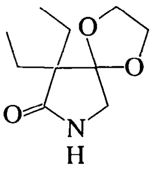

(I)

The molecules of (I) are linked into centrosymmetric dimers through two N–H···O(=C) hydrogen bonds of length 2·91 Å. The pyrrolidine ring is in the envelope conformation with C(4) 0·467 Å above the least-squares plane through the other ring atoms [unit weights, distances from the plane: N(1) −0·005, C(2) 0·005, C(3) −0·003, C(5) 0·003, O(21) −0·001 Å]. A similar conformation is adopted by the 1,3-dioxole ring [unit weights, distances from the plane: C(4) −0·018, O(41) −0·395, C(42) 0·017, C(43) −0·028, O(44) 0·029 Å]. Bond lengths and angles are normal (Tables 3 and 4). As a result of π interaction the N(1)—C(2) distance of 1·330 (3) Å is much shorter than the N(1)—C(5) distance of 1·461 (3) Å. A projection of the unit cell perpendicular to [001] is given in Fig. 2.

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5,5′-Dibromo-3,3′-diethyl-4,4′-dimethyl-2,2′-pyrromethene Hydrobromide

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Abstract. $C_{15}H_{19}N_2Br_2^+Br^-$, monoclinic, $C2/c$, a = 16·140 (8), b = 8·871 (6), c = 12·537 (8) Å, β = 106·57 (5)°, M_r = 467·0, D_x = 1·73 g cm^{-3}, Z = 4. The molecule contains a space-group C_2 axis with the Br^- anion in a disordered site ±0·793 Å from the best least-squares plane of the pyrromethene system. The chromophore displays a slightly twisted *syn-Z* conformation (interplanar angle 13·0°) with a wide methine bridge angle of 133·8 (6)°. The disordered Br^- anions are each involved in two non-linear N—H···Br hydrogen bonds of length 3·228 and 3·225 Å.

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, λ = 1·54178 Å). Intensity measurements were carried out in the θ–2θ mode (3·5 ≤ 2θ ≤ 135·0°) with graphite-monochromated Cu $K\alpha$ radiation, at scan speeds varying linearly between 2·93 (150 counts s^{-1} and below) and 29·30° min^{-1} (1500 counts s^{-1} and above). Scan and background times were equal. Lorentz, polarization and a numerical absorption correction [μ(Cu $K\alpha$) = 81·2 cm^{-1}; crystal size: 0·106 × 0·088 × 1·2 mm] were applied. After application of the rejection criterion $I \leq 2{\cdot}0\sigma(I)$, 1420 unique reflexions were retained for the refinement. The structure was solved by Patterson and difference syntheses and refined by full-matrix least squares with anisotropic temperature factors for all the non-hydrogen atoms. The Br^- anion [Br(1)] occupies a disordered site. As a result of the shortness of the distance between these C_2 symmetry-related sites [1·590 Å] Br(1) has unrealistically high values of U_{11},

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U_{33} and U_{13} [0·160 (1), 0·110 (1) and 0·102 (1) Å^2] perpendicular to the diad axis, which contrast with the value of 0·028 (1) Å^2 for U_{22}. All anisotropic temperature factor components for the other atoms are physically reasonable. The H atom positions were refined under the geometrical constraints d(N–H) = 1·02 ± 0·01, d(C–H) = 1·08 ± 0·01 Å. A group isotropic temperature factor was introduced for the C–H protons. The terminal value of R_G $[=(\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}]$ was 0·049, with $R_w = \Sigma w^{1/2}\Delta/\Sigma w^{1/2}|F_o|$ = 0·046 and R = 0·046.* Although a refinement in the noncentrosymmetric space group Cc led to a significant increase in R_G (Hamilton, 1965) it was rejected on account of the unrealistic bond lengths in the pyrromethene moiety which it yielded. Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer & Liberman, 1970). The weights were those from the counting statistics. Calculations were carried out with *SHELX* 76 (G. M. Sheldrick) and local programs. Positional parameters, bond lengths and bond angles are given in Tables 1–4. Fig. 1 is a perspective drawing showing the numbering scheme.

