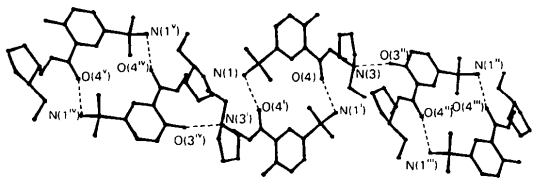


Fig. 2. Représentation de l'enchaînement des feuillets.

la fonction méthoxy amène les doublets de l'oxygène de part et d'autre de ce plan. Il en résulte deux possibilités pour l'établissement de la liaison hydrogène intramoléculaire, ce qui n'est pas sans répercussion sur la chaîne latérale de la molécule. Ceci explique sans doute le désordre rencontré dans cette zone de la molécule de sulpiride.

Des études complémentaires sur des composés de la même famille sont nécessaires pour confirmer ces résultats: c'est dans cette direction que s'orientent actuellement nos travaux.

Nous tenons à exprimer notre gratitude aux Laboratoires Delagrange qui ont mis à notre disposition les échantillons de métabolite nécessaires à cette étude. Nos remerciements vont également à l'Institut de Chimie Pharmaceutique de Lille qui nous a aidés à réaliser ce travail.

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# Structure of Bilirubin IXα (Isopropylammonium Salt) Chloroform Solvate, $C_{33}H_{34}N_4O_6^{2-}.2C_3H_{10}N^+.2CHCl_3$

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**Abstract.** $M_r = 941{\cdot}7$, monoclinic, $I2/c$, $a = 19{\cdot}952\ (2)$, $b = 12{\cdot}867\ (1)$, $c = 18{\cdot}941\ (2)$ Å, $\beta = 96{\cdot}09\ (1)°$, $V = 4835{\cdot}1\ (8)$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}289$, $D_x = 1{\cdot}293$ Mg m$^{-3}$, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 3{\cdot}71$ mm$^{-1}$, $F(000) = 1976$, room temperature. Final $R = 0{\cdot}067$ for 1951 observed reflections. The bile pigment (ridge-tile shaped, with *syn-Z* configurated lactamic oxodipyrromethenes) is in the salt form and its conformation is stabilized by intra- and intermolecular hydrogen bonds with the isopropylammonium cations and the molecules of chloroform. The torsion angles along the propionic chains are very different from those found in bilirubin itself and in related compounds. The chloroform molecules and the methyl and vinyl groups in rings *A* and *D* of the bilirubinate dianion are affected by disorder.

**Introduction.** A valuable point of interest concerned with the structure of bile pigments, particularly bilirubin (1) is the type of their bonding with albumin and other proteins which act as carriers of the pigment in the human organism (Brodersen, 1979); thermochemical and kinetic results obtained by Jacobsen (1977) were in favour of hydrogen bonds and salt linkages. On the other hand the crystal structures of bilirubin itself (Bonnett, Davies & Hursthouse, 1976; Bonnett, Davies, Hursthouse & Sheldrick, 1978) and of its chloroform–methanol solvate (Le Bas, Allegret & de Rango, 1977; Le Bas, Allegret, Mauguen, de Rango & Bailly, 1980) do not seem to suggest an answer, all the hydrogen bonds being intramolecular. Therefore it seemed to us worthwhile to study the structure of a complex of the bile pigment with a low-weight amine, as

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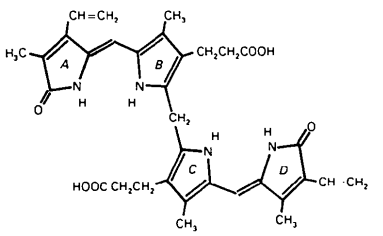
a model for the bilirubin–protein associations. A brief report of our findings has already been published (Mugnoli, Manitto & Monti, 1978). The refinement has since been completed and the final results are reported here.




