Structure of N-{4-[2,4-Bis(1,1-dimethylpropyl)phenoxy]butyl}-1-hydroxy-2-naphthalenecarboxamide

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Abstract. $C_{31}H_{41}NO_3$, $M_r = 475.68$, orthorhombic, $Pca2_1$, $a = 10.397$ (4), $b = 23.018$ (16), $c = 11.667$ (3) Å, $V = 2792$ (4) Å^3, $Z = 4$, $D_x = 1.132$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.67$ cm^{-1}, $F(000) = 1032$, $T = 295$ K, $R = 0.079$ for 1871 observed reflections [$I > \sigma(I)$]. The molecules are packed in (010) sheets, bounded on either side by *tert*-pentyl groups. The sheets consist of two intertwined layers related by the *a* glide. Disorder is evident in the ethyl groups on both *tert*-pentyl groups. The carbonyl O atom is doubly hydrogen bonded, intramolecularly to the hydroxyl proton and intermolecularly to the amide H atom on an adjacent molecule. These intermolecular hydrogen bonds yield molecular ribbons in the *a*-glide direction.

Introduction. The title compound (I) is a color photographic coupler, and reacts with oxidized color developer to yield cyan indoaniline image dyes in negative color films (Tong, 1977; Texter, 1988). Its structure was investigated because of the reactivity and crystallinity features it exhibits in various photographic applications. The usual method of incorporating this compound into a sensitized film layer is to prepare it as a nominally oil-in-water emulsion (submicrometre particle sizes) and then to remove the high-vapor-pressure solvent [leaving a largely amorphous particle consisting of (I) and a plasticizer such as di-*n*-butyl phthalate]. It was observed that dye forming rates were comparable to those of these small amorphous particles when microcrystallites (submicrometre in largest dimension) of (I) were dispersed by roller-milling methods (Wheeler, 1981) and subsequently coated with plasticizer by adsorption from solution (Texter, 1991).
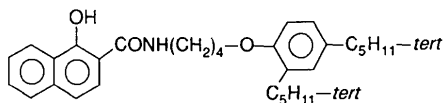
(I)

Experimental. The title compound was obtained from Mr W. F. Coffey of the Photographic Research Laboratories, Eastman Kodak Company. Large crystals were grown in saturated ethyl acetate solution at room temperature. One of these crystals was cut to a size of $0.41 \times 0.43 \times 0.48$ mm for data collection. Data (ω–2θ scans) were collected on an Enraf–Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. 2587 reflections were measured for (sinθ)/$\lambda < 0.59$ Å^{-1}. One octant was measured with maximum $h = 12$, $k = 27$ and $l = 13$. Unit-cell parameters were obtained by computer centering of 25 reflections ($8.8 < \theta < 15.6°$), followed by least-squares refinement of the setting angles. The scan range was from 2θ (Mo $K\alpha_1$) -0.65 to 2θ (Mo $K\alpha_2$) $+ 0.65°$. Backgrounds were measured by moving-crystal moving-counter counts at each end of the scan range. The ratio of scan time to background time was 2.0, which extended the scan range by 25% at each end. To check crystal and electronic stability, three reflections were remeasured periodically. No significant changes in intensities were noted during data collection.

