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A Rhodinol Dye Derivative. 2-Chloro-6-(dimethylamino)-9-phenyl-3*H*-xanthen-3-one Methylene Chloride Solvate, $C_{21}H_{16}ClNO_2.CH_2Cl_2$

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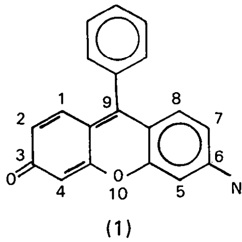
Abstract. $M_r = 434\cdot75$, monoclinic, $P2_1/c$, $a = 10\cdot237\,(2)$, $b = 9\cdot728\,(3)$, $c = 21\cdot329\,(2)$ Å, $\beta = 92\cdot83\,(1)^\circ$, $U = 2121$ Å^3, $Z = 4$, $D_m = 1\cdot35\,(1)$, $D_x = 1\cdot361$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0\cdot71069$ Å) $= 0\cdot45$ mm^{-1}, $F(000) = 896$, $T = 295\,(1)$ K, $R_F = 0\cdot081$, for 1871 reflections. The structure contains discrete $C_{21}H_{16}ClNO_2$ dye molecules arranged in two-dimensional sheets separated by protruding phenyl groups and disordered solvate molecules. Within each sheet, centrosymmetrically related dye molecules are separated by distances of 3·45 and 3·56 Å, and show two distinct types of overlap, one typical of ladder-type *H* aggregates and one typical of *J* or staircase aggregates.

Introduction. The present structural investigation was undertaken as part of a project designed to prepare new organic materials for photovoltaic cells. For effective devices, such materials should have high exciton mobility and a low probability for exciton degradation. According to current theory, the greatest exciton mobility will be achieved for molecules which pack as red-shifted *J*-aggregates [*i.e.* like a slipped deck of cards (Smith, 1974)], while energy dissipation *via* torsional



(1)

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photoisomerization may be avoided by using rigid, fully cyclized chromophores. With these considerations in mind, a series of rhodinol (1) dye derivatives, in which the phenyl substituent would act as an indexing group for *J*-aggregate formation, were prepared by condensation of the appropriately substituted resorcinol with 2-[4-(dimethylamino)-2-hydroxybenzoyl]benzoic acid, followed by decarboxylation of the resulting product (Sauers & Husain, 1983). We report here the structure of the 2-chloro-6-(dimethylamino) derivative.

Experimental. Crystals, grown by evaporation from methylene chloride, were supplied by Professor R. Sauers.

Crystal 0·3 × 0·4 × 0·7 mm, mounted in a glass capillary. Cell dimensions by least-squares fit of the setting angles of 15 reflections centered on a Syntex $P2_1$ diffractometer, graphite monochromator. With $Z = 4$ and the assumption of one solvate molecule per dye molecule, the observed ($ZnCl_2$ solution) and calculated densities agreed well.

θ–2θ scan ($4 < 2\theta < 45°$; $0 \le h \le 11$, $0 \le k \le 10$, $-22 \le l \le 22$); three standard reflections, recorded at 47-reflection intervals, decayed approximately 10% during data collection, presumably because of loss of solvate. 2701 unique reflections measured, 1871 with $F_o^2 > 2\sigma(F_o^2)$ considered observed and corrected for decay, Lp effects, and absorption ($1{\cdot}14 < A < 1{\cdot}16$). $\sigma(F^2) = (\mathrm{Lp})^{-1}[N_t + (0{\cdot}03\,N_n)^2]^{1/2}$, where N_t is the total count and N_n is the net count. Direct methods [*MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978)]; refinement on *F* by full-matrix least-squares techniques described previously (Hughey, Fawcett, Rudich, Lalancette, Potenza & Schugar, 1979). Neutral-atom scattering factors and anomalous-dispersion corrections for Cl (*International Tables for X-ray Crystallography*, 1974).

An *E* map based on 400 phases revealed all non-hydrogen atoms of the dye molecule and three possible sites for the two CH_2Cl_2 Cl atoms. Subsequent electron density maps confirmed that the solvate Cl atoms were indeed disordered. Attempts to refine the Cl atoms on the three sites isotropically led to unusually large temperature factors. Careful examination of electron density maps at this point revealed broad, double peaks at the three Cl sites, and a model consisting of three independent CH_2Cl_2 molecules, each of $\frac{1}{3}$ occupancy, was chosen to take this into account. Refinement using this model led to better agreement between observed and calculated structure factors, and to more reasonable temperature factors.