(1)

**Experimental.** $D_m$ measured by flotation. Orange needle [from isomerically pure bilirubin IXα (1) in chloroform containing 1% isopropylamine], $0{\cdot}32 \times 0{\cdot}29 \times 0{\cdot}25$ mm, sealed in thin glass capillary. Philips PW 1100 diffractometer, graphite-monochromatized Cu $K\alpha$. Cell dimensions from a least-squares fit for 40 reflections ($\theta$ range 5 to 47°). 3130 unique $\pm hkl$ with $\theta < 56°$, $h$ −20–20, $k$ 0–13, $l$ 0–20, 1951 with $F \geq 4\sigma(F)$. Lp correction. Three standard reflections, overall decay 4%. Systematic absences observed in agreement with space groups *Ic* and *I2/c*.

$Z$ being 4, and because of the anticipated lack of molecular symmetry, the structure was solved in space group *Ic*, based on its four general equivalent positions. Direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) allowed most of the non-H atoms of the asymmetric unit (one molecule of bilirubin, two of chloroform and two of isopropylamine) to be recognized. The terminal C atoms of both the vinyl groups were amongst the missing atoms. Block-diagonal and then full-matrix isotropic least squares process on $F$ led, however, to awkward values for many geometrical parameters; difference Fourier syntheses showed just very low peaks near the positions expected for the second C atom of both vinyl groups, whereas a region of positive electron density was found near the methyl groups of rings *A* and *D*. Therefore, and in agreement with observed statistics over several functions of $|E|$, we moved to the corresponding centrosymmetric space group *I2/c*,* by assuming a crystallographic twofold axis of symmetry running through atom C(10) of the bilirubin moiety (this being allowed by the relative positions and orientations found for the molecules of isopropylamine and of chloroform) and by locating two terminal C atoms, both with a site occupancy of 50%, close to atoms C(11) and C(12) respectively. After translation of the whole structure to put atom C(10) at $\frac{1}{2}$, $y$, $\frac{1}{4}$, the refinement was started again by isotropic, and then anisotropic full-matrix least squares. Soon a splitting of the terminal atom bonded to C(12) was observed in $\Delta F$ maps. Apart from the region involving the disordered C atoms, the overall geometry became quite reasonable; the $R$ index fell to 0·09. The convergence, however, was slow; moreover, in subsequent cycles the anisotropic temperature factors for the three Cl atoms became markedly large, suggesting some rotational disorder of the chloroform molecule.

Last part of refinement performed using *SHELX*76 (G. M. Sheldrick, 1976). Starting from some residual peaks found on $\Delta F$ maps, splitting of each Cl atom over two positions assessed. Refinement continued by considering the six split Cl atoms as isotropic and then anisotropic, with one site-occupation factor (s.o.f.) as single free variable for Cl(1), Cl(2), Cl(3), and its difference from unity for Cl′(1), Cl′(2) and Cl′(3). Bond-length constraints applied to C—Cl and C—Cl′ distances. S.o.f. of C(111) (see Fig. 1*a*) held fixed at 0·50, those of C(121) and C(122) constrained so that their sum was 0·50. H atoms (from $\Delta F$ syntheses) included in $F_c$ with $U(\mathrm{H}) = U_{eq.}$ of bonded atom. Final $R = 0{\cdot}067$, $R_w = 0{\cdot}084$, $S = 1{\cdot}6$; $w = 1/\sigma^2$. Shifts < corresponding e.s.d.'s. In final $\Delta F$ synthesis $\rho$ between 0·32 and −0·28 e Å$^{-3}$.

**Discussion** Final parameters of the heavier atoms are listed in Table 1.* Fig. 1 shows the three fragments of the asymmetric unit with the atom numbering. Bond distances and bond angles are collected in Table 2. Molecular parameters have been calculated by means of the program *PARST* (Nardelli, 1982).

The structure of the complex corresponds to the salt of the bilirubin dianion with two isopropylammonium cations, in the presence of solvate molecules of chloroform. In fact the C(16)—O(2) and C(16)—O(3) bond distances, 1·267 (7) and 1·265 (7) Å respectively, correspond to values expected for a carboxylate ion; moreover, all the three H atoms bonded to N(3) have been localized through $\Delta F$ maps.

