References

BRATAN-MAYER, S., STROHBUSCH, F. & HÄNSEL, W. (1976). *Z. Naturforsch. Teil B*, **31**, 1106–1115.

DEWAR, M. J. S. & SCHMEISING, H. N. (1960). *Tetrahedron*, **11**, 96–120.

FAYOS, J. & MARTÍNEZ-RIPOLL, M. (1975). *HSEARCH* program. Instituto 'Rocasolano', CSIC, Serrano 119, Madrid 6, Spain.

GRADNIK, R. & FLEISCHMANN, L. (1973). *Pharm. Acta Helv.* **48**, 181–192.

HÄNSEL, W. (1976*a*). *Justus Liebigs Ann. Chem.* pp. 1380–1394.

HÄNSEL, W. (1976*b*). *Justus Liebigs Ann. Chem.* pp. 1680–1688.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–102. Birmingham: Kynoch Press.

MAIN, P., WOOLFSON, M. M., DECLERCQ, J. P. & GERMAIN, G. (1974). *MULTAN 74. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS* program. Instituto 'Rocasolano', CSIC, Serrano 119, Madrid 6, Spain.

MELTZER, B. (1978). Univ. of Freiburg. Private communication.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

RUNDLE, R. E. (1964). *J. Phys. (Paris)*, **25**, 487–492.

SMITH, D. L. & BARRETT, E. K. (1969). *Acta Cryst.* B**25**, 2355–2361.

SMITH, D. L. & BARRETT, E. K. (1971). *Acta Cryst.* B**27**, 2043–2057.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1980). B**36**, 3007–3011

The Structure of Triclinic Bilirubin Chloroform–Methanol Solvate

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Abstract

Crystals of bilirubin ($C_{33}H_{36}N_4O_6$) grown from a chloroform–methanol solution are triclinic [space group $P\bar{1}$, $a = 9{\cdot}58$ (4), $b = 11{\cdot}96$ (4), $c = 15{\cdot}60$ (5) Å, $\alpha = 93{\cdot}3$ (1), $\beta = 99{\cdot}9$ (1), $\gamma = 84{\cdot}8$ (1)°, $Z = 2$, at 223 K]. Solvent molecules are present in the crystal structure. The structure was solved by direct methods and was refined to $R = 0{\cdot}11$ for 2140 unique diffractometer data, with $F_{obs} \geq 4\sigma$. The refinement with individual atomic parameters gave satisfactory bond lengths for the bilirubin molecule; the determination of the positions of the H atoms makes possible an unequivocal assignment of the bilirubin formulation. Bilirubin is shown to have two molecular planes interrelated by a non-crystallographic 2 axis; the lactam configuration involves six intramolecular hydrogen bonds. The vinyl groups appear to be disordered.

Bilirubin, one of the most important components of the bile pigments, is the end product of hæm catabolism in man and most animals; excess of bilirubin provokes the yellow colour in all jaundices. Neonatal jaundice is particularly frequent and, although usually benign, if there is a high concentration of this pigment it may diffuse into the brain and cause irreversible damage. Bilirubin is removed from infants by exchange transfusion and irradiation to avoid intoxication.

Among other unusual physical and chemical properties, bilirubin presents a remarkable Cotton effect when complexed with serum albumin. This extremely large Cotton effect in the visible region is 'very likely associated with a high degree of inherent dissymmetry' as in the case of hexahelicene (Blauer & King, 1970).

Fischer, Plieninger & Weissbarth (1941) first elucidated the basic structure of bilirubin (Fig. 1). Several spectroscopic studies were devoted to the conformation of bilirubin, and Kuenzle proposed (Kuenzle, 1970; Kuenzle, Weibel, Pelloni & Hemmerich, 1973) a model consisting of two molecular planes separated by the central methylene bridge. This model, stabilized by strong intramolecular hydrogen bonds, is corroborated by subsequent spectroscopic

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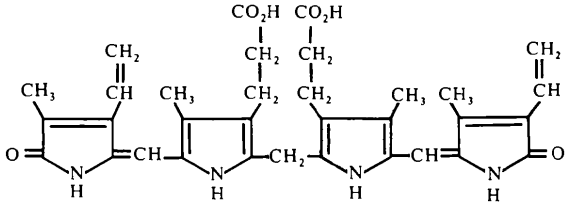

Fig. 1. Structural formula of bilirubin IX .

and chemical work (Manitto, Ricca & Monti, 1974; Manitto & Monti, 1976).