Following isotropic refinement, H atoms were added as described previously (Potenza, Johnson, Williams, Toby, Lalancette & Efraty, 1981), and not refined. The disordered C atom of the solvate molecule, C(22), was refined isotropically; all other atoms were refined anisotropically. Refinement with unit weights gave $R_F = 0{\cdot}081$, and $R_{wF} = 0{\cdot}097$. For the final cycle, $\Delta/\sigma < 0{\cdot}5$ where σ is the e.s.d. from the inverse matrix. Background $\Delta\rho$ in final difference map $= \pm 0{\cdot}25$ e Å^{-3}; the only peaks (0·4–0·6 e Å^{-3}) above background were within 0·8 Å of the disordered Cl atoms.

Discussion. Final atomic parameters are given in Table 1* and a sketch of the dye molecule, showing the atom-numbering scheme and bond distances and angles, is given in Fig. 1.

The structure contains discrete $C_{21}H_{16}ClNO_2$ dye molecules packed into layers and separated by CH_2Cl_2 solvate molecules and the protruding phenyl rings. Bond distances suggest that the dye exists in the solid state as an admixture of the quinoid form (1) and the zwitterion form (2), with the major contribution from form (1). Both the alternation of bond lengths in the C(1)—C(6) ring, a characteristic of quinone derivatives

Table 1. *Fractional atomic coordinates and isotropic thermal parameters*

Estimated standard deviations are given in parentheses. Equivalent isotropic temperature factors B_{eq}(Å^2) have been calculated by $B_{\mathrm{eq}} = (B_{11}a^{*2}a^2 + B_{12}a^*b^*\,ab\cos\gamma + \cdots)/3$.

	x	*y*	*z*	B_{eq}/B
Cl(1)	0·2363 (3)	0·0447 (3)	0·43129 (14)	5·48 (7)
O(1)	0·2366 (7)	−0·0478 (7)	0·5635 (3)	5·4 (2)
O(2)	0·5840 (6)	−0·3609 (7)	0·5565 (3)	4·3 (2)
N	0·9200 (8)	−0·6963 (9)	0·5650 (4)	5·3 (2)
C(1)	0·5133 (9)	−0·2443 (9)	0·4607 (4)	3·7 (2)
C(2)	0·4261 (10)	−0·1444 (10)	0·4327 (5)	4·1 (2)
C(3)	0·3387 (9)	−0·0785 (10)	0·4664 (4)	4·0 (2)
C(4)	0·3237 (10)	−0·1049 (10)	0·5339 (5)	4·2 (3)
C(5)	0·4142 (10)	−0·2021 (11)	0·5615 (5)	4·3 (2)
C(6)	0·5035 (9)	−0·2682 (10)	0·5256 (4)	3·7 (2)
C(7)	0·6739 (9)	−0·4351 (10)	0·5252 (4)	3·7 (2)
C(8)	0·7501 (10)	−0·5249 (10)	0·5608 (5)	4·3 (3)
C(9)	0·8451 (9)	−0·6052 (10)	0·5322 (5)	4·2 (3)
C(10)	1·0139 (11)	−0·7877 (12)	0·5336 (6)	6·2 (3)
C(11)	0·9128 (13)	−0·7111 (14)	0·6322 (6)	7·2 (4)
C(12)	0·8592 (10)	−0·5859 (11)	0·4672 (5)	4·6 (3)
C(13)	0·7804 (10)	−0·4966 (11)	0·4330 (5)	4·5 (3)
C(14)	0·6838 (9)	−0·4170 (10)	0·4600 (4)	3·8 (2)
C(15)	0·6011 (9)	−0·3218 (10)	0·4274 (5)	3·9 (2)
C(16)	0·6089 (10)	−0·3091 (10)	0·3580 (5)	4·2 (3)
C(17)	0·6647 (11)	−0·1953 (12)	0·3312 (5)	5·4 (3)
C(18)	0·6757 (13)	−0·1866 (14)	0·2676 (5)	6·5 (4)
C(19)	0·6284 (13)	−0·292 (2)	0·2285 (5)	6·8 (4)
C(20)	0·5729 (14)	−0·408 (2)	0·2556 (6)	7·7 (4)
C(21)	0·5636 (13)	−0·4150 (13)	0·3198 (6)	6·6 (4)
Cl(3*A*)	0·9930 (7)	0·0419 (7)	0·2863 (3)	4·2 (2)
Cl(4*A*)	0·7962 (7)	0·2778 (8)	0·2870 (3)	4·5 (2)
Cl(2*B*)	1·0564 (6)	0·2889 (7)	0·3483 (3)	3·7 (2)
Cl(4*B*)	0·7611 (9)	0·2246 (10)	0·2832 (4)	5·8 (2)
Cl(2*C*)	1·0195 (9)	0·3008 (9)	0·3309 (4)	5·7 (2)
Cl(3*C*)	0·9461 (8)	0·0302 (8)	0·2879 (4)	4·7 (2)
C(22*A*)	0·925 (3)	0·191 (3)	0·328 (1)	5·2 (7)
C(22*B*)	0·915 (3)	0·160 (4)	0·327 (1)	5·8 (8)
C(22*C*)	0·877 (4)	0·176 (4)	0·332 (1)	6·7 (9)

