

Table 4. *Hydrogen-bond parameters in (II)*

	D...A(Å)	H...A(Å)	D-H(Å)	H-D...A(°)	D-H...A(°)
W(1)-HW(11)...W(3)	2.835 (2)	2.07 (3)	0.76 (3)	4 (2)	174 (3)
W(1)-HW(12)...W(3)	2.920 (2)	1.91 (5)	1.03 (5)	8 (2)	168 (4)
W(2)-HW(21)...O(1)	2.819 (2)	1.97 (3)	0.85 (3)	2 (2)	177 (3)
W(2)-HW(22)...W(1 ^b)	2.865 (2)	1.87 (5)	1.02 (5)	9 (3)	166 (4)
W(3 ^b)-HW(31)...W(2)	2.824 (2)	1.94 (3)	0.91 (3)	12 (2)	163 (3)
W(3 ^b)-HW(32)...O(1)	2.824 (2)	2.03 (3)	0.79 (3)	0 (3)	180 (3)

Symmetry code: none x, y, z ; (i) $2-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, 1+y, z$; (iv) $1-x, -y, 1-z$.

W(1) deviates by 0.215 (1) Å from the plane through its three hydrogen-bonded neighbours, W(2) deviates 0.781 (1) Å and W(3) 2.119 (2) Å. [The illustrations were made with ORTEPII (Johnson 1976).]

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N,N'-Bis(2-methylphenyl)guanidine, C₁₅H₁₇N₃

BY C. J. BROWN AND D. J. GASH

Department of Metallurgy and Materials Engineering, City of London Polytechnic, Central House, Whitechapel High Street, London E1 7PF, England

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Abstract. $M_r = 239.32$, orthorhombic, *Pcab* {non-standard setting of *Pbca*, equivalent positions $\pm[x, y, z; \frac{1}{2}-x, y, \frac{1}{2}+z; \frac{1}{2}+x, \frac{1}{2}-y, z; x, \frac{1}{2}+y, \frac{1}{2}-z]$ }, $a = 21.558$ (12), $b = 13.588$ (10), $c = 8.980$ (5) Å, $V = 2630.51$ Å³, $Z = 8$, $D_m = 1.218$ (1), $D_x = 1.208$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.62$ mm⁻¹, $F(000) = 1024$, $T = 295$ K, $R = 0.053$ for 1245 observed [$I > 3\sigma(I)$] reflexions. The material was supplied by Imperial Chemical Industries Limited (Organics Division) under the trade name 'Vulcafor DOTG'. Molecules in the crystal are linked in chains along *c* by N-H...N hydrogen bonds.

Introduction. The title compound is widely used as an accelerator in the curing of rubber and, as there is a scarcity of structural information on guanidine compounds, the structure determination was undertaken to improve our understanding of the industrial process.

Experimental. Recrystallized from ethanol, colourless acicular crystals, m.p. 451 K; density by flotation in NaI solution; crystal $2.0 \times 0.5 \times 0.2$ mm used for obtaining intensities by the multiple-film technique, Stoe Weissenberg camera, layers $hk0 \rightarrow hk7$, and $h0l$ which was used for inter-layer scaling; lattice parameters

Table 1. Final atomic parameters and e.s.d.'s

$$B_{\text{eq}} = \frac{4}{3} \left(\frac{\beta_{11}}{a^*2} + \frac{\beta_{22}}{b^*2} + \frac{\beta_{33}}{c^*2} \right).$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
C(1)	0.0952 (2)	0.0519 (3)	-0.0248 (5)	5.93 (8)
C(2)	0.1329 (2)	-0.0008 (2)	0.0986 (4)	3.76 (6)
C(3)	0.1077 (2)	-0.0791 (3)	0.1777 (4)	5.10 (8)
C(4)	0.1438 (2)	-0.1230 (3)	0.2892 (4)	4.90 (7)
C(5)	0.2051 (2)	-0.0937 (3)	0.3172 (4)	5.54 (8)
C(6)	0.2294 (2)	-0.0142 (3)	0.2360 (4)	4.60 (7)
C(7)	0.1936 (2)	0.0331 (3)	0.1292 (4)	4.15 (7)
C(8)	0.2689 (2)	0.1663 (3)	0.0574 (4)	4.18 (6)
C(9)	0.3596 (2)	0.2149 (3)	0.1834 (4)	4.17 (6)
C(10)	0.3666 (2)	0.2956 (3)	0.2800 (4)	4.93 (7)
C(11)	0.4234 (2)	0.3424 (4)	0.2976 (5)	5.92 (8)
C(12)	0.4760 (2)	0.3026 (4)	0.2299 (4)	6.07 (9)
C(13)	0.4682 (2)	0.2245 (3)	0.1334 (4)	4.70 (7)
C(14)	0.4110 (2)	0.1783 (2)	0.1095 (4)	4.11 (6)
C(15)	0.4080 (2)	0.0916 (3)	0.0017 (5)	5.74 (9)
N(1)	0.2149 (1)	0.1142 (2)	0.0508 (3)	3.98 (5)
N(2)	0.2830 (1)	0.2262 (2)	-0.0622 (3)	3.94 (5)
N(3)	0.3026 (1)	0.1680 (2)	0.1861 (3)	4.02 (5)