Bonnett, Davies & Hursthouse (1976) and Bonnett, Davies, Hursthouse & Sheldrick (1978) reported an X-ray analysis of bilirubin crystals (grown by diffusion of diethyl ether into a solution of bilirubin in pyridine). They confirmed the pleated-sheet structure, the *Z* configuration and the six hydrogen bonds. However, this crystal form yielded very limited X-ray data ($\theta <$ 40°, 1323 observed reflections for two independent molecules in the asymmetric unit). Consequently, these authors were not able to refine individual atomic positions and had to assume bond lengths in their refinement calculations. The structure was not accurately resolved and the positions of the H atoms in the hydrogen bonds could not be determined in order to make a clear assignment of either the lactam or lactim formulation.

The crystal form we obtained (from a mixture of chloroform and methanol) gave much better data (to a limit of $\theta = 50°$, 2140 observed reflections for one molecule in the asymmetric unit, at 223 K). An initial diffraction study was performed at room temperature [preliminary results have already been reported (Le Bas, Allegret & de Rango, 1977)]. Although this study gave satisfactory bond lengths for the bilirubin molecule, the H atoms could not be located. This failure led us to examine the X-ray diffraction pattern at low temperature. The present paper deals with this second study. The refinement of individual atomic parameters allows us to give here a detailed account of all the bond lengths in crystallized bilirubin and the determination of the positions of the H atoms makes possible an unequivocal assignment of the bilirubin formulation.

The present work is part of a more general study dealing with the relationship between optical-rotation properties and the conformation of some organic molecules having a twofold axis.

Experimental

The instability of bilirubin made the crystallization and recording of X-ray diffraction intensities extremely difficult.

Crystals were obtained by diffusion of methanol into a solution of bilirubin in chloroform (dark room, temperature 277 K) and they were protected during X-ray intensity recording by a plastic film. Weissenberg photographs showed the crystals to be triclinic.

Two complete data sets were collected on an automated Nonius CAD-4 four-circle diffractometer using Cu $K\alpha$ radiation. The first was recorded at room temperature, two crystals being necessary for this data collection; systematic corrections were applied to account for the loss of intensity during X-ray exposure; this was less than 10% for each crystal (2090 observed reflections with $F_{obs} > 4\sigma$ to a limit of $\theta = 45°$). The second data set was recorded with only one crystal at 223 K. The crystal did not alter despite intense exposure to X-rays (loss of intensity was less than 3%) and yielded significantly better data (2140 observed reflections were measured up to $\theta = 50°$).

Crystal data

$C_{33}H_{36}N_4O_6.CHCl_3.CH_3OH$, space group $P\bar{1}$, $Z = 2$.

Room temperature	223 K
$a = 9{\cdot}65\ (4)$ Å	$a = 9{\cdot}58\ (4)$ Å
$b = 12{\cdot}03\ (4)$	$b = 11{\cdot}96\ (4)$
$c = 15{\cdot}68\ (5)$	$c = 15{\cdot}60\ (5)$
$\alpha = 93{\cdot}1\ (1)°$	$\alpha = 93{\cdot}3\ (1)°$
$\beta = 99{\cdot}8\ (1)$	$\beta = 99{\cdot}9\ (1)$
$\gamma = 84{\cdot}5\ (1)$	$\gamma = 84{\cdot}8\ (1)$
$V = 1780$ Å^3	$V = 1750$ Å^3

Structure refinement

The structure was solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971). The *E* map calculated using the phases with the best figure of merit revealed the positions of 38 atoms of the tetrapyrrole skeleton. The remaining C, N, and O atoms of the bilirubin molecule with disorder of the vinyl and methyl groups of rings *A* and *D*, a disordered chloroform molecule and one probable methanol molecule were obtained from difference syntheses. These initial results were similar for the two data sets. The second set was used in the structure refinement detailed below. The isotropic refinement was carried out by block-diagonal methods (*SHELX* 76, Sheldrick, 1976). Several cycles of refinement reduced *R* to 0·19; bond lengths and angles of the chloroform molecule were chemically unreasonable and ΔF syntheses revealed large residual electron density peaks close to this molecule. The high scattering power of the Cl atom suggests that the very high value of the *R* index is mainly due to the disorder of the solvent. In the hope of

