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References

AHMED, F. R. (1968). *NRC*-10: a structure factor least-squares program. National Research Council of Canada, Ottawa, Canada.
CRUMP, D. R., FRANCK, R. W., GRUSKA, R., OZORIO, A. A., PAGNOTTA, M., SIUTA, G. J. & WHITE, J. G. (1977). *J. Org. Chem.* **42**, 105–108.
HUBER, C. P. & BRISSE, F. R. (1970). *NRC*-5: a direct phasing methods program. National Research Council of Canada, Ottawa, Canada.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., pp. 202–203. Birmingham: Kynoch Press.
KARLE, I. L., BRITTS, K. & GUM, P. (1964). *Acta Cryst.* **17**, 496–499.
KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63–76.
SIUTA, G. J., FRANCK, R. W. & OZORIO, A. A. (1974). *J. Chem. Soc. Chem. Commun.* p. 910.

Acta Cryst. (1978). B**34**, 2055–2058

1-*tert*-Butoxycarbonyl-2,7,12-tris(2-methoxycarbonylethyl)-8,13-bis(methoxycarbonylmethyl)-3,14-dimethyl-5,16-dihydro-15*H*-tripyrrin Hydrobromide

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Abstract. $C_{39}H_{52}N_3O_{12}^+Br^-$, triclinic $P\bar{1}$, $a = 13{\cdot}27\,(1)$, $b = 16{\cdot}97\,(2)$, $c = 10{\cdot}85\,(1)$ Å, $\alpha = 103{\cdot}1\,(1)$, $\beta = 113{\cdot}0\,(1)$, $\gamma = 71{\cdot}0\,(1)°$, $Z = 2$, $M_r = 834{\cdot}8$, $D_x = 1{\cdot}31$ g cm^{-3}. The pyrromethene chromophore displays a slightly twisted *syn-Z* conformation (interplanar angle 10·3°) with a wide methine bridge angle of 135·1 (4)°. The Br^- anion is situated 0·077 Å from the best least-squares plane of the pyrromethene system and makes two non-linear N—H···Br hydrogen bonds of length 3·26 and 3·30 Å. The N—H proton of the non-conjugated pyrrole ring is involved in an N—H···O intermolecular bond.

Introduction. Cell dimensions were obtained from a least-squares fit to the settings for 15 reflexions ($\pm hkl$) on a Syntex $P2_1$ diffractometer (Cu K, $\lambda = 1{\cdot}54178$ Å). Intensity measurements were carried out in the θ–2θ mode ($3{\cdot}5 \le 2\theta \le 135{\cdot}0°$) with graphite-monochromated Cu $K\alpha$ radiation. No absorption correction [μ(Cu $K\alpha$) = 17·1 cm^{-1}] was applied. After application of the rejection criterion $I < 2{\cdot}0\sigma(I)$, 4075 unique reflexions were retained for the refinement. The structure was solved by Patterson and difference

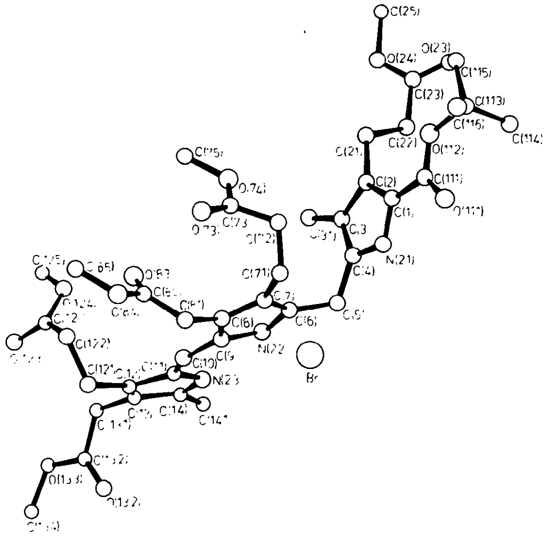

Fig. 1. The molecule of (I) in perspective with atom numbering.

