

Journal of The Chemical Society, Chemical Communications

NUMBER 2/1978

18 JANUARY

X-Ray Crystal and Molecular Structure of 1,19-Diethoxycarbonyl-2,3,7,8,12,13,17,18-octamethylbilatriene-*abc* Hydrobromide

BY GERHARD STRUCKMEIER

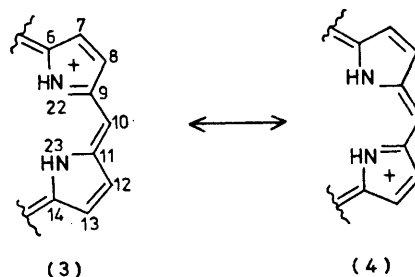
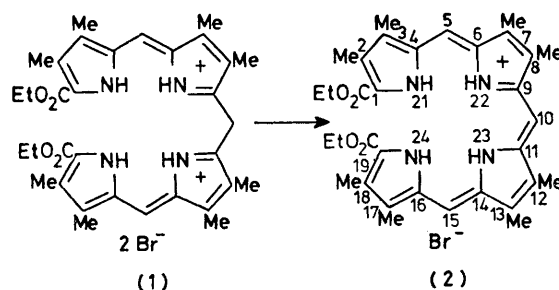
(Institut für Anorganische Chemie der Technischen Universität, D-3300 Braunschweig, Pochelstrasse, W. Germany)

and JÜRGEN ENGEL*†

(Institut für Organische Chemie A der Technischen Universität, D-3300 Braunschweig, Schleinitzstrasse, W. Germany)

Summary The molecular structure of the title compound (2), the deprotonation product of the corresponding biladiene-*ac* salt (1), has been determined by X-ray diffraction; on deprotonation the linear 'ridge-like' arrangement of (1) is changed to a helical conformation of the bilatriene chromophore.

BILADIENE-*ac* SALTS *e.g.* (1) are important building blocks for the synthesis of tetrapyrrolic compounds such as porphyrins,¹ azaporphyrins,² tetrahydrocorrins,¹ corroles,^{1,2} and bilanes.^{3,4} Johnson and his co-workers showed that they are readily deprotonated in solution by bases. This property is important with respect to their cyclisation behaviour; if deprotonation is hindered no cyclisation occurs.⁶ In the course of our investigations of the influence of protonation and deprotonation on the structure of open-chain polypyrroles we have recently determined by X-ray diffraction the molecular structure of 1,19-diethoxycarbonyloctamethylbiladiene-*ac* dihydrobromide⁷ and its 1,19-dimethyl substituted derivative,⁸ and 5,5'-diethoxycarbonyl-3,3'-diethyl-4,4'-dimethylpyrromethene hydrobromide⁸ and its free base.⁹ We now report the structure of 1,19-diethoxycarbonyloctamethylbilatriene-*abc* hydrobromide (2), the deprotonation product of (1). Bilatriene salts of type (2) were previously only described as occurring in solution,⁵ and this is the first report of a solid bilatriene-*abc* salt. The salt (2) was isolated by heating a methanolic solution of (1) followed by slow



cooling, as deep green crystals. The spectroscopic data are compatible with the formulation shown. Green parallelepipeds suitable for X-ray work were obtained by slow diffusion of ether into a methylene dichloride-ethanol solution of (2).

* Present address: Chemiewerk Homburg, ZN Degussa, D-6000 Frankfurt, Daimler Str. 25, W. Germany.

Crystal data: triclinic, space group $P1$, $a = 15.386(7)$, $b = 15.528(7)$, $c = 9.230(5)$ Å, $\alpha = 123.8(2)$, $\beta = 70.6(2)$, $\gamma = 108.8(2)^\circ$ and $Z = 2$. The intensity data were collected on a Stoe 4-circle-diffractometer using graphite-monochromated Mo- K_α radiation. The structure was solved by the heavy-atom technique using 2606 reflections with $I \geq 3\sigma(I)$. $R = 0.095$ after full-matrix least-squares refinement¹⁰ with anisotropic temperature factors for all atoms.†