Table 1. *Positional* ($\times 10^4$) *and isotropic temperature factors of the non-hydrogen atoms of the bilirubin and solvent molecules*

	x	y	z	U(Å^2)	s.o.f.
Bilirubin molecule					
C(1)	8967 (14)	3610 (13)	6028 (9)	0·078	1·00
O(1)	8744 (9)	2594 (8)	5997 (6)	0·096	1·00
C(2)	10072 (16)	4175 (15)	6532 (9)	0·091	1·00
C(20)	11181 (15)	3687 (15)	7230 (10)	0·115	1·00
C(200)	11042 (61)	2633 (28)	7440 (39)	0·150	0·25
C(3)	9883 (15)	5312 (14)	6315 (9)	0·086	1·00
C(30)	10752 (18)	6209 (15)	6736 (10)	0·134	1·00
C(300)	11136 (42)	7045 (24)	6346 (22)	0·178	0·50
C(301)	12076 (35)	5983 (39)	7148 (45)	0·170	0·25
C(4)	8641 (14)	5402 (13)	5639 (8)	0·079	1·00
N(21)	8154 (10)	4334 (9)	5462 (6)	0·077	1·00
C(5)	8037 (14)	6337 (11)	5202 (9)	0·083	1·00
C(6)	6857 (15)	6498 (10)	4535 (8)	0·074	1·00
C(7)	6215 (15)	7514 (10)	4179 (9)	0·081	1·00
C(70)	6647 (15)	8684 (10)	4498 (9)	0·110	1·00
C(8)	5068 (14)	7264 (9)	3526 (9)	0·078	1·00
C(80)	4102 (14)	8111 (10)	2982 (9)	0·086	1·00
C(81)	4775 (14)	8779 (10)	2386 (9)	0·087	1·00
C(82)	5266 (15)	8115 (12)	1668 (9)	0·086	1·00
O(84)	4989 (9)	7163 (7)	1441 (6)	0·087	1·00
O(83)	6128 (10)	8642 (7)	1271 (6)	0·110	1·00
C(9)	5030 (14)	6112 (10)	3453 (8)	0·073	1·00
N(22)	6098 (11)	5673 (7)	4088 (6)	0·071	1·00
C(10)	4043 (12)	5332 (10)	2945 (8)	0·074	1·00
C(11)	4719 (12)	4465 (10)	2414 (7)	0·064	1·00
C(12)	4762 (12)	3286 (10)	2358 (7)	0·066	1·00
C(120)	4110 (13)	2567 (9)	2920 (8)	0·078	1·00
C(121)	5135 (15)	1803 (10)	3525 (9)	0·087	1·00
C(122)	6015 (14)	2369 (12)	4237 (9)	0·078	1·00
O(123)	6883 (9)	1697 (7)	4769 (5)	0·088	1·00
O(124)	5874 (8)	3385 (7)	4396 (5)	0·081	1·00
C(13)	5482 (13)	2915 (10)	1689 (8)	0·071	1·00
C(130)	5713 (15)	1717 (10)	1356 (8)	0·089	1·00
C(14)	5879 (13)	3842 (10)	1325 (8)	0·074	1·00
N(23)	5400 (10)	4771 (7)	1776 (6)	0·066	1·00
C(15)	6648 (13)	3834 (10)	621 (8)	0·080	1·00
C(16)	7051 (12)	4736 (11)	244 (8)	0·072	1·00
C(17)	7938 (12)	4697 (11)	−451 (8)	0·077	1·00
C(170)	8480 (14)	3610 (10)	−822 (8)	0·090	1·00
C(171)	9516 (61)	3538 (36)	−1299 (43)	0·188	0·25
C(18)	8144 (13)	5783 (12)	−592 (8)	0·075	1·00
C(180)	8954 (14)	6092 (12)	−1256 (9)	0·103	1·00
C(181)	9142 (21)	7177 (18)	−1307 (13)	0·114	0·75
C(19)	7403 (13)	6505 (12)	−51 (8)	0·079	1·00
O(19)	7292 (9)	7576 (8)	48 (6)	0·096	1·00
N(24)	6814 (10)	5877 (9)	483 (6)	0·077	1·00
Solvent molecule					
Cl(10)	11388	656	2946	0·0894	0·21
Cl(20)	10068	180	4409	0·0894	0·21
Cl(40)	8697	−295	2643	0·0894	0·21
C(500)	10294	−210	3356	0·0894	0·21
Cl(60)	11603	597	3262	0·1322	0·25
Cl(50)	10074	−727	1839	0·1322	0·25
Cl(30)	8749	119	3237	0·1322	0·25
C(600)	10379	−421	2966	0·1322	0·25
Cl(80)	11497	432	2763	0·1254	0·21
Cl(90)	8943	−564	2191	0·1254	0·21
Cl(70)	9436	453	3899	0·1254	0·21
C(700)	10233	−346	3110	0·1254	0·21
Cl(11)	8598	221	2838	0·1150	0·20
Cl(13)	9807	709	4619	0·1150	0·20
Cl(14)	11505	679	3237	0·1150	0·20
C(800)	10140	47	3595	0·1150	0·20
O(101)	8066	271	9729	0·180	0·70
C(101)	8797	541	251	0·180	0·70