Intensities were calculated according to $I = ASK(C - RB)$, where A is the attenuation factor, S is the scan rate, K is a scale factor, C is the total integrated peak count, R is the ratio of peak time to background time and B is the total background count. Standard deviations were calculated according to $\sigma^2 = (ASK)^2(C + R^2B)$ and $\sigma_o = \{[I + \sigma(I)]/Lp\}^{1/2} - F_o$, where $(Lp)^{-1}$ is the Lorentz–polarization correction and $F_o = (I/Lp)^{1/2}$ is the observed structure factor. Lorentz and polarization corrections were made. Corrections for changes in intensity of the standard reflections and for absorption were not necessary. The structure was solved by direct methods (*MULTAN*11/82; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). The E map calculated with the phase set (264 E's > 1.60) having the best combined figure of merit gave all atoms except those on the *tert*-pentyl groups. Sub-
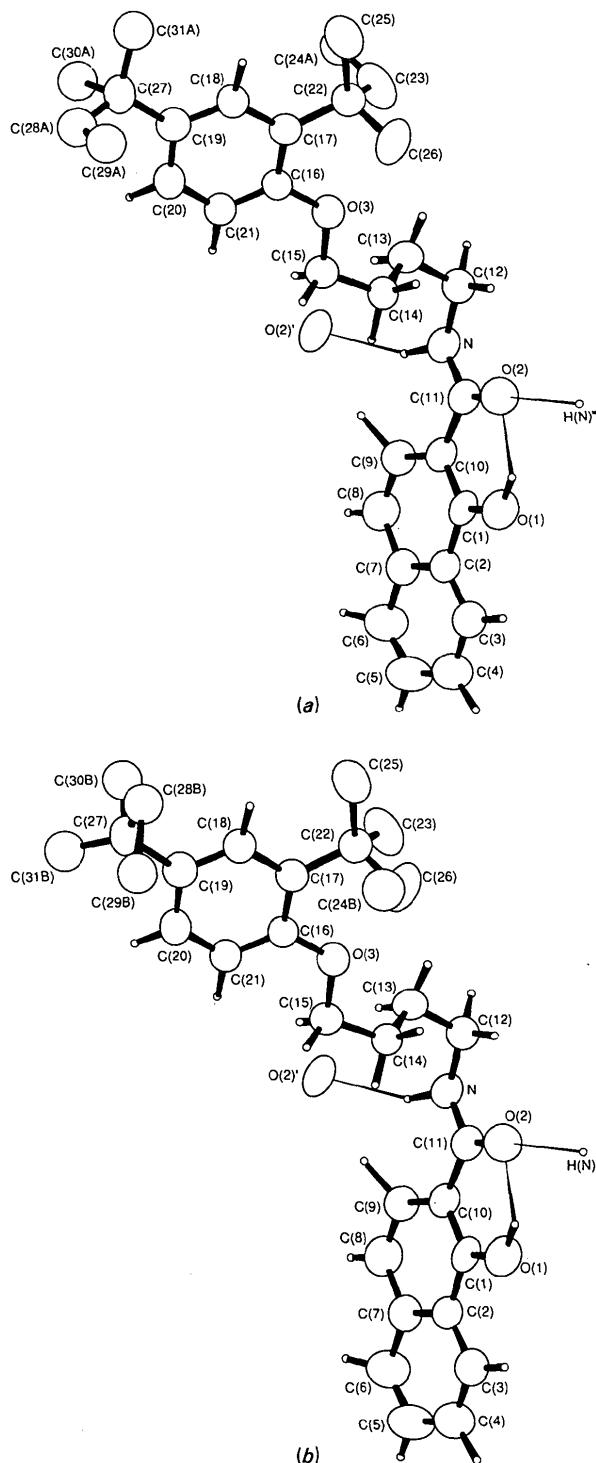
(a)

(b)

Fig. 1. (a) Conformation where the *tert*-pentyl groups are in the A positions. The labeling of the non-H atoms is illustrated. Thin bonds represent intramolecular hydrogen bonding {O(1)—H[O(1)]⋯O(2)} and intermolecular hydrogen bonding to O(2)′ (symmetry $-\frac{1}{2}+x$, $-y$, z) and to H(N)″ ($\frac{1}{2}+x$, $-y$, z). Thermal ellipsoids are drawn at the 40% probability level. (b) Conformation where the *tert*-pentyl groups are in the B positions. The hydrogen bonding is identical to that described in (a).

sequently, difference electron density maps yielded the disordered *tert*-pentyl C atoms and all H atoms not involved in the disorder. Refinement was performed by full-matrix least squares on F using 1871 observed reflections with $I > \sigma(I)$ (*SDP-Plus*; Frenz, 1985). Anisotropic thermal parameters were applied to all atoms, except those involved in the disorder and H atoms. The function minimized was $\Sigma w(|F_o| - \kappa|F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + (0.03F_o)^2$. Scattering factors and anomalous-dispersion corrections for all atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). At convergence, the final $R = 0.079$, $wR = 0.097$, $S = 2.46$ and $\kappa = 2.79$ (2). Only two shifts/e.s.d.'s were greater than 0.1σ on the final cycle. Residual electron density in the final difference Fourier map was ± 0.24 e Å^{-3}, except for one peak of 0.76 e Å^{-3} near disordered atom C(30A).

Discussion. The refinement was complicated by disorder in both *tert*-pentyl groups. In one case, the ethyl group occupies either positions C(23) and C(24A) (Fig. 1a) or C(26) and (C24B) (Fig. 1b). In the second case, the entire *tert*-pentyl group occupies either position A (Fig. 1a) or B (Fig. 1b). The occupancy parameters were fixed at 0.5/0.5 for C(24A/B) and 0.7/0.3 for C(28A)–C(31A)/C(28B)–C(31B) from considerations of relative peak heights and temperature factors. Atom C(30A) did not refine well, so it was fixed at a calculated position in the final cycles of refinement.