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syntheses and refined by full-matrix least squares with anisotropic temperature factors for the non-hydrogen atoms. Respective group isotropic temperature factors, which refined to 0·068 (7), 0·061 (7) and 0·111 (3) Å^2, were introduced for the N—H, the C(5) and C(10), and the remaining protons. One methylene proton on C(123) and the methyl protons on C(25) and C(125), which could not be located in difference syntheses, were not included in the refinement. The terminal value of $R_w = (\sum w^{1/2}\Delta/\sum w^{1/2}|F_o|)$ was 0·059 with R 0·055. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). The weights were given by $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$, where k and g refined to 1·961 and 0·001012 respectively. Positional parameters, bond lengths and bond angles are given in Tables 1–4.[*] Fig. 1 is a perspective drawing showing the numbering scheme.

Discussion. Tripyrrenes (5,16-dihydro-15*H*-tripyrrins), which have the linear tripyrrolic skeleton depicted in Fig. 2, are useful intermediates for the stepwise synthesis of unsymmetrically substituted biladienes-*a*,*c*, which are precursors of porphyrins and related tetrapyrrole macrocycles (Engel & Gossauer, 1976). They are usually isolated as their red crystalline mineral acid salts, which are more stable than the corresponding free bases (Gossauer & Engel, 1978). As would be expected, the characteristic light absorption of the tripyrrenes (as free bases) lies in the range of the excitation energy of the pyrromethene chromophore (*i.e.* near 455 nm). The corresponding hydrobromides absorb at around 490 nm (Jackson, Kenner & Sach, 1967). As part of our systematic study of the structures of linear polypyrrolic compounds (including the natural bile pigments), we have reported the structure of the pyrromethene free base 5,5′-diethoxycarbonyl-3,3′-diethyl-4,4′-dimethyl-2,2′-pyrromethene (II) (Sheldrick, Borkenstein, Struckmeier & Engel, 1978) and the hydrobromide of 5,5′-dibromo-3,3′-diethyl-4,4′-dimethyl-2,2′-pyrromethene (III) (Becker, Sheldrick & Engel, 1978). We present here results of the first X-ray analysis of a tripyrrolic derivative, the tripyrrene hydrobromide (I) (Engel & Gossauer, 1976).

The protonated pyrromethene moiety in (I) displays a slightly twisted *syn-Z* conformation with an interplanar angle of 10·3° similar to that of 13·0° in (III), which contrasts with the planar conformation of the free base (II). The Br$^-$ anion in (I) lies 0·077 Å from the best least-squares plane of the pyrromethene

Table 1. *Positional parameters* ($\times 10^4$)