Table 1. *Positional parameters for the nonhydrogen atoms*

	x	y	z
N(1)	0·9485 (2)	0·3848 (3)	0·8440 (2)
Br(1)	0·9553 (1)	0·0837 (1)	0·7022 (1)
C(2)	0·9532 (2)	0·5368 (4)	0·8165 (3)
C(21)	0·0000 (1)	0·5981 (6)	0·7500 (1)
C(3)	0·9039 (2)	0·6198 (4)	0·8760 (3)
C(31)	0·8854 (3)	0·7845 (4)	0·8677 (4)
C(32)	0·8002 (3)	0·8203 (6)	0·7805 (5)
C(4)	0·8715 (2)	0·5163 (4)	0·9380 (3)
C(41)	0·8160 (3)	0·5486 (6)	1·0131 (4)
C(5)	0·9009 (2)	0·3753 (4)	0·9167 (3)
Br(51)	0·8836 (1)	0·1918 (1)	0·9773 (1)

Table 2. *Positional parameters and isotropic temperature factors for the hydrogen atoms*

	x	y	z	U (Å^2)
H(1)	0·969 (3)	0·285 (3)	0·821 (4)	0·060 (16)
H(211)	0·000 (0)	0·713 (1)	0·750 (0)	0·099 (10)
H(311)	0·875 (4)	0·824 (7)	0·944 (3)	0·099 (10)
H(312)	0·931 (3)	0·865 (6)	0·853 (5)	0·099 (10)
H(321)	0·789 (4)	0·940 (2)	0·771 (6)	0·099 (10)
H(322)	0·746 (3)	0·757 (7)	0·789 (6)	0·099 (10)
H(323)	0·796 (4)	0·813 (8)	0·693 (2)	0·099 (10)
H(411)	0·830 (4)	0·482 (5)	1·088 (3)	0·099 (10)
H(412)	0·753 (2)	0·588 (6)	0·968 (4)	0·099 (10)
H(413)	0·826 (4)	0·653 (4)	1·058 (4)	0·099 (10)

Discussion. Pyrromethenes are important model compounds for the study of conformational preference and bonding characteristics in the natural series of bile pigments. Their chromophore is formally equivalent to that of the *B* and *C* rings of biliverdin dimethyl ester (BDME) (Sheldrick, 1976). The red crystalline mineral-acid salts of the pyrromethenes are usually more stable than the corresponding free bases (Gossauer & Engel, 1978). The most characteristic property of the pyrromethenes is their ability to form stable metal chelates, the structures of several of which, bis(4,4′-diethoxycarbonyl-3,3′,5,5′-tetramethylpyrromethenato)copper(II) (Elder & Penfold, 1969), bis(3,3′,5,5′-tetramethylpyrromethenato)nickel(II) (Cotton, De Boer & Pipal, 1970) and bis(4,4′-diethoxycarbonyl-3,3′,5,5′-tetramethylpyrromethenato)palladium(II) (March, Couch, Emerson, Fergusson & Robinson, 1971), have been characterized by X-ray analysis. As part of our systematic study of the structures of linear polypyrrolic compounds, we have reported the structure of

Table 3. *Bond lengths* (Å)

C(2)–N(1)	1·399 (5)	C(5)–N(1)	1·351 (6)
Br(1)–Br(1)	1·590 (3)	C(21)–C(2)	1·386 (5)
C(3)–C(2)	1·438 (6)	C(31)–C(3)	1·489 (6)
C(4)–C(3)	1·397 (6)	C(32)–C(31)	1·526 (7)
C(41)–C(4)	1·502 (9)	C(5)–C(4)	1·390 (6)
Br(51)–C(5)	1·851 (4)		

Table 4. *Bond angles* (°)

C(5)–N(1)–C(2)	107·9 (4)	C(3)–C(2)–N(1)	106·7 (4)
C(21)–C(2)–N(1)	127·1 (4)	C(2)–C(21)–C(2)	133·8 (6)
C(3)–C(2)–C(21)	126·0 (4)	C(4)–C(3)–C(2)	107·6 (4)
C(31)–C(3)–C(2)	126·5 (4)	C(32)–C(31)–C(3)	112·1 (4)
C(4)–C(3)–C(31)	125·8 (4)	C(5)–C(4)–C(3)	106·4 (4)
C(41)–C(4)–C(3)	127·5 (4)	C(4)–C(5)–N(1)	111·3 (4)
C(5)–C(4)–C(41)	126·1 (4)	Br(51)–C(5)–C(4)	127·8 (4)
Br(51)–C(5)–N(1)	120·9 (3)		

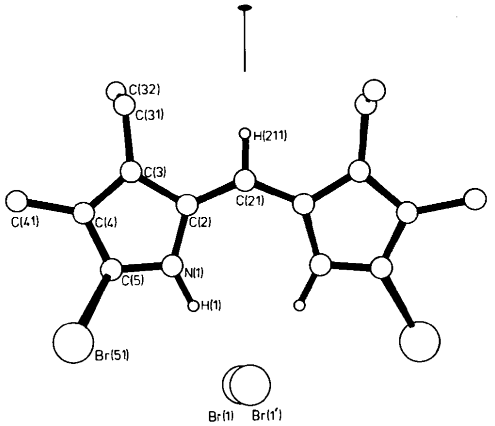

Fig. 1. Molecule of (I) in perspective with the atom numbering.