Atomic positional and isotropic thermal parameters are listed in Table 1, and selected bond distances and bond angles are listed in Table 2.* The
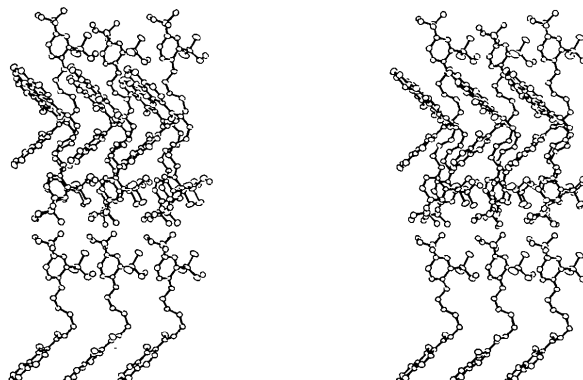
Fig. 2. Stereographic plot (100) of the molecular packing. The c axis is horizontal (left to right) and the b axis is vertical (top to bottom). The disordered atoms are illustrated here in the A positions.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$*
O(1)	0·9887 (3)	0·0622 (2)	0·0000	6·4 (1)
O(2)	0·9157 (4)	0·0002 (2)	0·1653 (4)	6·6 (1)
O(3)	0·6417 (4)	−0·2231 (1)	0·1983 (4)	5·96 (9)
N	0·7134 (4)	0·0013 (2)	0·2295 (4)	5·0 (1)
C(1)	0·8684 (5)	0·0833 (2)	−0·0030 (6)	4·6 (1)
C(2)	0·8453 (5)	0·1269 (2)	−0·0871 (5)	4·7 (1)
C(3)	0·9422 (6)	0·1505 (3)	−0·1551 (6)	6·3 (1)
C(4)	0·9164 (7)	0·1923 (3)	−0·2332 (7)	7·3 (2)
C(5)	0·7912 (8)	0·2123 (3)	−0·2480 (7)	8·1 (2)
C(6)	0·6937 (7)	0·1913 (3)	−0·1810 (6)	7·7 (2)
C(7)	0·7164 (5)	0·1489 (2)	−0·0993 (6)	5·6 (1)
C(8)	0·6190 (6)	0·1269 (3)	−0·0240 (7)	6·5 (2)
C(9)	0·6455 (6)	0·0861 (2)	0·0541 (6)	5·6 (1)
C(10)	0·7716 (5)	0·0639 (2)	0·0706 (6)	4·5 (1)
C(11)	0·8054 (5)	0·0202 (2)	0·1588 (6)	5·0 (1)
C(12)	0·7311 (6)	−0·0440 (2)	0·3139 (6)	5·4 (1)
C(13)	0·6697 (6)	−0·1011 (2)	0·2791 (6)	5·6 (1)
C(14)	0·7196 (5)	−0·1265 (2)	0·1682 (6)	5·3 (1)
C(15)	0·6366 (6)	−0·1742 (2)	0·1210 (6)	5·8 (1)
C(16)	0·5712 (5)	−0·2716 (2)	0·1709 (5)	4·6 (1)
C(17)	0·5866 (6)	−0·3204 (2)	0·2400 (6)	5·4 (1)
C(18)	0·5118 (6)	−0·3686 (2)	0·2132 (6)	6·4 (1)
C(19)	0·4263 (7)	−0·3717 (3)	0·1210 (7)	7·0 (2)
C(20)	0·4168 (6)	−0·3214 (3)	0·0552 (6)	6·1 (1)
C(21)	0·4876 (5)	−0·2726 (2)	0·0800 (6)	5·1 (1)
C(22)	0·6803 (7)	−0·3218 (3)	0·3421 (7)	7·5 (2)
C(23)	0·639 (1)	−0·2743 (3)	0·4345 (8)	10·9 (3)
C(24A)	0·524 (2)	−0·2899 (8)	0·475 (2)	9·8 (4)*
C(24B)	0·855 (2)	−0·3493 (8)	0·247 (2)	11·1 (5)*
C(25)	0·6783 (9)	−0·3838 (3)	0·4048 (8)	10·4 (2)
C(26)	0·8180 (7)	−0·3077 (4)	0·304 (1)	11·5 (3)
C(27)	0·3502 (9)	−0·4251 (4)	0·0952 (8)	10·8 (2)
C(28A)	0·332 (2)	−0·4387 (7)	−0·014 (2)	12·9 (5)*
C(28B)	0·436 (4)	−0·482 (1)	0·116 (3)	12 (1)*
C(29A)	0·453 (1)	−0·4578 (6)	−0·045 (1)	10·6 (4)*
C(29B)	0·509 (4)	−0·471 (1)	−0·011 (3)	11·3 (9)*
C(30A)	0·206	−0·408	0·109	15·5 (6)*
C(30B)	0·291 (4)	−0·444 (1)	0·185 (4)	13 (1)*
C(31A)	0·364 (1)	−0·4736 (5)	0·186 (1)	8·9 (3)*
C(31B)	0·236 (3)	−0·421 (1)	0·027 (2)	7·8 (6)*
H(N)	0·623 (5)	0·012 (2)	0·195 (6)	7(1)
H[O(1)]	1·017 (8)	0·031 (3)	0·041 (8)	12 (3)

