

by Bent (1968) for the I—I distances in the closely related  $I_3^-$  ions.

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## *N,N'*-Diisopropyl-2,5-diphenyl-1,4-phenylenediamine

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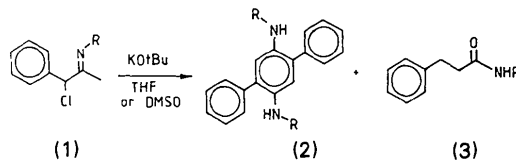
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**Abstract.**  $C_{24}H_{28}N_2$ ,  $M_r = 344.5$ , triclinic,  $P\bar{1}$ ,  $a = 9.926$  (13),  $b = 6.187$  (8),  $c = 8.034$  (7) Å,  $\alpha = 90.65$  (9),  $\beta = 97.68$  (9),  $\gamma = 100.48$  (10)°,  $V = 480.5$  (9) Å<sup>3</sup>,  $Z = 1$ ,  $D_x = 1.191$  g cm<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.749$  cm<sup>-1</sup>,  $F(000) = 186$ ,  $T = 291$  K,  $R = 0.055$  for 907 observed reflections. As regards the relative conformation of the three rings, this molecule is rather different from *p*-terphenyl, but very similar to 2,5-diphenylhydroquinone.

**Introduction.** During investigation of the Favorskii rearrangement of various  $\alpha$ -halogenated ketimines, a curious side reaction was observed (De Kimpe, Sulmon, Moëns, Schamp, Declercq & Van Meerssche, 1986). The reaction of  $\alpha$ -chloroketimines (1) ( $R = iPr$ , cycloHex) with potassium *tert*-butoxide in tetrahydro-

furan or dimethyl sulfoxide afforded, besides minor amounts of the rearranged amide (3), condensation products (22–41%) which were identified as *N,N'*-dialkyl-2,5-diphenyl-*p*-phenylenediamines (2) ( $R = iPr$ , cycloHex). The mechanism was interpreted in terms of a double intramolecular nucleophilic substitution or a cyclocondensation of a zwitterionic Favorskii intermediate.



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Both processes were followed by air oxidation of the resulting six-membered 1,4-diimine or the corresponding electron-rich cyclohexadienes. As mechanistic routes were also plausible for the formation of

the isomeric *N,N'*-dialkyl-2,3-diphenyl-*p*-phenylenediamines, an unambiguous structural assignment of the self-condensation products by means of an X-ray crystallographic analysis was undertaken.

**Experimental.** The title compound (2) (*R* = *i*Pr) was obtained from the reaction of *N*-(1-chloro-1-phenyl-2-propylidene)isopropylamine (1) (*R* = *i*Pr) and potassium *tert*-butoxide in tetrahydrofuran (room temperature, 3h) as a yellow solid (m.p. 427 K from pentane/ether). Recrystallization from acetone.  $D_m$  not measured. Parallelepipedal crystal with dimensions  $0.25 \times 0.25 \times 0.15$  mm. Lattice parameters refined using 15 reflections in the range  $4 \leq 2\theta \leq 16^\circ$ . Syntex  $P2_1$ , graphite-monochromatized Mo  $K\alpha$  radiation. 1411 independent reflections ( $-10 \leq h \leq 10$ ,  $-6 \leq k \leq 6$ ,  $0 \leq l \leq 8$ ) with  $(\sin\theta)/\lambda \leq 0.561 \text{ \AA}^{-1}$ , 907 with  $I \geq 2.5\sigma(I)$ . Standard reflection (112) checked every 50 reflections: no significant deviation. Structure solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). H atoms from difference Fourier synthesis. Anisotropic least-squares refinement (*SHELX*76; Sheldrick, 1976) using *F*; H isotropic with common refined temperature factor ( $B = 4.8 \text{ \AA}^2$ ).  $w = 1/(\sigma^2 + 0.0012F^2)$ ,  $R = 0.055$ ,  $wR = 0.057$ ,  $S = 1.4$  for 907 observed reflections. Final maximum shift to e.s.d. = 0.68. Maximum and minimum heights in final difference Fourier synthesis = 0.20 and  $-0.22 \text{ e \AA}^{-3}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** There is only one half molecule in the asymmetric unit: a crystallographic centre of symmetry coincides with the middle of the central ring. The atomic parameters are given in Table 1.\* Fig. 1 is a view of the molecule, showing the numbering of the atoms (program *PLUTO*; Motherwell & Clegg, 1978). Bond distances and angles are given in Table 2.

