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 $a:b = 22\cdot13\ (5)°$, $b:c = 106\cdot13\ (5)°$ and $a:c = 85\cdot90\ (5)°$. Other than the hydrogen bonds, the

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

closest intermolecular contacts between non-H atoms are $C(4)\cdots N(2') = 3\cdot292\ (5)$ and $C(5)\cdots N(2') = 3\cdot361\ (5)$ Å, both *b*-glide related.

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α-(4-Methyl-2-nitrophenylhydrazono)acetoacetanilide, $C_{17}H_{16}N_4O_4$

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Abstract. $M_r = 340\cdot3$, monoclinic, $P2_1/a$, $a = 12\cdot034\ (11)$, $b = 20\cdot388\ (13)$, $c = 7\cdot623\ (10)$ Å, $\beta = 120\cdot5\ (3)°$, $V = 1611\cdot50$ Å³, $Z = 4$, $D_m = 1\cdot395\ (1)$, $D_x = 1\cdot403$ Mg m⁻³, Cu $K\alpha$, $\lambda = 1\cdot5418$ Å, $\mu = 0\cdot87$ mm⁻¹, $F(000) = 712$, $T = 295$ K, $R = 0\cdot044$ 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 × 0·25 × 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 Lp effects but not for absorption or extinction, index range h 0–9, k 0–24, l –8–8, $\theta_{max} = 60°$; structure solved by trial-and-error since direct methods failed and Patterson map indicated only that molecules lay in (001) with $z = 0\cdot25$; 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_{ij} with weights $w^{1/2} = 1/F_o$ until shifts all $< 0\cdot25\sigma$, H parameters calculated and included in structure factors but not refined, $\Delta\rho$ excursions in final difference Fourier map within

± 0·1 e Å⁻³, scattering factors from *International Tables for X-ray Crystallography* (1962), $R_w = 0.093$.

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

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

	x	y	z	$B_{eq}(\text{Å}^2)$
C(1)	0·9600 (4)	0·6780 (2)	0·3289 (7)	4·89 (9)
C(2)	0·8478 (4)	0·6360 (2)	0·2971 (6)	4·78 (8)
C(3)	0·8522 (4)	0·5683 (2)	0·2884 (6)	4·55 (8)
C(4)	0·7494 (3)	0·5287 (2)	0·2659 (5)	3·41 (7)
C(5)	0·6417 (3)	0·5570 (2)	0·2583 (5)	4·02 (7)
C(6)	0·6366 (4)	0·6259 (2)	0·2642 (6)	4·51 (8)
C(7)	0·7390 (4)	0·6628 (2)	0·2838 (6)	5·43 (9)
C(8)	0·2895 (4)	0·6365 (2)	0·2948 (7)	4·27 (9)
C(9)	0·2608 (4)	0·5647 (2)	0·2663 (6)	4·17 (8)
C(10)	0·3528 (3)	0·5198 (2)	0·2530 (5)	4·45 (7)
C(11)	0·3384 (3)	0·4464 (2)	0·2396 (5)	4·43 (7)
C(12)	0·1850 (3)	0·3575 (2)	0·2103 (5)	4·10 (7)
C(13)	0·2652 (4)	0·3028 (2)	0·2369 (6)	5·01 (8)
C(14)	0·2120 (4)	0·2410 (2)	0·2208 (6)	5·03 (9)
C(15)	0·0892 (4)	0·2314 (2)	0·1836 (6)	5·83 (8)
C(16)	0·0122 (4)	0·2869 (2)	0·1547 (6)	4·49 (8)
C(17)	0·0630 (3)	0·3495 (2)	0·1716 (6)	4·99 (8)
N(1)	0·7640 (3)	0·4588 (1)	0·2547 (5)	3·92 (6)
N(2)	0·5414 (2)	0·5195 (2)	0·2477 (4)	3·37 (6)
N(3)	0·4490 (3)	0·5507 (2)	0·2560 (4)	4·28 (6)
N(4)	0·2300 (3)	0·4236 (1)	0·2269 (5)	4·61 (6)
O(1)	0·8581 (3)	0·4376 (1)	0·2537 (5)	6·06 (7)
O(2)	0·6812 (3)	0·4224 (1)	0·2454 (5)	5·45 (6)
O(3)	0·4232 (2)	0·4122 (1)	0·2413 (4)	4·64 (5)
O(4)	0·1620 (3)	0·5450 (1)	0·2611 (5)	5·71 (6)