The bilirubin moiety is present in the typical *syn-Z* configuration (see Figs. 1*a* and 2), as found in pure bilirubin IXα (Bonnett *et al.*, 1976; Bonnett *et al.*, 1978), in bilirubin chloroform–methanol solvate (Le Bas *et al.*, 1977; Le Bas *et al.*, 1980), in mesobilirubin chloroform solvate (Becker & Sheldrick, 1978) and in diethoxybilirubin diethyl ester (Sheldrick & Becker, 1979). Atoms C(1) to C(10), O(1), N(1), N(2) lie on a plane within 0·04 Å. The whole bilirubin dianion is

* General equivalent positions: (0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) + $x, y, z$; $-x, -y, -z$; $-x, y, \frac{1}{2}-z$; $x, -y, \frac{1}{2}+z$. The corresponding conventional space group $C2/c$ would imply an angle $\beta = 130{\cdot}3°$.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38598 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) *of the non-H atoms with e.s.d.'s in parentheses*

The s.o.f. values are unitary for all atoms, except for the following: C(10) 0·50, C(111) 0·50, C(121) 0·35 (1), C(122) 0·15 (1), Cl 0·485 (6), Cl′ 0·515 (6).

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| C(1) | 7105 (3) | 9851 (5) | 4332 (4) | 70 (3) |
| C(2) | 7674 (3) | 10343 (4) | 4029 (4) | 66 (2) |
| C(3) | 7669 (3) | 9989 (4) | 3361 (3) | 63 (2) |
| C(4) | 7114 (3) | 9263 (4) | 3208 (3) | 56 (2) |
| C(5) | 6960 (3) | 8740 (4) | 2596 (3) | 55 (2) |
| C(6) | 6461 (3) | 8017 (4) | 2333 (3) | 51 (2) |
| C(7) | 6391 (3) | 7575 (4) | 1655 (3) | 52 (2) |
| C(8) | 5825 (3) | 6911 (4) | 1602 (3) | 46 (2) |
| C(9) | 5569 (3) | 6943 (4) | 2253 (3) | 50 (2) |
| C(10) | 5000 | 6344 (6) | 2500 | 60 (3) |
| C(11) | 8144 (3) | 11089 (5) | 4412 (4) | 97 (2) |
| C(111) | 8076 (6) | 11516 (10) | 4944 (7) | 91 (3) |
| C(12) | 8151 (3) | 10254 (6) | 2832 (3) | 91 (2) |
| C(121) | 8484 (11) | 10939 (17) | 2885 (11) | 110 (5) |
| C(122) | 8077 (23) | 11147 (34) | 2706 (23) | 110 (5) |
| C(13) | 6840 (3) | 7764 (5) | 1084 (3) | 71 (3) |
| C(14) | 5564 (3) | 6286 (4) | 967 (3) | 58 (2) |
| C(15) | 4854 (3) | 6609 (4) | 632 (3) | 56 (2) |
| C(16) | 4805 (3) | 7771 (4) | 541 (3) | 56 (2) |
| C(17) | 4039 (3) | 7021 (6) | 6011 (4) | 89 (2) |
| C(18) | 5994 (3) | 9644 (5) | 6291 (3) | 67 (2) |
| C(19) | 5441 (4) | 9733 (7) | 6735 (4) | 122 (4) |
| C(20) | 6352 (4) | 8625 (6) | 6357 (4) | 113 (4) |
| N(1) | 6790 (2) | 9216 (4) | 3818 (3) | 63 (2) |
| N(2) | 5954 (2) | 7614 (3) | 2690 (2) | 50 (2) |
| N(3) | 5756 (2) | 9824 (3) | 5534 (3) | 69 (2) |
| O(1) | 6931 (2) | 9962 (4) | 4936 (2) | 90 (2) |
| O(2) | 5141 (2) | 8214 (3) | 96 (2) | 65 (2) |
| O(3) | 4416 (2) | 8268 (3) | 905 (2) | 79 (2) |
| Cl(1) | 3775 (5) | 7978 (7) | 6579 (5) | 148 (3) |
| Cl(2) | 3308 (3) | 6322 (6) | 5720 (4) | 119 (2) |
| Cl(3) | 4721 (5) | 6341 (8) | 6450 (4) | 147 (3) |
| Cl′(1) | 3619 (5) | 7955 (7) | 6400 (5) | 158 (3) |
| Cl′(2) | 3615 (5) | 5924 (5) | 5781 (4) | 155 (3) |
| Cl′(3) | 4684 (4) | 6633 (8) | 6593 (6) | 180 (3) |