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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 33213 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

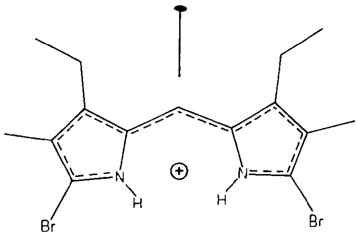

Fig. 2. Delocalized protonation in (I).

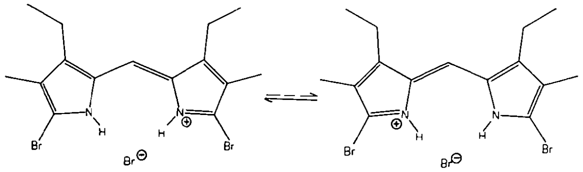

Fig. 3. The two mesomeric forms of the protonated pyrromethene system.

the pyrromethene free base 5,5′-diethoxycarbonyl-3,3′-diethyl-4,4′-dimethyl-2,2′-pyrromethene (II) (Sheldrick, Borkenstein, Struckmeier & Engel, 1978). We present here the results of the first X-ray analysis of a protonated pyrromethene (I).

It may be deduced from the position and shape of the N_{1s} level in their X-ray photoelectron spectra, that both the N atoms in symmetrically and unsymmetrically substituted protonated pyrromethenes are equivalent and that, therefore, the positive charge is delocalized on the time-scale of electronic excitement (Falk, Hofer & Lehner, 1974). The observations of crystallographic C_2 symmetry for the chromophore of (I) and of the equivalence of the two independent N···Br distances to the disordered Br^- anions (3·228 and 3·225 Å) are in accordance with a delocalized protonation (Fig. 2). The protonated pyrromethene moiety displays a slightly twisted *syn-Z* conformation with an interplanar angle of 13·0°, which contrasts with the planar conformation of the free base (II) [interplanar angle = 0·6°]. A fundamentally planar *syn-Z* conformation has been predicted for protonated pyrromethenes in solution on the basis of lanthanide-induced-shift measurements (Falk, Gergely & Hofer, 1974). The bond-length distribution in the protonated pyrromethene system in (I) is very similar to that in the free base (II), for which a 50:50 equilibrium of the two proton-jump-related valence tautomers was observed. The shortness of N(1)–C(5) in comparison with N(1)–C(2) [1·351 (6) *vs* 1·400 (5) Å] is explicable in terms of contributions from the two mesomeric forms (Fig. 3). The former bond possesses a formal order of 1·5, the latter 1·0. The bond-angle distribution in (I) is, however, strikingly different from that in (II). As a result of the formation of two N–H···Br hydrogen bonds rather than the N–H···N intramolecular hydrogen bonds as in (II), the angles C(2)–C(21)–C(2)′, N(1)–C(2)–C(21) and H(1)–N(1)–C(2) are significantly larger in (I) than in (II) [133·8 (6), 127·1 (4) and 136 (3)° *vs* 126·1 (2), 122·2 (2) and 131 (2)° respectively]. This leads to an intramolecular N···N distance of 3·25 Å in (I) as opposed to 2·75 Å in (II). Bond angles and an N···N distance similar to those in (I) were observed in a planar *syn-Z* configurated pyrromethenone (Cullen, Black, Meyer, Lightner, Quistad & Pak, 1977) in which both N–H protons were involved in N–H···O hydrogen bonds [C–C–C 133·3 (9), N–C–C 126·4 (9)°, N···N 3·17 Å].