explaining this disorder the chloroform molecule was then refined as a rigid body, with a common variable isotropic temperature factor. The introduction of four possible positions with site-occupation factors of 0·25 reduced R below 0·15. At this stage difference syntheses revealed all H atoms except those of the disordered groups and H(22) and H(23). 22 H atoms were found, four of which correspond to hydrogen bonds with sensible distances [H(83), H(123), H(21), H(24)]. As the configuration of the H atoms, associated with the methyl groups on rings B and C and with the CH_2 atoms of the propionic acid, was unsatisfactory, these H positions were recalculated. The fixed positions of all these 22 atoms and the calculated positions of H(22) and H(23) were used in subsequent refinements. Difference syntheses showed that the vinyl groups attached to rings A and D were distributed on C(18), C(3), C(17), and C(2) with a site-occupation factor (s.o.f.) < 1. The site of the first C atom of each vinyl group is the same as that of the C atom of the methyl group for which it is substituted: this site appeared fully occupied. The terminal C atom of the vinyl appeared as a fractionally occupied site. One appeared clearly on C(18) with a s.o.f. of 0·75. On C(3), two positions [C(300), C(301)] appeared with s.o.f.'s of 0·5 and 0·25 respectively. The other two vinyls bound to C(17) and C(2) were obtained with s.o.f.'s of 0·25. All were refined in a constrained geometry. H atoms of the methyl groups with a s.o.f. of 0·75 were included as a rigid group as well. The methanol molecule also displays disorder; a simplified model was used.

Final refinement, where only the molecule of bilirubin was treated as anisotropic, yielded an R factor of 0·11.* The final difference synthesis showed some small residual peaks close to the positions of the solvent molecules.

The atomic coordinates are listed in Tables 1 and 2; the ring and atom labelling are in Fig. 2(*a*), the bond distances in Fig. 2(*b*) and the bond angles in Fig. 2(*c*).

Discussion

The folding of the molecule is clearly represented in Fig. 2(*c*). The molecule can be described by two planes,

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35231 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

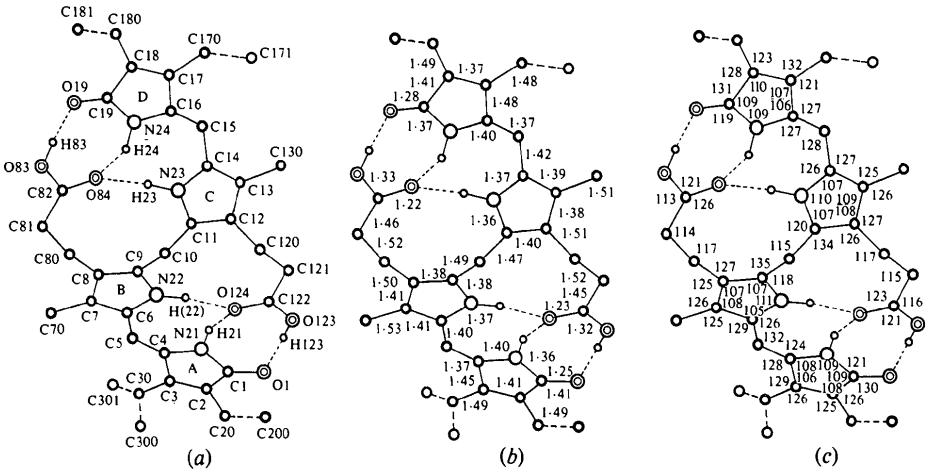

Fig. 2. (*a*) Molecular conformation and atomic labelling, (*b*) bond lengths (Å) (standard deviations 0·015–0·02 Å), and (*c*) bond angles (°) (standard deviations 1·0–1·5°) of the bilirubin molecule.