	x	y	z
Br	288 (1)	3415 (1)	2106 (1)
N(21)	4284 (3)	1781 (2)	6627 (3)
C(1)	5317 (4)	1366 (2)	6490 (4)
C(2)	5384 (3)	1649 (2)	5426 (4)
C(3)	4359 (4)	2259 (2)	4919 (4)
C(4)	3710 (4)	2328 (2)	5678 (4)
C(5)	2531 (3)	2867 (2)	5561 (4)
N(22)	1649 (3)	4318 (2)	5000 (3)
C(6)	2437 (3)	3782 (2)	5876 (4)
C(7)	3001 (3)	4255 (2)	7045 (4)
C(8)	2492 (3)	5090 (2)	6868 (4)
C(9)	1627 (3)	5140 (2)	5549 (4)
C(10)	993 (3)	5859 (2)	4949 (4)
N(23)	9815 (3)	5478 (2)	2592 (3)
C(11)	241 (3)	6033 (2)	3687 (4)
C(12)	9801 (4)	6841 (2)	3210 (5)
C(13)	9137 (4)	6735 (3)	1851 (5)
C(14)	9145 (4)	5886 (3)	1505 (4)
C(111)	6087 (4)	734 (2)	7401 (5)
O(111)	5843 (3)	564 (2)	8259 (3)
O(112)	7058 (2)	381 (2)	7181 (3)
C(113)	7912 (4)	9659 (3)	7851 (5)
C(114)	7400 (5)	8937 (3)	7476 (7)
C(115)	8824 (6)	9507 (4)	7264 (9)
C(116)	8336 (5)	9896 (4)	9364 (7)
C(21)	6339 (4)	1339 (2)	4884 (4)
C(22)	6282 (5)	509 (3)	3971 (5)
C(23)	7280 (7)	109 (5)	3529 (6)
O(23)	7663 (5)	9339 (3)	3406 (7)
O(24)	7666 (5)	595 (3)	3290 (6)
C(25)	8739 (9)	227 (6)	2970 (12)
C(31)	4034 (5)	2757 (3)	3780 (5)
C(71)	3995 (4)	3895 (2)	8240 (4)
C(72)	5127 (4)	3618 (3)	8014 (5)
C(73)	5493 (4)	4334 (3)	7861 (5)
O(73)	5554 (4)	4955 (2)	8615 (4)
O(74)	5780 (4)	4174 (2)	6782 (4)
C(75)	6249 (8)	4782 (5)	6581 (7)
C(81)	2730 (4)	5825 (2)	7896 (4)
C(82)	3277 (4)	6380 (3)	7614 (5)
O(82)	3398 (4)	6373 (2)	6585 (4)
O(83)	3580 (4)	6914 (2)	8710 (3)
C(84)	4126 (8)	7494 (5)	8615 (7)
C(121)	73 (5)	7624 (3)	4049 (6)
C(122)	1213 (6)	7724 (3)	4139 (8)
C(123)	1148 (6)	7921 (4)	2794 (9)
O(123)	543 (5)	8543 (3)	2327 (6)
O(124)	1821 (4)	7356 (3)	2274 (6)
C(125)	1811 (7)	7552 (6)	987 (9)
C(131)	8548 (4)	7392 (3)	883 (6)
C(132)	7406 (4)	7877 (2)	848 (4)
O(132)	6881 (3)	7739 (2)	1386 (4)
O(133)	7008 (3)	8492 (2)	102 (4)
C(134)	5905 (6)	9043 (4)	9997 (8)
C(141)	8548 (6)	5446 (5)	208 (7)

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33422 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Hydrogen atom positional parameters and isotropic temperature factors* (*all values* × 10³)

	x	y	z	U (Å²)
H(21)	400 (3)	176 (3)	733 (3)	68 (7)
H(22)	121 (4)	414 (3)	430 (4)	68 (7)
H(23)	985 (4)	499 (3)	259 (4)	68 (7)
H(51)	202 (3)	276 (2)	474 (4)	61 (7)
H(52)	233 (3)	273 (2)	616 (4)	61 (7)
H(101)	115 (3)	630 (2)	543 (4)	61 (7)
H(111)	796 (5)	849 (3)	782 (5)	111 (3)
H(112)	655 (5)	908 (3)	762 (6)	111 (3)
H(113)	694 (5)	889 (3)	646 (6)	111 (3)
H(114)	944 (5)	901 (3)	767 (5)	111 (3)
H(115)	916 (4)	12 (3)	748 (5)	111 (3)
H(116)	848 (5)	911 (3)	638 (5)	111 (3)
H(117)	854 (5)	45 (4)	965 (5)	111 (3)
H(118)	779 (5)	18 (3)	976 (5)	111 (3)
H(119)	902 (5)	945 (3)	983 (5)	111 (3)
H(211)	633 (5)	185 (3)	446 (5)	111 (3)
H(212)	711 (5)	130 (3)	557 (5)	111 (3)
H(213)	558 (5)	66 (3)	322 (5)	111 (3)
H(214)	613 (5)	6 (3)	430 (5)	111 (3)
H(311)	340 (5)	320 (4)	360 (6)	111 (3)
H(312)	437 (5)	314 (3)	409 (6)	111 (3)
H(313)	397 (5)	237 (4)	298 (5)	111 (3)
H(711)	400 (4)	427 (4)	897 (5)	111 (3)
H(712)	388 (5)	345 (4)	838 (5)	111 (3)
H(713)	574 (5)	330 (3)	872 (6)	111 (3)
H(714)	510 (5)	316 (3)	714 (5)	111 (3)
H(715)	636 (5)	452 (3)	569 (5)	111 (3)
H(716)	690 (5)	486 (3)	741 (5)	111 (3)
H(717)	577 (5)	542 (3)	686 (5)	111 (3)
H(811)	319 (5)	566 (3)	866 (5)	111 (3)
H(812)	211 (5)	616 (4)	793 (5)	111 (3)
H(813)	362 (5)	792 (3)	799 (5)	111 (3)
H(814)	437 (5)	779 (4)	941 (6)	111 (3)
H(815)	481 (5)	712 (4)	871 (5)	111 (3)
H(121)	4 (5)	764 (3)	500 (5)	111 (3)
H(122)	950 (5)	802 (3)	374 (6)	111 (3)
H(123)	176 (5)	732 (3)	438 (5)	111 (3)
H(131)	−147 (5)	718 (3)	989 (5)	111 (3)
H(132)	911 (4)	777 (3)	126 (5)	111 (3)
H(133)	583 (5)	922 (4)	87 (6)	111 (3)
H(134)	572 (5)	942 (4)	930 (6)	111 (3)
H(135)	537 (6)	878 (4)	925 (6)	111 (3)
H(141)	789 (6)	557 (4)	4 (7)	111 (3)
H(142)	879 (6)	488 (4)	7 (6)	111 (3)
H(143)	878 (5)	544 (4)	946 (6)	111 (3)