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* Lists of anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38599 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

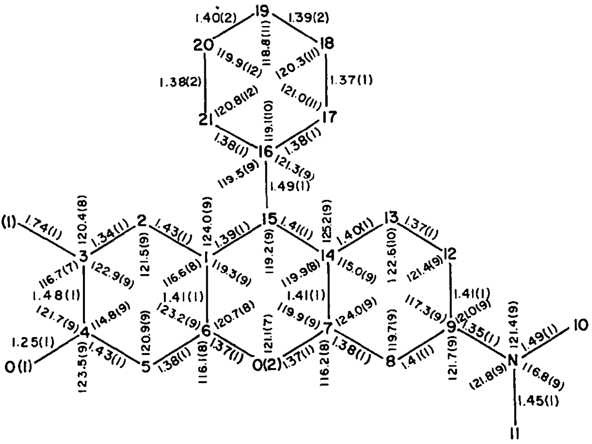
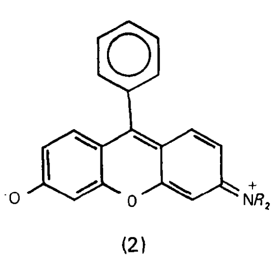


Fig. 1. The title complex showing the atom-numbering scheme and bond distances (Å) and angles (°). Additional distances are: Cl(3*A*)–C(22*A*), 1·85 (3); Cl(4*A*)–C(22*A*), 1·76 (3); Cl(2*B*)–C(22*B*), 1·95 (3); Cl(4*B*)–C(22*B*), 1·90 (3); Cl(2*C*)–C(22*C*), 1·90 (4); Cl(3*C*)–C(22*C*), 1·86 (4) Å.

(Desiraju, Paul & Curtin, 1977), and the C(4)—O(1) bond length, which lies within experimental error of the C=O bond distances reported for several quinones [1·221 (2) Å; Hanson, 1977; 1·2350 (6) Å; Semmingsen, 1977], support a major contribution from form (1). On the other hand, the C(9)—N distance is shorter than the C(aromatic)—N(amine) single-bond distances reported for 1,8-bis(dimethylamino)naphthalene [1·396 (8), 1·399 (8) Å; Einspahr, Robert, Marsh & Roberts, 1973] and for two anilino derivatives of thiazole [1·405 (4), 1·399 (5) Å; Declercq, Germain, Touillaux, Van Meerssche, Henriet & Ghosez, 1981], suggesting some contribution from form (2). In general, rhodinol and related merocyanine dyes are characterized by large dipole moments, consistent with some contribution from the zwitterionic form, and by solvent-sensitive spectra which have been interpreted in terms of varying admixtures of quinoid and zwitterionic forms (Platt, 1956; Brooker, Craig, Heseltine, Jenkins & Lincoln, 1965).



(2)

In the dye, the tricyclic fragment [O(2), C(1)–C(9), C(12)–C(15)] is planar with an average deviation of ±0·018 Å from the least-squares plane. The phenyl group (planar to ±0·004 Å) is twisted substantially from this plane [phenyl, tricyclic dihedral angle 72·8 (9)°] suggesting little conjugation between these groups. The N atom deviates only slightly (–0·016 Å) from the tricyclic-fragment plane while Cl(1) shows a much larger deviation (0·062 Å). A bowing of the quinoid moiety [C(1)–C(6), O(1)] is evident from the rather large deviations of O(1) and C(4) from the tricyclic-fragment plane (–0·140 and –0·045 Å, respectively); bowing effects of this magnitude have been reported previously for other quinoid structures (Desiraju *et al.*, 1977). Finally, the methyl C atoms deviate in opposite directions from the tricyclic-fragment plane and the dimethylamino plane [N, C(10), C(11)] makes an angle of 4·2 (9)° with that of the tricyclic fragment.

As shown in Fig. 2, the dye molecules are arranged in two-dimensional sheets perpendicular to **c**. Adjacent sheets are related by the glide-plane operation and are separated by protruding phenyl groups. The CH_2Cl_2 solvate molecules lie between the dye layers, and the disordered methylene chloride C atoms [C(22*A*)–C(22*C*)] show distances to O(1′) of 2·85 (3), 3·07 (3) and 3·23 (3) Å.

