substituted derivative (Mez, 1968).

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