Table 3. *Bond lengths* (Å)

C(1)–N(21)	1·372 (6)	C(4)–N(21)	1·365 (6)
C(2)–C(1)	1·390 (8)	C(111)–C(1)	1·467 (6)
C(3)–C(2)	1·408 (5)	C(21)–C(2)	1·495 (8)
C(4)–C(3)	1·371 (9)	C(31)–C(3)	1·499 (8)
C(5)–C(4)	1·506 (6)	C(6)–C(5)	1·488 (6)
C(6)–N(22)	1·349 (5)	C(9)–N(22)	1·382 (5)
C(7)–C(6)	1·414 (5)	C(8)–C(7)	1·378 (6)
C(71)–C(7)	1·514 (6)	C(9)–C(8)	1·443 (5)
C(81)–C(8)	1·499 (6)	C(10)–C(9)	1·373 (6)
C(11)–C(10)	1·373 (6)	C(11)–N(23)	1·390 (5)
C(14)–N(23)	1·346 (6)	C(12)–C(11)	1·433 (7)
C(13)–C(12)	1·397 (7)	C(121)–C(12)	1·492 (7)
C(14)–C(13)	1·400 (7)	C(131)–C(13)	1·510 (8)
C(141)–C(14)	1·483 (8)	O(111)–C(111)	1·214 (8)
O(112)–C(111)	1·322 (7)	C(113)–O(112)	1·473 (6)
C(114)–C(113)	1·492 (9)	C(115)–C(113)	1·503 (13)
C(116)–C(113)	1·515 (9)	C(22)–C(21)	1·532 (7)
C(23)–C(22)	1·485 (12)	O(23)–C(23)	1·234 (10)
O(24)–C(23)	1·220 (14)	C(25)–O(24)	1·499 (15)
C(72)–C(71)	1·522 (9)	C(73)–C(72)	1·510 (10)
O(73)–C(73)	1·182 (7)	O(74)–C(73)	1·313 (9)
C(75)–O(74)	1·458 (14)	C(82)–C(81)	1·503 (10)
O(82)–C(82)	1·186 (8)	O(83)–C(82)	1·331 (6)
C(84)–O(83)	1·440 (13)	C(122)–C(121)	1·540 (12)
C(123)–C(122)	1·535 (14)	O(123)–C(123)	1·178 (9)
O(124)–C(123)	1·275 (10)	C(125)–O(124)	1·502 (14)
C(132)–C(131)	1·461 (8)	O(132)–C(132)	1·170 (9)
O(133)–C(132)	1·309 (7)	C(134)–O(133)	1·435 (8)

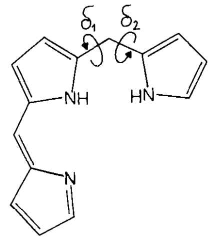

Fig. 2. The tripyrrene skeleton.