Within each sheet, adjacent dye molecules are related in a 'head to tail' arrangement by centers of symmetry, while every other molecule is related by cell translations along **a** or **b**. In a given sheet, the dye molecules are stacked in two non-equivalent ways (Fig. 3). One pair is separated by an interplanar spacing of 3·45 Å and shows extensive overlap between the tricyclic fragments. The remaining pair is separated by a slightly larger interplanar distance (3·56 Å) and shows substantially less overlap. Interplanar spacings of 3·3–3·6 Å are common for dye structures (Smith, 1974).

The overlap depicted in Fig. 3(*a*) is typical of *H* or 'ladder-type' aggregates, while that in Fig. 3(*b*) is

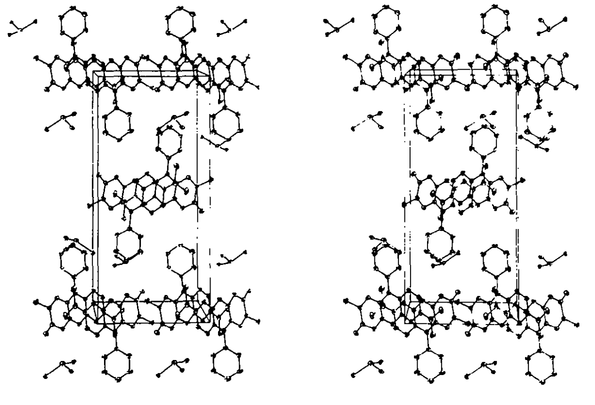


Fig. 2. *ORTEP* view (Johnson, 1965) of the unit-cell contents along **a*** showing the sheet structure. The *c* axis is vertical.

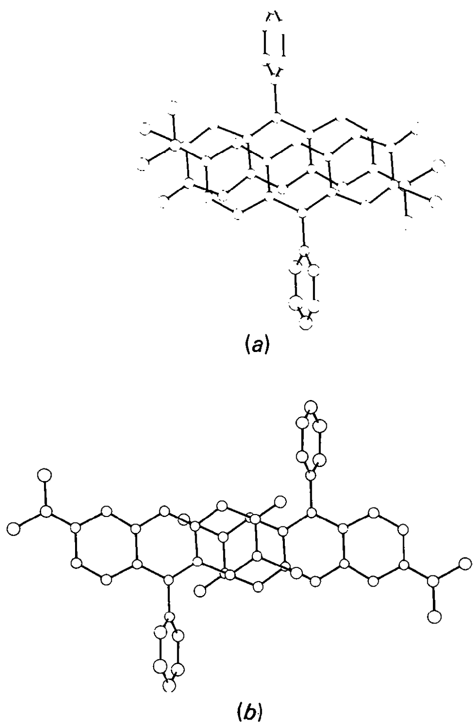


Fig. 3. The relative orientation of centrosymmetrically related dye molecules. (*a*) The molecule with coordinates *x,y,z* shown above that with coordinates $1-x$, $-1-y$, $1-z$. (*b*) The molecule with coordinates $1-x$, $-y$, $1-z$ above that with coordinates *x,y,z*.

characteristic of *J* or staircase aggregates. Thus, the present structure may be described as a combination of both types. The protruding phenyl group has caused separation of the dye layers, but has not entirely prevented the extensive overlap of pairs of dye molecules characteristic of *H* aggregates. Further, because of its size and twist relative to the dye plane, the phenyl ring yields gaps in the structure which are available to be filled by solvent molecules. A structure containing solvent molecules is not a favored candidate for photovoltaic applications since loss of solvent is expected to have the same effect on conductivity as a disordering phase transition. To prevent both solvation and mixed-aggregate formation, slightly smaller out-of-plane substituents at both the 9 and 10 positions are suggested.

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Structures of 1,3-Dicyclohexyl-1-(1*H*-indol-3-ylacetyl)urea, $C_{23}H_{31}N_3O_2$ (I), and 3-Cyclohexyl-1-[2-(1*H*-indol-3-yl)ethyl]urea, $C_{17}H_{23}N_3O$ (II)

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(*Received* 21 *April* 1983; *accepted* 1 *June* 1983)

Abstract. (I): $M_r = 381{\cdot}5$, $P2_1/a$, $a = 9{\cdot}527\,(2)$, $b = 21{\cdot}437\,(5)$, $c = 11{\cdot}046\,(3)$ Å, $\beta = 92{\cdot}05\,(4)°$, $V = 2254\,(1)$ Å^3, $Z = 4$, $D_m = 1{\cdot}123\,(1)$, $D_x = 1{\cdot}124$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu(\text{Cu } K\alpha) = 5{\cdot}39$ cm^{-1}, $F(000) = 824$, $T = 294$ K, R and $R_w = 0{\cdot}084$ and $0{\cdot}105$ for 3418 non-zero reflections. (II):

0108-2701/83/091294-04$01.50