Table 2. *Bond distances* (Å) *and angles* (°) *with their e.s.d.'s*

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·469 (9) | C(3)–C(12) | 1·500 (8) |
| C(2)–C(3) | 1·344 (9) | C(12)–C(121) | 1·10 (3)* |
| C(3)–C(4) | 1·454 (8) | C(12)–C(122) | 1·18 (4)* |
| C(4)–N(1) | 1·384 (8) | C(7)–C(13) | 1·496 (8) |
| C(1)–N(1) | 1·371 (9) | C(8)–C(14) | 1·494 (8) |
| C(4)–C(5) | 1·347 (8) | C(14)–C(15) | 1·546 (8) |
| C(5)–C(6) | 1·414 (8) | C(15)–C(16) | 1·507 (7) |
| C(6)–C(7) | 1·398 (8) | C(1)–O(1) | 1·239 (8) |
| C(7)–C(8) | 1·411 (8) | C(16)–O(2) | 1·267 (7) |
| C(8)–C(9) | 1·384 (8) | C(16)–O(3) | 1·265 (7) |
| C(9)–N(2) | 1·373 (7) | C(17)–Cl | 1·75 (1)* |
| C(6)–N(2) | 1·376 (7) | C(17)–Cl′ | 1·68 (1)* |
| C(9)–C(10) | 1·488 (7) | C(18)–C(19) | 1·46 (1)* |
| C(2)–C(11) | 1·477 (9) | C(18)–C(20) | 1·49 (1)* |
| C(11)–C(111) | 1·17 (2)* | C(18)–N(3) | 1·480 (8) |

| | | | |
|---|---|---|---|
| C(1)–C(2)–C(3) | 107·0 (5) | C(6)–C(7)–C(13) | 126·1 (5) |
| C(2)–C(3)–C(4) | 109·6 (5) | C(8)–C(7)–C(13) | 125·7 (5) |
| C(3)–C(4)–N(1) | 106·0 (5) | C(7)–C(8)–C(14) | 126·2 (5) |
| C(4)–N(1)–C(1) | 110·3 (5) | C(9)–C(8)–C(14) | 127·1 (5) |
| N(1)–C(1)–C(2) | 107·1 (6) | C(8)–C(9)–C(10) | 129·1 (5) |
| N(1)–C(1)–O(1) | 124·9 (6) | C(9)–C(10)–C(9$^{i}$) | 117·6 (6)† |
| C(2)–C(1)–O(1) | 128·0 (6) | N(2)–C(9)–C(10) | 122·2 (5) |
| C(1)–C(2)–C(11) | 124·4 (7) | N(2)–C(6)–C(5) | 127·0 (5) |
| C(3)–C(2)–C(11) | 128·6 (6) | C(8)–C(14)–C(15) | 114·3 (5) |
| C(2)–C(11)–C(111) | 127 (1)* | C(14)–C(15)–C(16) | 111·0 (5) |
| C(2)–C(3)–C(12) | 127·6 (5) | C(15)–C(16)–O(2) | 119·3 (5) |
| C(4)–C(3)–C(12) | 122·8 (5) | C(15)–C(16)–O(3) | 118·4 (5) |
| C(3)–C(12)–C(121) | 123 (1)* | O(2)–C(16)–O(3) | 122·3 (5) |
| C(3)–C(12)–C(122) | 10o (2)* | Cl(1)–C(17)–Cl(2) | 105 (1)* |
| C(3)–C(4)–C(5) | 126·3 (5) | Cl(2)–C(17)–Cl(3) | 118 (1)* |
| N(1)–C(4)–C(5) | 127·8 (5) | Cl(3)–C(17)–Cl(1) | 109 (1)* |
| C(4)–C(5)–C(6) | 136·0 (6) | Cl′(1)–C(17)–Cl′(2) | 117 (1)* |
| C(5)–C(6)–C(7) | 126·1 (5) | Cl′(2)–C(17)–Cl′(3) | 105 (1)* |
| C(6)–C(7)–C(8) | 108·2 (5) | Cl′(3)–C(17)–Cl′(1) | 108 (1)* |
| C(7)–C(8)–C(9) | 106·7 (5) | C(19)–C(18)–C(20) | 114 (1)* |
| C(8)–C(9)–N(2) | 108·7 (5) | C(19)–C(18)–N(3) | 111 (1)* |
| C(9)–N(2)–C(6) | 109·5 (4) | C(20)–C(18)–N(3) | 109 (1)* |
| N(2)–C(6)–C(7) | 106·9 (5) | | |