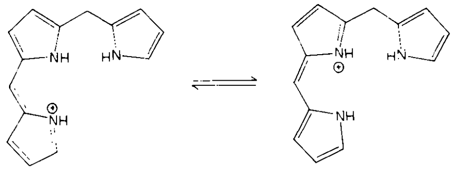

Fig. 3. The two mesomeric forms of the protonated tripyrrene system.

chromophore and is involved in two non-linear N–H···Br bonds of similar length, 3·26 and 3·30 Å. The conformation of the non-conjugated pyrrole ring with respect to the first pyrrole ring of the pyrromethene system, *i.e.* N(22), may be uniquely described in terms of the dihedral angles shown in Fig. 2 (Blauer & Wagnière, 1975) which here are 104·1 and 172·7° respectively. N(21) is involved in an intermolecular N–H···O bond to O(132), 2·95 Å, rather than in an N–H···Br bond which would require the tripyrrole skeleton to adopt a more cyclic structure (*i.e.* with δ_1, δ_2 close to zero). The bond-length distribution in the pyrromethene chromophore of (I) is very similar to that in (II) and (III), *i.e.* the positive charge is delocalized over both N atoms so that the bonding in both the component rings is equivalent. Thus N(22)–C(6) and N(23)–C(14), 1·349 (5) and 1·346 (6) Å, are much

Table 4. *Bond angles* (°)

C(4)–N(21)–C(1)	108·1 (5)	O(24)–C(23)–C(22)	115·0 (7)	N(23)–C(11)–C(10)	128·4 (4)
C(111)–C(1)–N(21)	118·2 (5)	C(25)–O(24)–C(23)	116·8 (7)	C(12)–C(11)–N(23)	105·9 (4)
C(3)–C(2)–C(1)	106·8 (5)	C(73)–C(72)–C(71)	113·5 (4)	C(121)–C(12)–C(11)	124·2 (4)
C(21)–C(2)–C(3)	126·5 (5)	O(74)–C(73)–C(72)	111·1 (5)	C(14)–C(13)–C(12)	107·7 (4)
C(31)–C(3)–C(2)	126·9 (6)	C(75)–O(74)–C(73)	116·7 (5)	C(131)–C(13)–C(14)	124·8 (4)
C(3)–C(4)–N(21)	109·4 (4)	O(82)–C(82)–C(81)	126·9 (5)	C(141)–C(14)–N(23)	121·8 (5)
C(5)–C(4)–C(3)	130·0 (4)	O(83)–C(82)–O(82)	124·5 (7)	O(111)–C(111)–C(1)	122·6 (5)
C(9)–N(22)–C(6)	110·7 (3)	C(122)–C(121)–C(12)	113·6 (5)	O(112)–C(111)–O(111)	124·7 (4)
C(7)–C(6)–C(5)	131·1 (3)	O(123)–C(123)–C(122)	122·0 (8)	C(114)–C(113)–O(112)	109·0 (4)
C(8)–C(7)–C(6)	107·1 (3)	O(124)–C(123)–O(123)	125·0 (6)	C(115)–C(113)–C(114)	112·2 (5)
C(71)–C(7)–C(8)	127·4 (4)	C(132)–C(131)–C(13)	115·7 (6)	C(116)–C(113)–C(114)	111·7 (7)
C(81)–C(8)–C(7)	126·3 (3)	O(133)–C(132)–C(131)	111·7 (6)	C(22)–C(21)–C(2)	111·1 (5)
C(8)–C(9)–N(22)	105·4 (3)	C(134)–O(133)–C(132)	118·5 (6)	O(23)–C(23)–C(22)	121·2 (6)
C(10)–C(9)–C(8)	126·2 (4)	C(2)–C(1)–N(21)	108·5 (4)	O(24)–C(23)–O(23)	123·8 (6)
C(14)–N(23)–C(11)	110·6 (4)	C(111)–C(1)–C(2)	133·3 (5)	C(72)–C(71)–C(7)	113·5 (5)
C(12)–C(11)–C(10)	125·6 (4)	C(21)–C(2)–C(1)	126·7 (4)	O(73)–C(73)–C(72)	125·9 (7)
C(13)–C(12)–C(11)	107·3 (4)	C(4)–C(3)–C(2)	107·2 (4)	O(74)–C(73)–O(73)	123·0 (7)
C(121)–C(12)–C(13)	128·5 (5)	C(31)–C(3)–C(4)	125·9 (4)	C(82)–C(81)–C(8)	117·0 (5)
C(131)–C(13)–C(12)	127·4 (5)	C(5)–C(4)–N(21)	120·6 (5)	O(83)–C(82)–C(81)	108·6 (5)
C(13)–C(14)–N(23)	108·5 (4)	C(6)–C(5)–C(4)	114·2 (4)	C(84)–O(83)–C(82)	115·9 (6)
C(141)–C(14)–C(13)	129·7 (5)	N(22)–C(6)–C(5)	120·3 (3)	C(123)–C(122)–C(121)	111·3 (5)
O(112)–C(111)–C(1)	112·7 (5)	C(7)–C(6)–N(22)	108·5 (3)	O(124)–C(123)–C(122)	113·0 (6)
C(113)–O(112)–C(111)	122·9 (5)	C(71)–C(7)–C(6)	125·5 (4)	C(125)–O(124)–C(123)	114·0 (7)
C(115)–C(113)–O(112)	101·8 (6)	C(9)–C(8)–C(7)	108·3 (3)	O(132)–C(132)–C(131)	125·6 (5)
C(116)–C(113)–O(112)	110·1 (4)	C(81)–C(8)–C(9)	125·2 (3)	O(133)–C(132)–O(132)	122·7 (5)
C(116)–C(113)–C(115)	111·6 (6)	C(10)–C(9)–N(22)	128·2 (3)		
C(23)–C(22)–C(21)	114·3 (6)	C(11)–C(10)–C(9)	135·1 (4)		