*Starred atoms were refined isotropically.

Table 2. *Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

O(1)—C(1)	1·342 (5)	O(2)—C(11)	1·239 (5)
O(3)—C(15)	1·443 (6)	O(3)—C(16)	1·373 (5)
N—C(11)	1·336 (5)	N—C(12)	1·447 (6)
N—H(N)	1·05 (5)	O(2)—H(N)''	2·20 (5)*
C(1)—C(2)	1·425 (6)	C(1)—C(10)	1·396 (6)
C(2)—C(3)	1·392 (7)	C(2)—C(7)	1·439 (6)
C(3)—C(4)	1·353 (8)	C(4)—C(5)	1·391 (9)
C(5)—C(6)	1·368 (8)	C(6)—C(7)	1·383 (8)
C(7)—C(8)	1·434 (7)	C(8)—C(9)	1·336 (7)
C(9)—C(10)	1·420 (6)	C(10)—C(11)	1·482 (6)
C(12)—C(13)	1·516 (6)	C)13)—C(14)	1·512 (7)
C(14)—C(15)	1·502 (7)	C(16)—C(17)	1·392 (6)
C(16)—C(21)	1·372 (6)	C(17)—C(18)	1·390 (6)
C(17)—C(22)	1·540 (7)	C(18)—C(19)	1·397 (7)
C(19)—C(20)	1·393 (7)	C(19)—C(27)	1·492 (7)
C(20)—C(21)	1·375 (6)	C(22)—C(23)	1·595 (10)
C(22)—C(25)	1·602 (7)	C(22)—C(26)	1·535 (9)
C(23)—C(24A)	1·33 (2)	C(26)—C(24B)	1·23 (2)
C(27)—C(28A)	1·33 (2)	C(27)—C(28B)	1·60 (3)
C(27)—C(30A)	1·554 (10)	C(27)—C(30B)	1·29 (4)
C(27)—C(31A)	1·54 (1)	C(27)—C(31B)	1·43 (2)
C(28A)—C(29A)	1·38 (2)	C(28B)—C(29B)	1·69 (5)
O(1)—H[O(1)]	0·91 (8)	H[O(1)]—O(2)	1·93 (8)*
C(15)—O(3)—C(16)	117·9 (3)	C(11)—N—C(12)	124·3 (4)
C(11)—N—H(N)	109 (3)	C(12)—N—H(N)	123 (3)
O(1)—C(1)—C(2)	115·4 (4)	O(1)—C(1)—C(10)	122·7 (4)
C(2)—C(3)—C(4)	121·2 (5)	C(3)—C(4)—C(5)	120·3 (6)
C(4)—C(5)—C(6)	120·3 (6)	C(5)—C(6)—C(7)	121·1 (6)
C(2)—C(7)—C(6)	118·3 (5)	C(2)—C(7)—C(8)	118·2 (4)
C(6)—C(7)—C(8)	123·5 (5)	C(7)—C(8)—C(9)	121·4 (4)
C(2)—C(1)—C(10)	121·8 (4)	C(1)—C(2)—C(3)	123·0 (4)
C(1)—C(2)—C(7)	118·2 (4)	C(3)—C(2)—C(7)	118·7 (4)
C(8)—C(9)—C(10)	122·3 (5)	C(1)—C(10)—C(9)	117·9 (4)
C(1)—C(10)—C(11)	118·2 (3)	O(3)—C(15)—C(14)	108·7 (5)
O(3)—C(16)—C(17)	117·4 (4)	O(3)—C(16)—C(21)	122·1 (4)
C(17)—C(16)—C(21)	120·5 (4)	C(16)—C(17)—C(18)	116·7 (4)
C(16)—C(17)—C(22)	122·6 (4)	C(18)—C(17)—C(22)	120·7 (4)
C(17)—C(18)—C(19)	124·8 (5)	C(18)—C(19)—C(20)	115·2 (4)
C(18)—C(19)—C(27)	122·4 (5)	C(20)—C(19)—C(27)	122·4 (5)
C(19)—C(20)—C(21)	121·8 (5)	C(16)—C(21)—C(20)	121·0 (4)
C(17)—C(22)—C(23)	109·6 (5)	C(17)—C(22)—C(25)	111·4 (4)
C(17)—C(22)—C(26)	111·2 (6)	C(23)—C(22)—C(25)	107·4 (5)
C(23)—C(22)—C(26)	107·8 (6)	C(25)—C(22)—C(26)	109·5 (5)
O(2)—C(11)—N	120·2 (4)	O(2)—C(11)—C(10)	121·0 (4)
N—C(11)—C(10)	118·7 (3)	N—C(12)—C(13)	112·9 (4)
C(12)—C(13)—C(14)	114·8 (4)	C(13)—C(14)—C(15)	113·5 (4)
C(22)—C(23)—C(24A)	107·4 (8)	C(22)—C(26)—C(24B)	107 (1)
C(19)—C(27)—C(28A)	117·6 (9)	C(19)—C(27)—C(28B)	110 (1)
C(19)—C(27)—C(30A)	106·1 (6)	C(19)—C(27)—C(30B)	112 (2)
C(19)—C(27)—C(31A)	114·1 (6)	C(19)—C(27)—C(31B)	120 (1)
C(28A)—C(27)—C(30A)	91·4 (9)	C(28A)—C(27)—C(31A)	120 (1)
C(28B)—C(27)—C(30B)	82 (2)	C(28B)—C(27)—C(31B)	126 (2)
C(30A)—C(27)—C(31A)	101·7 (7)	C(30B)—C(27)—C(31B)	94 (2)
C(27)—C(28A)—C(29A)	101 (1)	C(27)—C(28B)—C(29B)	90 (2)
C(1)—O(1)—H[O(1)]	127 (5)	O(1)—H[O(1)]—O(2)	120 (6)*
C(11)—O(2)—H[O(1)]	109 (2)*	C(11)—O(2)—H(N)''	165 (1)*
H[O(1)]—O(2)—H(N)''	68 (3)*	N—H(N)—O(2)'	155 (4)*