* See text.
† See Fig. 2.

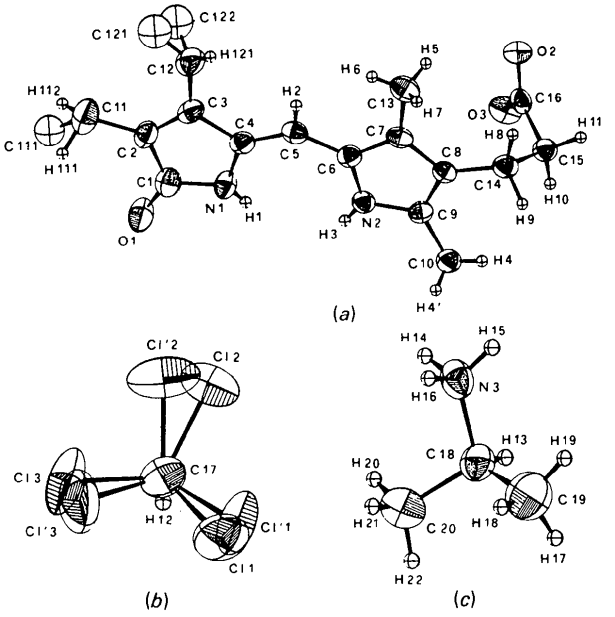



Fig. 1. (*a*) The oxodipyrromethene anion. (*b*) The chloroform molecule in the two different orientations. (*c*) The isopropylammonium cation. Drawings (*b*) and (*c*) are on the same scale. Thermal ellipsoids are drawn at 0·30 probability level. H atoms are on an arbitrary scale.

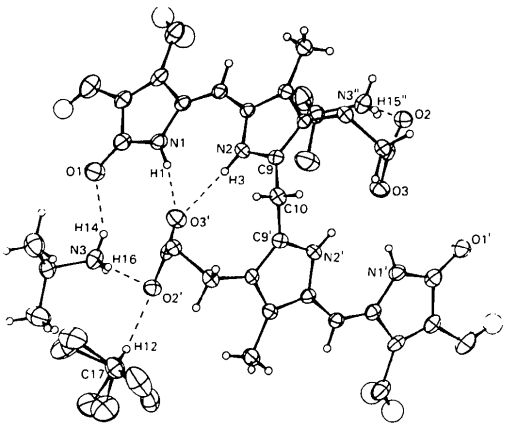



Fig. 2. The six crystallographically independent inter- and intramolecular hydrogen bonds in the complex (dashed lines), as viewed at a 5° tilt from the (vertical) twofold axis through atom C(10). Equivalent positions are: (i) $1-x, y, \frac{1}{2}-z$; (ii) $x, 2-y, -\frac{1}{2}+z$. For clarity, some H atoms not involved in hydrogen bonds have been omitted.

ridge-tile shaped with a dihedral angle of 97·2 (3)°, the torsion angle N(2)—C(9)—C(10)—C(9$^{i}$) (Fig. 2) being 60·8 (8)°.