Table 2. *Positional coordinates* ($\times 10^4$) *and isotropic temperature factors of the hydrogen atoms of the bilirubin molecule*

	x	*y*	*z*	*U* (Å²)	s.o.f.
H(200)	11931	4268	7523	0·08	0·75
H(201)	11811	2947	6964	0·08	0·75
H(202)	10716	3347	7748	0·08	0·75
H(21)	7272	3980	5175	0·08	1·00
H(50)	8363	7115	5380	0·08	1·00
H(70)	6271	9054	3872	0·08	1·00
H(71)	7762	8773	4689	0·08	1·00
H(72)	6069	9118	4977	0·08	1·00
H(800)	3248	7645	2581	0·08	1·00
H(801)	3593	8688	3418	0·08	1·00
H(810)	5708	9137	2773	0·08	1·00
H(811)	4030	9441	2127	0·08	1·00
H(83)	6405	8067	695	0·08	1·00
H(22)	6191	4843	4256	0·08	1·00
H(100)	3670	5196	3495	0·08	1·00
H(101)	3248	5574	2477	0·08	1·00
H(1200)	3515	3116	3306	0·08	1·00
H(1201)	3416	2032	2488	0·08	1·00
H(1211)	5808	1299	3140	0·08	1·00
H(1210)	4503	1267	3808	0·08	1·00
H(123)	7654	2103	5257	0·08	1·00
H(130)	5253	1258	1820	0·08	1·00
H(131)	6840	1526	1470	0·08	1·00
H(132)	5253	1467	710	0·08	1·00
H(23)	5327	5661	1699	0·08	1·00
H(15)	7052	2940	457	0·08	1·00
H(24)	6025	6275	800	0·08	1·00
H(1700)	9126	3763	−1329	0·08	0·75
H(1701)	7635	3116	−1133	0·08	0·75
H(1702)	9180	3120	−333	0·08	0·75

each involving a dipyrromethene moiety and the propionic acid chains attached to the other dipyrromethene moiety. The interplanar angle is 96°, and the r.m.s. distance of atoms from their associated plane is 0·13 Å, for each plane; in the calculation, we included all the atoms of the molecule except the disordered atoms. These two planes are interrelated by a non-crystallographic twofold axis (vinyl group excluded) passing through C(10) (r.m.s. deviation: 0·06 Å) and approximately perpendicular to the line C(8)C(10)-C(12). The conformation of bilirubin appears to be highly dissymmetric as was pointed out by Blauer & King. The dissymmetry permits dipole–dipole coupling between the two dipyrromethene halves. Although no optical activity is observed with bilirubin in solution, the complex bilirubin serum albumin exhibits a large Cotton effect; a change of pH causes an inversion of the sign of this Cotton effect. It was proposed that a conformational change of the protein alters its preferential avidity for either one of the two chiral pigment conformations (Blauer & King, 1970; Blauer, Harmatz & Snir, 1972). In the crystallographic cell the two enantiomeric bilirubin conformations are present.

The conformation of bilirubin is stabilized through a system of six intramolecular hydrogen bonds: two outer O–H···O strong bonds (mean distance 2·61 Å) and four inner N–H···O bonds (mean distance 2·84 Å). These six intramolecular hydrogen bonds may explain the insolubility of bilirubin in aqueous conditions since all potential sites are occupied by the intramolecular hydrogen bonds (Kuenzle, Weibel, Pelloni & Hemmerich, 1973). The observed positions of H(83), H(23), H(24), and H(124) in the hydrogen bonds provide an absolute proof for the lactam configuration of bilirubin. The bond distances of the carbonyl groups C(1)–O(1) and C(19)–O(19) (1·25 and 1·28 Å respectively) and the bond distances of the propionic acid groups which are bound to the outer rings by hydrogen bonds confirmed that these outer rings are in the lactam [bis(pyrrolenone)] structure: C(122)–O(123) and C(82)–O(83) are close to the usual single-bond value of carboxylic acid (1·32 and 1·33 Å respectively) whereas C(122)–O(124) and

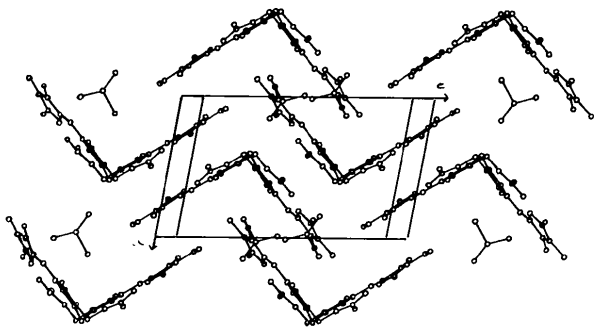

Fig. 3. Molecular packing in the projection (010).