The N–H···Br distances are in good agreement with those found in other structures containing Br^-, which vary from 3·12 to 3·48 Å (Anderson, Bartczak & Hodgkin, 1974). In general, such bonds are not linear and the bend may be as high as 30° (Donohue, 1968). The H···Br distances in (I) are not identical: H(1)–Br(1) is 2·30 (4) Å with a Br···H–N angle of 151 (4)°, whereas H(1′)–Br(1) is 2·23 (4) Å with a corresponding angle of 167 (4)°. These findings must, of course, be regarded with caution in view of the lack of precision in the location of H(1) in a structure containing three Br atoms. However, this apparent asymmetry is further illustrated by the fact that Br(1) is −1·22 Å from the plane of the atoms 1–5, but only −0·353 Å from that of atoms 1′–5′. The distances from the weighted least-squares plane are: N(1) −0·005, C(2) 0·004, C(3) 0·000, C(4) −0·004, C(5) 0·006, C(21) 0·081, Br(51) 0·067 Å.

This analysis of a model protonated pyrromethene has relevance to the structures of the natural bilatriene bile pigments. The angle of twist of 13·0° in (I) is not dissimilar to those of 20·8, 9·8 and 19·3° in the helical BDME, for which, however, much narrower methine bridge angles in the range 125·3–127·4 (6)° are observed. It is, therefore, possible that protonation of the bilatriene chromophore will lead to a widening of the helix, due to an increase in the bond angles at the methine bridges, but not to a lengthening of the molecule perpendicular to its molecular plane. This has, indeed, recently been observed for a related model bilatriene hydrobromide, for which methine bridge angles of 128–124 (1)° were reported (Struckmeier & Engel, 1977).

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1,2-Epoxy-3-hydroxy-α-lycoran-7-one

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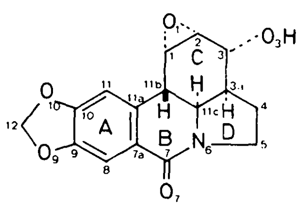
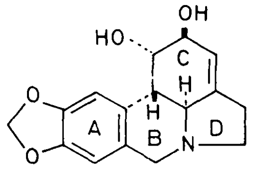
Abstract. $C_{16}H_{15}NO_5$. Monoclinic, $P2_1/c$, $a = 17{\cdot}06$ (2), $b = 9{\cdot}33$ (1), $c = 8{\cdot}25$ (1) Å, $\beta = 98{\cdot}4$ (2)°, $D_c = 1{\cdot}54$ g cm^{-3}, $Z = 4$. Full-matrix least-squares refinement gave $R = 0{\cdot}08$ for 199 parameters and 1453 significant reflexions [$I > 2\sigma(I)$]. The compound is an intermediate in the synthesis of lycorine.

Introduction. The title compound (I) is an intermediate in the total synthesis (Møller, Steinberg & Torssell, 1978) of lycorine (II). The structure was solved to determine the configuration of the epoxy and hydroxy groups relative to the junction of rings *B* and *D*.



(I)



(II)

Single crystals were obtained from an aqueous solution by controlled cooling (10°C d^{-1}). A crystal, 0·4 × 0·6 × 0·7 mm, was mounted on a Picker FACS-1 diffractometer and intensities were measured out to $2\theta = 45°$ with monochromated Mo $K\alpha$ radiation. Data were collected with the ω–2θ step-scanning technique, with a step length of 0·04° and a scan width of $(3{\cdot}92 + 0{\cdot}692 \tan \theta)°$. 1712 independent reflexions were obtained of which 1453 has $I > 2\sigma(I)$ according to counting statistics. No corrections were made for absorption.

The structure was determined with *MULTAN* (Germain, Main, & Woolfson, 1971). Least-squares

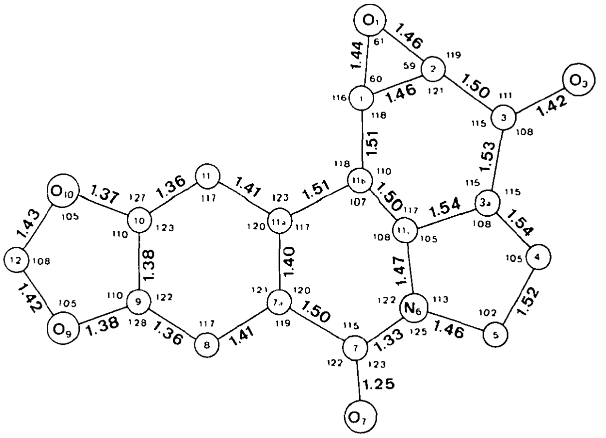


Fig. 1. Bond distances (Å) and angles (°). The mean estimated standard deviations are 0·006 Å for bond lengths and 0·4° for angles.