*These bond lengths and angles involve the hydrogen bonds illustrated in Fig. 1.

orthorhombic unit cell contains four molecules. The molecules pack in (010) sheets that consist of two intertwined layers related by the *a* glide. This sheet structure, illustrated in the (100) stereographic plot in Fig. 2, effectively buries the naphthyl ends of the molecules within the sheet and exposes the *tert*-pentyl groups at the surfaces, where contact occurs with the adjacent sheets. The naphthyl rings are not coplanar, and there is little overlap between them. Intermolecular hydrogen bonds (2·20 Å; angles given in Table 2) exist between the carbonyl [O(2)] and the nitrogen [through H(N)''] of these *a*-glide-related molecules. This bonding results in polymeric ribbons along **a**. The hydrogen bonds, including the intramolecular O(1)—H[O(1)]···O(2) bond (1·93 Å; angles given in Table 2) are illustrated in Fig. 1. Adjacent molecules along **c** are related by the *c* glide (symmetry $\frac{3}{2} - x, y, \frac{1}{2} + z$).

References

FRENZ, B. A. (1985). *Enraf–Nonius SDP–Plus Structure Determination Package.* Version 1.1. Enraf-Nonius, Delft, The Netherlands.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

TEXTER, J. (1988). *J. Photogr. Sci.* **36**, 14–17.

TEXTER, J. (1991). In preparation.

TONG, L. K. J. (1977). *The Theory of the Photographic Process*, edited by T. H. JAMES, pp. 339–353. New York: Macmillan.

WHEELER, D. A. (1981). *Dispersion of Powders in Liquids*, edited by G. D. PARFITT, pp. 327–361. London: Applied Science Publishers.