X-Ray Molecular Structure of 1,19-Diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethylbiladiene-ac Dihydrobromide

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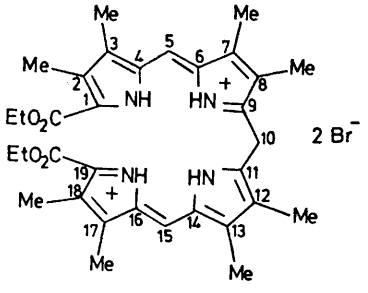
Summary The molecular structure of 1,19-diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethylbiladiene-ac dihydrobromide (**1**) has been determined by *X*-ray diffraction; the molecule shows a linear arrangement and consists of two planar units around the methylene carbon atom C(10) with an interplanar angle of 107°.

PROTONATED biladienes-ac (1,19-dideoxy-biladiene-ac; 10,-23-dihydro-21*H*-bilin) and their corresponding metal chelates, which were synthesized for the first time by Johnson *et al.*[1] represent by far the most useful class of open-chain tetrapyrroles as intermediates for the synthesis of porphyrins[2] and related macrocycles.[3] Recently their importance has been shown in the synthesis of natural occuring porphyrins, such as isocoproporphyrin,[4] uroporphyrin III,[5,6] and phyriaporphyrin III,[6] and bilanes[7] of biological interest. The mechanism of their cyclisations has been discussed,[8] but an investigation of the molecular structure of biladiene-ac salts, biladiene-ac free bases, and their corresponding metal complexes could perhaps explain more clearly their

unique behaviour on cyclisation to tetrapyrrole macrocycles. As far as we know no *X*-ray studies of protonated open-chain polypyrroles have been reported. Red-green needle-shaped crystals of (**1**)[9] were obtained directly from the reaction of 3,3′,4,4′-tetramethyl-dipyrromethanedicarboxylic acid with ethyl 5-formyl-3,4-dimethylpyrrole-2-carboxylate in glacial AcOH in the presence of HBr by slow cooling from 100 °C (reaction temperature) to room temperature. *Crystal data:* monoclinic, space group $P2_1/n$, with cell dimensions: $a = 18{\cdot}350(8)$, $b = 13{\cdot}138(3)$, $c = 14{\cdot}476(4)$ Å, $\beta = 99{\cdot}10(7)°$; $Z = 4$. Intensity data were collected



(1)

using monochromated Mo-K_α radiation on a Stoe 4-circle-diffractometer. 1206 reflections with $I > 3\sigma(I)$ were used for the structure solution by the heavy-atom technique. The R index after full-matrix least squares refinement[10] with anisotropic temperature factors for the Br atoms is 0·092. As can be seen from the Figure the molecule is composed of two nearly planar units around the methylene carbon atom C(10). Including the atoms C(1^1), O(1^2), O($1^{2'}$) C(19^1), O(19^2), and O($19^{2'}$) the deviations from the least-squares planes are within ± 0·2 Å. The dihedral angle between these planes is 107°. The angle C(9)–C(10)-C(11) is 107(2)°. The two bromide anions do not lie in the two best planes, but deviate from them by more than 0·75 Å. The C-C bond lengths and angles in the Figure show that

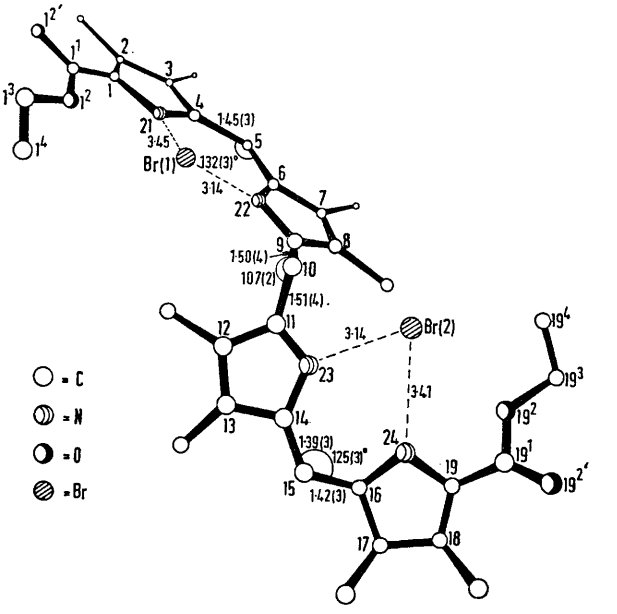


FIGURE. Perspective view of the structure of the title compound (**1**). Bond lengths are given in Å and bond angles in degrees.

the four pyrrole rings are attached by two methine and one methylene bridge. The bromine–nitrogen distances indicate protonation of N(22) and N(23). A similar linear structure for bilirubin, which is stabilised by intramolecular N· · · · H–O and O–H · · · · O hydrogen bonds to the propionic acid side-chains was proposed by Kuenzle[11] and has recently been confirmed by *X*-ray analysis.[12]

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