The oxodipyrromethene fragment is in the lactam form, from the experimental location of atom H(1) and the typical C(1)—O(1) bond length of 1·24 (1) Å. The tight intramolecular contact H(1)···H(3) (2·39 Å) accounts, at least in part, for the very large C(4)—C(5)—C(6) bond angle [136·0 (6)°]. A value of 132·11 (4)° has been found in 3,4-dimethyl-2,2′-pyrromethen-5(1*H*)-one (Cullen, Pèpe, Meyer, Falk & Grubmayr, 1979) and of 133·3 (9)° in another 5(1*H*)-pyrromethenone (Cullen, Black, Meyer, Lightner, Quistad & Pak, 1977). The methyl and vinyl groups of rings *A* and *D* (1) are disordered; in the asymmetric unit they are both linked to atoms C(11) and C(12). The terminal C atom of a vinyl group is further split over two positions: C(121) and C(122) in Fig. 1(*a*). Similar features were observed in the bilirubin chloroform–methanol solvate (Le Bas *et al.*, 1980) and in the dimethyl ester of biliverdin IXα (W. S. Sheldrick, 1976). In the last compound, as in the present one, very short bond distances involving the disordered C atoms have been found.*

The chloroform molecule is affected by rotational disorder, even if to a lesser extent than that found in the bilirubin chloroform–methanol solvate. In the present compound the Cl s.o.f. value refined to 0·485 (6), and the C(17)—Cl and C(17)—Cl′ bond lengths to 1·75 (1) and 1·68 (1) Å respectively. Values corrected for riding motion range from 1·74 to 1·81 Å. Disorder on one chloroform molecule was noticed even in the crystal structure of mesobilirubin chloroform solvate (Becker & Sheldrick, 1978). In the present complex some rotational disorder is probably present even around the N(3)—C(18) bond of the isopropylammonium ion, owing to the high anisotropic temperature factor components for C(19) and C(20).

As one of its more interesting results, the present crystal-structure determination describes the bilirubin molecule in the salt form. Moreover, the pattern of hydrogen bonds is quite different from that found in related compounds having a ridge-tile conformation. Whereas in bilirubin itself (compound *A*; Bonnett *et al.*, 1978) and in bilirubin chloroform–methanol solvate (compound *B*; Le Bas *et al.*, 1980) all the hydrogen bonds are intramolecular, as are most of those in mesobilirubin chloroform solvate (compound *C*; Becker & Sheldrick, 1978),† in the present complex there are only four intramolecular hydrogen bonds, each of the carboxylic 'external' O atoms, O(2) and O(2)′, being engaged in two hydrogen bonds with two isopropylammonium ions and in a third with the C atom of a chloroform molecule.* Correspondingly a different sequence of torsion angles along the propionic chain can be observed. The relevant values for the considered compounds are compared in Table 3, where for each torsion the average over four values (for compound *A*) or over two values (for compounds *B* and *C*) is reported. Whereas each of the considered angles has essentially the same value in compounds *A*, *B* and *C*, striking differences are observed by comparison with the present compound, where all the three torsion angles are (+)-synclinal (Klyne & Prelog, 1960) and the first one in particular deviates by nearly 180° from the other values in the same row. This result indeed should be referred back to the effect of intermolecular hydrogen bonds between the carboxylate anion and the cation and chloroform. Even the O(1) atom is strongly hydrogen-bonded with an isopropylammonium ion (rather than with the carboxyl group, as in compounds *A*, *B* and *C*).

This complex therefore conforms to the predictions of Jacobsen (1977) for bilirubin–protein interactions and could be considered as a model for the complex formed by the pigment in the biological system. The pattern of the hydrogen bonds is shown in the thermal-ellipsoid plot (Johnson, 1965) of Fig. 2; the relevant distances and angles are reported in Table 4.