Table 2. Bond lengths (Å) and inter-bond angles (°)

C(1)–C(2)	1.551 (6)	C(8)–N(3)	1.365 (4)
C(2)–C(3)	1.390 (5)	C(9)–N(3)	1.385 (5)
C(2)–C(7)	1.413 (5)	C(9)–C(10)	1.407 (5)
C(3)–C(4)	1.402 (6)	C(9)–C(14)	1.385 (5)
C(4)–C(5)	1.402 (6)	C(10)–C(11)	1.388 (6)
C(5)–C(6)	1.405 (6)	C(11)–C(12)	1.395 (6)
C(6)–C(7)	1.389 (5)	C(12)–C(13)	1.380 (6)
C(7)–N(1)	1.386 (4)	C(13)–C(14)	1.401 (5)
C(8)–N(1)	1.364 (4)	C(14)–C(15)	1.526 (6)
C(8)–N(2)	1.382 (4)		
C(1)–C(2)–C(3)	120.9 (3)	C(10)–C(9)–N(3)	116.4 (3)
C(1)–C(2)–C(7)	118.2 (3)	C(14)–C(9)–N(3)	123.6 (3)
C(3)–C(2)–C(7)	120.8 (3)	C(10)–C(9)–C(14)	119.3 (3)
C(2)–C(3)–C(4)	118.2 (4)	C(9)–C(10)–C(11)	121.5 (4)
C(3)–C(4)–C(5)	122.0 (4)	C(10)–C(11)–C(12)	119.4 (4)
C(4)–C(5)–C(6)	118.5 (4)	C(11)–C(12)–C(13)	118.2 (4)
C(5)–C(6)–C(7)	120.4 (4)	C(12)–C(13)–C(14)	123.2 (4)
C(2)–C(7)–C(6)	119.9 (3)	C(13)–C(14)–C(15)	118.7 (3)
C(2)–C(7)–N(1)	117.9 (3)	C(13)–C(14)–C(9)	118.0 (3)
C(6)–C(7)–N(1)	122.3 (3)	C(15)–C(14)–C(9)	123.2 (3)
N(1)–C(8)–N(2)	117.4 (3)	C(7)–N(1)–C(8)	132.3 (3)
N(1)–C(8)–N(3)	120.0 (3)	C(8)–N(3)–C(9)	117.7 (3)
N(2)–C(8)–N(3)	122.0 (3)		

measured by least-squares fit to 13 selected reflexions; region examined showed 1817 independent hkl of which 1245 were observed with $I > 3\sigma(I)$; index range h $0 \rightarrow 26$, k $0 \rightarrow 16$, l $0 \rightarrow 11$; $\theta_{\text{max}} = 70^\circ$; structure solved by \sum_2 relationships in the NRC series of programs (Ahmed, Hall, Pippy & Huber, 1970) implemented on our DEC-10 computer; E map showed all non-H atoms, refined by least squares on F , initially using B_{150} for each atom commencing with $B(\text{overall}) = 4.05 \text{ \AA}^2$ given by a Wilson plot; scattering factors from *International Tables for X-ray Crystallography* (1962); finally β_{ij} introduced and refinement continued with $w^{1/2} = 1/F_o$ until convergence with shifts $< 0.3\sigma$; approximate H positions in the guanidine residue and the two methyl groups were obtained from difference Fourier map, but these together with the eight phenyl H atoms were regularized by calculation assuming C–H and N–H = 1.08 Å, and not refined, although included

in the structure-factor calculations; min. and max. $\Delta\rho$ excursions in final difference Fourier map $\pm 0.2 e \text{ \AA}^{-3}$, $R_w = 0.108$.

Discussion. The final atomic parameters are given in Table 1,* and bond lengths and inter-bond angles for the non-H atoms are listed in Table 2.

The packing of the molecules and the numbering of the atoms are shown in Fig. 1. The molecules are linked in chains along c by hydrogen bonds $\text{N}(2)\text{--H}(9)\cdots\text{N}(3') = 3.024 (4) \text{ \AA}$ (c -glide related). This length may be compared with 2.873 Å in anthranilic acid (Brown, 1968), and 3.08 and 3.15 Å in guanine hydrochloride monohydrate (Broomhead, 1951). Lists of N–H \cdots N bonds published by Pimentel & McClellan (1960) show a spread 2.88–3.38 Å, mean 3.10 (13) Å. The difference Fourier map indicated that all three H atoms of the guanidine residue are bonded to N(2); this is confirmed by the C(8)–N(2) bond being significantly longer than C(8)–N(1) and C(8)–N(3). N(1) and N(3) are thus without primary bonded H atoms, although N(3) accepts a H bond from N(2') of the neighbouring molecule related by a c glide; this results in the bond angle at N(3) being $\sim 118^\circ$, while that at N(1) is $\sim 132^\circ$ [cf. 129.6° for corresponding bond angle in Paludrine (Brown, 1967) and 128.3° in *p*-chlorophenylbiguanide HCl (Brown & Sengier, 1984)].