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

C(1)–C(2)	1·511 (7)	C(11)–O(3)	1·231 (5)
C(2)–C(3)	1·385 (6)	C(12)–C(13)	1·419 (6)
C(2)–C(7)	1·374 (8)	C(12)–C(17)	1·353 (7)
C(3)–C(4)	1·412 (7)	C(12)–N(4)	1·436 (5)
C(4)–C(5)	1·393 (6)	C(13)–C(14)	1·390 (6)
C(4)–N(1)	1·444 (5)	C(14)–C(15)	1·370 (8)
C(5)–C(6)	1·408 (6)	C(15)–C(16)	1·408 (7)
C(5)–N(2)	1·396 (6)	C(16)–C(17)	1·392 (6)
C(6)–C(7)	1·387 (7)	N(1)–O(1)	1·216 (6)
C(8)–C(9)	1·493 (6)	N(1)–O(2)	1·215 (5)
C(9)–C(10)	1·478 (6)	N(2)–N(3)	1·309 (5)
C(9)–O(4)	1·237 (6)	N(4)[H(15)]···O(4)	2·819 (12)
C(10)–C(11)	1·504 (5)	N(2)[H(16)]···O(2)	3·069 (14)
C(10)–N(3)	1·309 (6)	N(2)[H(16)]···O(3)	2·899 (12)
C(11)–N(4)	1·341 (6)		
C(1)–C(2)–C(3)	121·3 (4)	C(10)–C(11)–N(4)	115·0 (3)
C(1)–C(2)–C(7)	121·7 (4)	C(10)–C(11)–O(3)	119·9 (4)
C(3)–C(2)–C(7)	116·9 (4)	N(4)–C(11)–O(3)	125·1 (4)
C(2)–C(3)–C(4)	121·5 (4)	C(13)–C(12)–C(17)	121·4 (4)
C(3)–C(4)–C(5)	120·5 (4)	C(13)–C(12)–N(4)	121·7 (4)
C(3)–C(4)–N(1)	116·5 (4)	C(17)–C(12)–N(4)	116·8 (4)
C(5)–C(4)–N(1)	123·0 (4)	C(12)–C(13)–C(14)	116·6 (4)
C(4)–C(5)–C(6)	117·8 (4)	C(13)–C(14)–C(15)	123·3 (4)
C(4)–C(5)–N(2)	122·4 (4)	C(14)–C(15)–C(16)	118·2 (4)
C(6)–C(5)–N(2)	119·8 (4)	C(15)–C(16)–C(17)	120·0 (4)
C(5)–C(6)–C(7)	119·6 (4)	C(12)–C(17)–C(16)	120·4 (4)
C(2)–C(7)–C(6)	123·6 (4)	C(4)–N(1)–O(1)	119·5 (4)
C(8)–C(9)–C(10)	119·4 (4)	C(4)–N(1)–O(2)	119·0 (4)
C(8)–C(9)–O(4)	118·1 (4)	O(1)–N(1)–O(2)	121·5 (4)
C(10)–C(9)–O(4)	122·5 (4)	C(5)–N(2)–N(3)	117·5 (3)
C(9)–C(10)–C(11)	123·9 (4)	C(10)–N(3)–N(2)	122·1 (3)
C(9)–C(10)–N(3)	112·8 (4)	C(11)–N(4)–C(12)	129·9 (4)
C(11)–C(10)–N(3)	123·4 (4)		

Discussion. The final positional and equivalent isotropic thermal parameters are in Table 1,* and bond lengths and inter-bond angles in Table 2. The numbering of the atoms and the packing arrangement, showing the internal hydrogen-bond arrangement, are in Fig. 1.

The molecule is almost planar, the average displacement of the 25 non-H atoms from their mean plane being 0·078 (4) Å, the largest being +0·236 (4) Å for C(16) and C(17) and −0·216 (4) Å for C(13) and C(14). If these four atoms are omitted, the average displacement is 0·052 (4) Å. The crystal is isostructural with the corresponding 4-chloro compound (Mez, 1968) but differs in its stereochemical configuration from the closely related α-(4-methyl-2-nitrophenyl-hydrazono)acetanilide (Brown & Yadav, 1984) and α,4-dibromo-α-(4-methyl-2-nitrophenylazo)acetanilide (Brown, 1967). A discussion of these relationships has been given by Brown & Yadav (1984).