Aside from the previously described hydrogen contacts and from contacts involving disordered atoms, there are only a few non-bonding distances remarkably shorter than the sum of the van der Waals radii concerned (Pauling, 1960): C(4)···C(13)($\frac{3}{2}-x$, $\frac{3}{2}-y$, $\frac{1}{2}-z$) 3·516 (8); C(8)···C(12)($\frac{3}{2}-x$, $\frac{3}{2}-y$, $\frac{1}{2}-z$) 3·552 (9); C(11)···C(20)($\frac{3}{2}-x$, $\frac{1}{2}+y$, $1-z$) 3·754 (10); C(12)···C(14)($\frac{3}{2}-x$, $\frac{3}{2}-y$, $\frac{1}{2}-z$) 3·800 (9); C(19)···C(19)($1-x$, $y$, $\frac{3}{2}-z$) 3·546 (11) Å.

* Still shorter C—C bond lengths have been reported for three ethyl groups in 3,8,12,17-tetraethyl-4,5-dimethoxy-2,7,13,18-tetramethyl-4,5-dihydrobilin-1,19(21*H*,24*H*)-dione (Cullen, Van Opdenbosch, Meyer, Smith & Eivazi, 1982).

† Short intermolecular contacts between the lactam O atoms and the chloroform C atoms are present in compound *C*.

* Such a type of hydrogen bond from a C atom has been reviewed by Green (1974).

Table 3. *Torsion angles* (°) *along the propionic chain*

Values of chemically equivalent torsion angles have been averaged. The labelling of atoms is that adopted in this work.

| | Compound *A* | Compound *B* | Compound *C* | This work |
|---|---|---|---|---|
| C(9)–C(8)–C(14)–C(15) | −122·0 | −114·0 | −118·9 | 65·7 (8) |
| C(8)–C(14)–C(15)–C(16) | 70·2 | 68·3 | 70·4 | 47·3 (7) |
| C(14)–C(15)–C(16)–O(2) | −171·7 | −173·5 | −170·6 | 67·7 (7) |
| Average e.s.d. | 2·7 | 1·3 | 1·0 | |

Table 4. *Geometry of hydrogen bonds*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N(1)—H(1)···O(3$^{i}$) | 0·81 Å | 2·01 Å | 2·797 (6) Å | 165·6° |
| N(2)—H(3)···O(3$^{i}$) | 0·84 | 2·13 | 2·958 (6) | 173·4 |
| N(3)—H(14)···O(1) | 0·83 | 1·98 | 2·716 (6) | 148·1 |
| N(3$^{ii}$)—H(15$^{ii}$)···O(2) | 0·81 | 2·08 | 2·890 (6) | 174·6 |
| N(3)—H(16)···O(2$^{i}$) | 0·79 | 2·12 | 2·910 (6) | 172·5 |
| C(17)—H(12)···O(2$^{i}$) | 0·83 | 2·36 | 3·187 (8) | 170·1 |

Equivalent positions: (i) $1-x$, $y$, $\frac{1}{2}-z$; (ii) $x$, $2-y$, $-\frac{1}{2}+z$.

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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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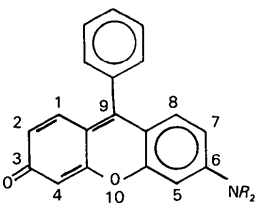
**Abstract.** $M_r = 434{\cdot}75$, monoclinic, $P2_1/c$, $a = 10{\cdot}237\ (2)$, $b = 9{\cdot}728\ (3)$, $c = 21{\cdot}329\ (2)$ Å, $\beta = 92{\cdot}83\ (1)°$, $U = 2121$ Å$^3$, $Z = 4$, $D_m = 1{\cdot}35\ (1)$, $D_x = 1{\cdot}361$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å) = $0{\cdot}45$ mm$^{-1}$, $F(000) = 896$, $T = 295\ (1)$ K, $R_F = 0{\cdot}081$, 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

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