The conformation of the *p*-terphenyl fragment can be described by one torsion angle along the bond between two phenyl rings. Several sets of structural parameters describing the *p*-terphenyl itself were retrieved by means of the Cambridge Structural Database (Allen *et al.*, 1979). The value of the above mentioned torsion ranges between  $0^\circ$  at room temperature (Rietveld, Maslen & Clews, 1970) and  $27^\circ$  at 113 K (Baudour, Delugeard & Cailleu, 1976). In the present case, the steric effect of the *N*-isopropyl substituents imposes a much larger torsion ( $56^\circ$ ), comparable to the value of  $52^\circ$  observed in 2,5-diphenyl hydroquinone (Kaftory, Tanaka & Toda, 1985). Nevertheless, there remains a

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51008 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors ( $\text{\AA}^2$ )

$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$
C1	8672 (3)	465 (5)	-540 (4)	2.60 (6)
C2	9395 (3)	1303 (5)	1005 (4)	2.46 (6)
C3	10700 (4)	833 (6)	1513 (4)	2.88 (7)
C4	8821 (3)	2705 (5)	2136 (4)	2.58 (6)
C5	8740 (4)	2219 (6)	3814 (4)	3.14 (7)
C6	8233 (4)	3543 (7)	4858 (5)	3.90 (8)
C7	7793 (4)	5415 (7)	4248 (5)	4.11 (8)
C8	7892 (4)	5938 (7)	2614 (5)	3.97 (8)
C9	8407 (4)	4635 (6)	1567 (5)	3.30 (7)
N10	7352 (3)	889 (5)	-1103 (4)	3.63 (6)
C11	6370 (4)	-434 (6)	-2363 (5)	3.16 (7)
C12	5916 (5)	-2779 (7)	-1873 (6)	4.74 (9)
C13	5122 (5)	670 (9)	-2750 (6)	4.43 (9)

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

C2-C1	1.391 (4)	N10-C1	1.399 (4)
C3-C2	1.389 (4)	C4-C2	1.484 (4)
C5-C4	1.394 (5)	C9-C4	1.394 (5)
C6-C5	1.370 (5)	C7-C6	1.383 (6)
C8-C7	1.367 (6)	C9-C8	1.367 (5)
C11-N10	1.440 (4)	C12-C11	1.512 (6)
C13-C11	1.519 (5)	C3*-C1	1.394 (4)
N10-C1-C2	121.5 (3)	C3-C2-C1	119.4 (3)
C4-C2-C1	122.2 (3)	C4-C2-C3	118.4 (3)
C5-C4-C2	121.9 (3)	C9-C4-C2	120.5 (3)
C9-C4-C5	117.5 (3)	C6-C5-C4	121.6 (4)
C7-C6-C5	119.7 (4)	C8-C7-C6	119.4 (4)
C9-C8-C7	121.3 (4)	C8-C9-C4	120.5 (4)
C11-N10-C1	124.3 (3)	C12-C11-N10	113.9 (3)
C2-C1-C3*	117.8 (3)	N10-C1-C3*	120.7 (3)
C2-C3-C1*	122.8 (3)		