C(82)–O(84) are consistent with double bonds (1·23 and 1·22 Å). The lactam configuration (*versus* lactim) is in agreement with the chemical properties of the molecule. It explains the difficulties encountered in the formation of bilirubin derivatives and bilirubin–divalent-metal complexes. It also accounts for the relative stability of bilirubin with respect to its esters (Lathe, 1972; Kuenzle, Pelloni & Weibel, 1972).

The arrangement of the molecules in the unit cell is shown in Fig. 3. The crystal structure has no intermolecular hydrogen bonds, the molecules being held together by van der Waals forces alone. We observe a channel containing solvent molecules; these are disordered and we cannot study this disorder completely. The model of four possible positions for the chloroform molecule produced significant improvement of the difference synthesis.

Since the report at the Fourth European Crystallographic Meeting (Le Bas, Allegret & de Rango, 1977) two studies have appeared on bilirubin derivatives: the structures of mesobilirubin (Becker & Sheldrick, 1978) and diisopropylammonium bilirubinate (Mugnoli, Manitto & Monti, 1978). The essential features of the bilirubin molecule shown above are retained in all these different structures. The conformation characterized by two molecular planes is very similar to those of mesobilirubin and the bilirubin bis(anion). Like bilirubin, the structure of mesobilirubin has a non-crystallographic twofold axis (the coordinates of Becker & Sheldrick show a r.m.s. deviation of 0·05 Å from the ideal symmetry), whereas the twofold axis is crystallographic in the structure of the bilirubin bis(anion). Six intramolecular hydrogen bonds are also found in the structure of bilirubin crystallized from pyridine (2·53 Å mean value for O–H···O distances and 2·70 Å for N–H···O) and mesobilirubin (2·64 Å for O–H···O, 2·87 Å for N–H···O). The four N–H···O hydrogen bonds remain in the molecule of the bilirubin bis(anion) (mean distance 2·86 Å). The lactam configuration, although undetermined in the bilirubin crystallized from pyridine, seems to be confirmed in mesobilirubin and in the bilirubin bis-(anion). There are strong similarities between the stacking pattern of the structures of bilirubin and that of mesobilirubin. In the structure of bilirubin crystallized from pyridine, no solvent molecule was mentioned; in the structure of mesobilirubin, an analogous channel containing two chloroform molecules has been reported. The packing seems to be compact only on the projection (010), and gives rise to infinite channels parallel to z and x, where disordered solvent molecules occur in the cases of bilirubin–chloroform and mesobilirubin–chloroform.

References

BECKER, W. & SHELDRICK, W. S. (1978). *Acta Cryst.* B**34**, 1298–1304.

BLAUER, G., HARMATZ, D. & SNIR, J. (1972). *Biochim. Biophys. Acta*, **278**, 68–88.

BLAUER, G. & KING, T. E. (1970). *J. Biol. Chem.* **245**, 372–381.

BONNETT, R., DAVIES, J. E. & HURSTHOUSE, M. B. (1976). *Nature (London)*, **262**, 326–328.

BONNETT, R., DAVIES, J. E., HURSTHOUSE, M. B. & SHELDRICK, G. M. (1978). *Proc. R. Soc. London Ser. B*, **202**, 249–268.

FISCHER, H., PLIENINGER, H. & WEISSBARTH, O. (1941). *Hoppe Seyler's Z. Physiol. Chem.* **268**, 231–260.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

KUENZLE, C. C. (1970). *Biochem. J.* **119**, 395–409.

KUENZLE, C. C., PELLONI, R. R. & WEIBEL, M. H. (1972). *Biochem. J.* **130**, 1145–1150.

KUENZLE, C. C., WEIBEL, M. H., PELLONI, R. R. & HEMMERICH, P. (1973). *Biochem. J.* **133**, 357–368.

LATHE, G. H. (1972). *Essays Biochem.* **8**, 107–148.

LE BAS, G., ALLEGRET, A. & DE RANGO, C. (1977). Abstract PI 107. Fourth European Crystallographic Meeting, Oxford, England.

MANITTO, P. & MONTI, D. (1976). *J. Chem. Soc. Chem. Commun.* pp. 122–123.

MANITTO, P., RICCA, G. S. & MONTI, D. (1974). *Gazz. Chim. Ital.* **104**, 633–637.

MUGNOLI, A., MANITTO, P. & MONTI, D. (1978). *Nature (London)*, **273**, 568–569.

SHELDRICK, G. M. (1976). *SHELX* 76. A program for crystal structure determination. Univ. of Cambridge, England.