The strict planarity of the atomic grouping C(9), C(10), C(11) and N(3) indicates that C(10) is trigonal and cannot have a H atom attached to it; this agrees with the conclusions of Mez (1968), and the standard chemical formulation for this compound, and possibly for other azo pigments, needs revision. There are three possible formulae (Fig. 2) and older textbooks generally give (*a*) whereas the *Colour Index* (1971) and Allen (1971) give (*b*) for this compound. Yagi (1963), however, gave (*c*) as the most probable arrangement on the basis of spectroscopic (electronic and infrared absorption) evidence.
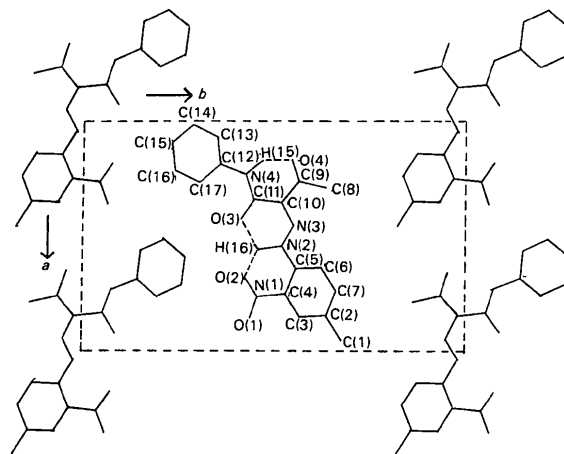
Fig. 1. Projection of unit cell on (001) showing numbering of atoms, packing of molecules and internal hydrogen-bonding system (dashed lines).
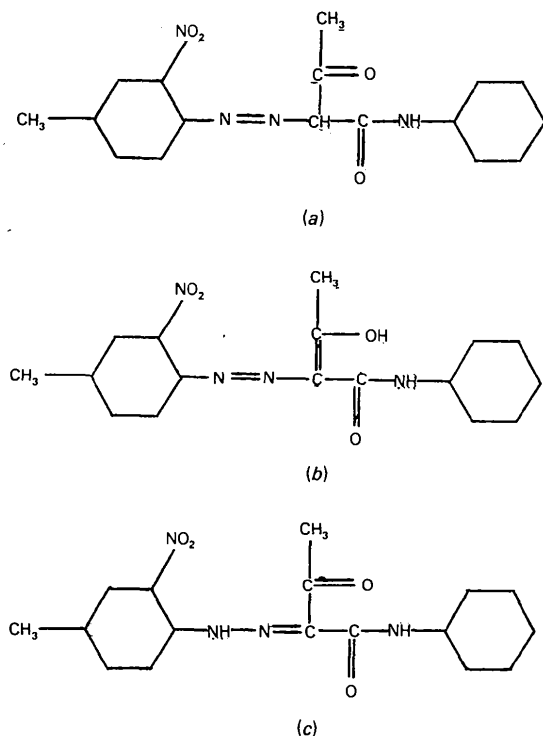
Fig. 2. Possible double-bond formulations around the azo group: (a) azo formula; (b) hydroxyazo formula; (c) hydrazone formula.

The relative merits of the hydroxyazo (b) and hydrazone (c) tautomeric forms have been discussed in detail by Prendergrass, Paul & Curtin (1972), by Kuder (1972) and by Guggenberger & Teufer (1975). Pren-

dergrass et al. list the ranges of bond lengths to be expected for the two tautomers by comparison with those found in a series of closely related compounds, and our values generally lie intermediate between their two extremes. Berrie, Hampson, Longworth & Mathias (1968) have studied the problem by NMR spectroscopy and give quantitative estimates of the amounts of the tautomers. They concluded that a resonance hybrid would be the best representation of the formula. Our X-ray results tend to favour the hydrazone (c) formulation, and this agrees with ideas of extensive π-electron resonance throughout the molecule which maintains geometric planarity and consequential exceptional stability and light fastness of the pigment.

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Ester of cis-(1R,3S)-3-tert-Butylcyclohexanol and (2R)-3,3,3-Trifluoro-2-methoxy-2-phenylpropionic Acid, $C_{20}H_{27}F_3O_3$

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Abstract. $M_r = 372.4$, orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 7.805$ (2), $b = 15.150$ (7), $c = 16.85$ (1) Å, $V = 1992.4$ Å^3, $D_x = 1.241$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.109$ mm^{-1}, $F(000) = 792$, room temperature. $R_w = 0.046$ for 1448 reflections with $I > 2\sigma(I)$, out of 2038 independent measurements. The cyclohexane ring has the chair conformation with the tert-butyl and the propionate groups at equatorial positions. The molecular geometry of the title compound is very

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