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares planes data and intermolecular contact distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39060 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

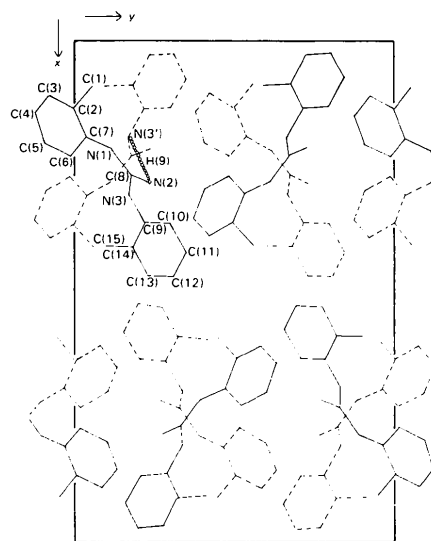


Fig. 1. Packing of molecules viewed in projection on (001).

The mean C—N length, 1.373 (4) Å, is appreciably longer than that found in many guanidinium compounds, e.g. 1.328 Å in Paludrine* (Brown, 1967), 1.323 Å in guanidinium chloride (Adams, 1978), 1.322 Å in guanidinium hydrochloride oxalate monohydrate (Haas, Harris & Mills, 1965) and 1.333 Å in *p*-chlorophenylbiguanide HCl (Brown & Sengier, 1984); these quoted values are, however, all guanidinium cations where the number and arrangement of H atoms is different from this structure.

The molecule lies in three planes defined by (a) C(1)—C(7), (b) C(8), N(1), N(2) and N(3) and (c) C(9)—C(15). The angles between these planes are $a:b = 22.13(5)^\circ$, $b:c = 106.13(5)^\circ$ and $a:c = 85.90(5)^\circ$. Other than the hydrogen bonds, the

closest intermolecular contacts between non-H atoms are C(4)⋯N(2') = 3.292 (5) and C(5)⋯N(2') = 3.361 (5) Å, both *b*-glide related.

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* 1-(*p*-Chlorophenyl)-5-isopropylbiguanide hydrochloride.

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α -(4-Methyl-2-nitrophenylhydrazono)acetoacetanilide, C₁₇H₁₆N₄O₄

BY C. J. BROWN AND H. R. YADAV

Department of Metallurgy and Materials Engineering, City of London Polytechnic, Central House, Whitechapel High Street, London E1 7PF, England

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Abstract. $M_r = 340.3$, monoclinic, $P2_1/a$, $a = 12.034(11)$, $b = 20.388(13)$, $c = 7.623(10)$ Å, $\beta = 120.5(3)^\circ$, $V = 1611.50$ Å³, $Z = 4$, $D_m = 1.395(1)$, $D_x = 1.403$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1.5418$ Å, $\mu = 0.87$ mm⁻¹, $F(000) = 712$, $T = 295$ K, $R = 0.044$ for 1156 observed reflexions [$I > 3\sigma(I)$]. The molecules are almost planar and stack in layers perpendicular to c^* with three intramolecular hydrogen bonds per molecule and no strong intermolecular forces. The carbon atom at which coupling occurs is trigonal with its hydrogen atom transferred to the nitrogen adjacent to the toluene ring so that the pigment exists in the hydrazone tautomeric form.

Introduction. The title compound is readily prepared by coupling diazotized 2-nitro-4-toluidine with acetoacetanilide. It is marketed under the trade name Monolite Fast Yellow (CI 11680), and is used commercially as a bright yellow pigment in paints and printing inks. Approximate dimensions of a variant unit cell have been given by Mez (1968). This structure determination was carried out to investigate further the stereochemical isomers obtaining in azo dyes and pigments.

Experimental. Sample from Imperial Chemical Industries Limited (Organics Division), recrystallized from nitrobenzene at room temperature, yellow needles elongated along a , m.p. 532 K, crystal $0.35 \times 0.25 \times 0.30$ mm, density by flotation in NaI solution, lattice parameters from rotation photographs and from least-squares analysis of 27 selected Weissenberg reflexions (in the absence of observable high-order reflexions), Stoe integrating Weissenberg camera with multiple films used for intensities about a ($0kl \rightarrow 9kl$) and c ($hk0$) (which was also used for inter-layer scaling), visual estimation with calibrated scale, 1156 reflexions out of a possible 1851 considered observed, corrections for L_p effects but not for absorption or extinction, index range h 0–9, k 0–24, l –8–8, $\theta_{\max} = 60^\circ$; structure solved by trial-and-error since direct methods failed and Patterson map indicated only that molecules lay in (001) with $z = 0.25$; refinement by least squares on F using the NRC programs (Ahmed, Hall, Pippy & Huber, 1970) on the London Polytechnics ICL 1905E computer, B_{iso} used initially and later β_j with weights $w^{1/2} = 1/F_o$ until shifts all $< 0.25\sigma$, H parameters calculated and included in structure factors but not refined, $\Delta\rho$ excursions in final difference Fourier map within