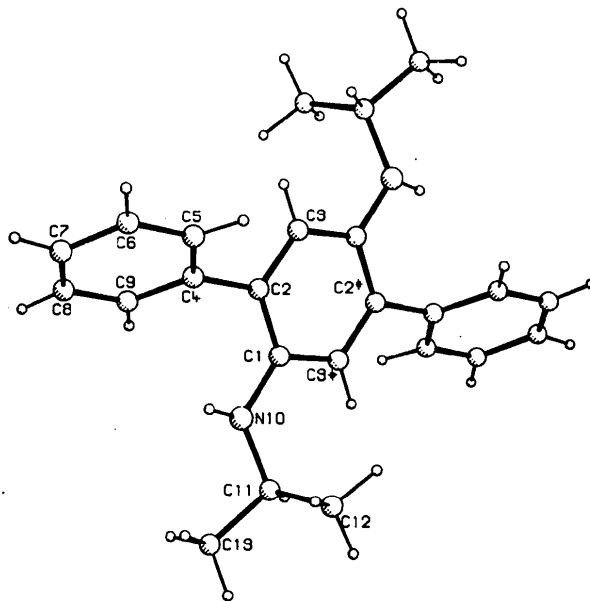


Fig. 1. The conformation of molecule (2) and the numbering of the atoms.

short intramolecular contact (2.50 Å) between C9 and HN10.

The pyramidal character of N10 is rather well marked: it lies 0.19 Å out of the plane defined by C1, C11 and HN10. However, there seems to be a partial conjugation with the central phenyl ring, suggested by the short C1–N10 bond [1.399 (4) Å] and the low value of the torsion angle C2–C1–N10–HN10: 10(1)°.

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## CI Pigment Yellow 60, 4-(2-Chlorophenylhydrazono)-3-methyl-1-phenyl-5-pyrazolone

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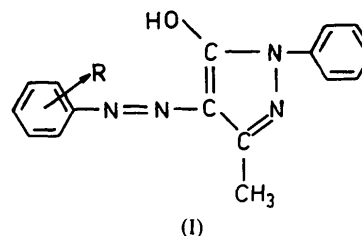
**Abstract.** C<sub>16</sub>H<sub>13</sub>ClN<sub>4</sub>O,  $M_r = 312.76$ , triclinic,  $P\bar{1}$ ,  $a = 11.1256$  (10),  $b = 9.4507$  (8),  $c = 7.5798$  (9) Å,  $\alpha = 80.708$  (9),  $\beta = 84.382$  (9),  $\gamma = 68.451$  (7)°,  $V = 730.9$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.4211$  (3),  $D_m = 1.420$  (3) Mg m<sup>-3</sup>, Cu  $K\alpha$ ,  $\lambda = 1.54184$  Å,  $\mu = 2.26$  mm<sup>-1</sup>,  $F(000) = 324$ , room temperature,  $R = 0.082$  for 2773 independent non-zero intensities. The planar molecule exists as the hydrazone tautomer with three intramolecular hydrogen bonds, one very weak. The molecules are linked by van der Waals forces into columns parallel to  $b$ .

**Introduction.** Some years ago, with the long-term aim of relating crystal structure and colour, work was published on the structure determination of several azo-pigments involving  $\beta$ -naphthol (Grainger & McConnell, 1969; Kobelt, Paulus & Kunstmann, 1972, 1974; Whitaker, 1977*a,b*, 1978*b*). A review (Whitaker, 1978*a*) of these six crystal structures concluded that for this group of pigments, the azo group was, in reality, a hydrazone group. Further crystal structure determinations (Whitaker, 1980, 1981; Paulus, 1982) on other members of this group of pigments supported this view.

Interest then moved to azo-pigments involving acetoacetanilide and again a series of crystal structures were determined (Whitaker, 1983*a,b*; Paulus, Rieper &

Wagner, 1983; Brown & Yadav, 1984; Whitaker, 1984*a*; Paulus, 1984; Whitaker, 1984*b*, 1985*a*; Whitaker & Walker, 1985; Whitaker, 1985*b*, 1986; Whitaker & Walker, 1987; Whitaker, 1987). The general conclusion from these was that this group of compounds should be classed as hydrazone rather than azo-pigments (Whitaker, 1988).

A third group of 'azo-pigments' are those involving pyrazolone. [General formula (I) according to the *Colour Index* (1971).] The structure of one member of this group, 4-(4-chlorophenylazo)-3-methyl-1-phenyl-5-pyrazolone, has been determined by Golinski, Reck & Kutschabsky (1982) who claimed that the molecule exists in the hydrazone form.



However, the quality of the work was poor, the residual was 13.7%, no direct evidence of the positions