shorter than N(22)–C(9) and N(23)–C(11), 1·382 (5) and 1·390 (5) Å. This difference may be explained in terms of contributions from the two mesomeric forms depicted in Fig. 3; the former bond possesses a formal order of 1·5, the latter 1·0. The bond-angle distribution in (I) is similar to that in (III). The very wide methine bridge angle of 135·1 (4)° [133·8 (6)° in (III)] and the N(22)–C(9)–C(10) and N(23)–C(11)–C(10) angles of 128·2 (3) and 128·4 (3)° lead to an N···N distance of 3·30 Å in (I), which is even longer than the 3·25 Å in (III). In the pyrromethene free base (II), for which intramolecular N–H···N bonding is observed, the N···N distance is only 2·75 Å. The two N–H···Br distances of 3·26 and 3·30 Å in (I) are significantly longer than those of 3·23 Å in (III). The Br$^-$ anion in (I) is much closer to the pyrromethene best least-squares plane than in (III), 0·077 *vs* ±0·793 Å. This and the concomitant increase of the N···N distance in (I) over that in (III) enable here both N–H···Br bonds to approach linearity more closely, 167 and 163° in (I) *vs* 151 and 167 (4)° in (III). The large displacement of the Br$^-$ anion in (III) from the pyrromethene plane is therefore presumably necessary in order to minimize the Br···Br steric interactions between the anion and the Br substituents at C(5): these contact distances are 4·00 and 4·09 Å in (III).

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References

Becker, W., Sheldrick, W. S. & Engel, J. (1978). *Acta Cryst.* B**34**, 1021–1024.

Blauer, G. & Wagnière, G. (1975). *J. Am. Chem. Soc.* **97**, 1949–1954.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Engel, J. & Gossauer, A. (1976). *Justus Liebigs Ann. Chem.* pp. 1637–1658.

Gossauer, A. & Engel, J. (1978). *Open-Chained Polypyrrolic Compounds* in *The Porphyrins*, edited by D. Dolphin. London, New York, San Francisco: Academic Press. To be published.

Jackson, A. H., Kenner, G. W. & Sach, G. S. (1967). *J. Chem. Soc. C*, pp. 2045–2059.

Sheldrick, W. S., Borkenstein, A., Struckmeier, G. & Engel, J. (1978). *Acta Cryst.* B**34**, 329–332.