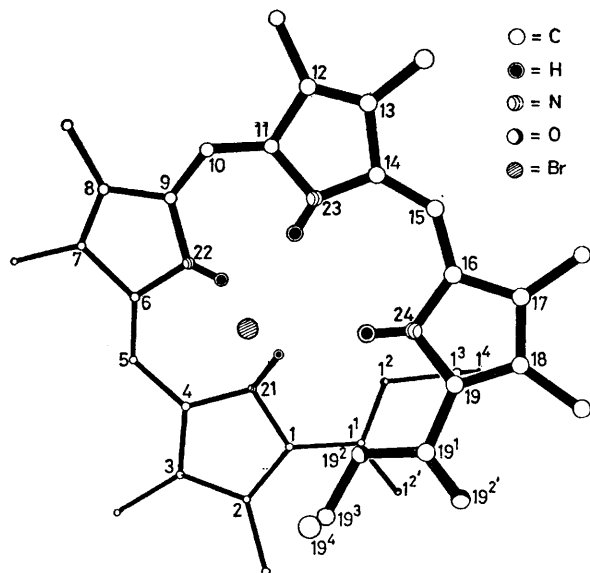


FIGURE. Perspective view of the structure of (2).

As can be seen from the Figure, on deprotonation, the linear 'ridge-like' arrangement of the biladiene-*ac* skeleton⁷ is changed into a helical conformation of the bilatriene chromophore (2). The intramolecular distance [C(1')-C(19')] between the two ethoxycarbonyl groups is 3.61 Å, and the

distances N(21)-N(23), N(22)-N(24), and C(1)-C(19) are 5.14, 4.69, and 4.78 Å, respectively. The bond lengths of the bridging carbon atoms C(5)-C(4), C(5)-C(6), C(10)-C(9), C(10)-C(11), C(15)-C(14), and C(15)-C(16) are 1.39(2), 1.38(2), 1.36(2), 1.37(2), 1.33(2), and 1.42(2) Å. Together with the angles C(4)-C(5)-C(6) [134.1(8)°], C(9)-C(10)-C(11) [132.9(7)°], and C(14)-C(15)-C(16) [128.3(9)°] the bond lengths clearly demonstrate that the pyrrole rings are attached to one another by three methine bridges. The bond lengths N(22)-C(9) [1.38(2)], C(9)-C(10) [1.36(2)], C(10)-C(11) [1.37(2)], C(11)-N(23) [1.38(2)], C(7)-C(8) [1.32(2)], C(12)-C(13) [1.30(2)], C(6)-C(7) [1.46(2)], C(13)-C(14) [1.52(2)], C(6)-N(22) [1.39(2)], C(14)-N(23) [1.42(2)], C(8)-C(9) [1.45(2)], and C(11)-C(12) [1.47(2) Å], as well as the interionic distances Br-N(21) [3.40], Br-N(22) [3.24], Br-N(23) [3.21], and Br-N(24) [3.86 Å] indicate protonation at N(22) or N(23). These results indicate that the molecule should be described by the two mesomeric structures (3) and (4). This was recently confirmed by the observation that the free base of (2) is present as the 21-H, 24-H tautomer.⁹ The bromide ion does not lie in the plane of any pyrrole ring. The crystal structure contains a disordered ethanol molecule, which has not as yet been unequivocally located.

As in the case of (1) the corresponding bile pigment of (2), namely the dimethylester of the natural occurring biliverdin, has a structure comparable with the reported one.¹¹ The observed helical conformation of (2) seems to be favourable for cyclisation to tetrahydrocorrins.¹² Starting from the hydroperchlorate of (2) we recently were successful in inserting platinum into the tetrahydrocorrin skeleton for the first time.¹²

We thank the Deutsche Forschungsgemeinschaft for support. One of us (J.E.) thanks Prof. H. H. Inhoffen for his support as well as for gifts of pyrrolic compounds and Dr. W. S. Sheldrick for his interest.

(Received, 31st August 1977; Com. 915.)

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¹ A. W. Johnson, *Chem. Soc. Rev.*, 1975, 29, 1.

² J. Engel and A. Gossauer, *J.C.S. Chem. Comm.*, 1975, 714.

³ J. Engel and A. Gossauer, *J.C.S. Chem. Comm.*, 1975, 570.

⁴ J. Engel and A. Gossauer, *Annalen*, 1977, 225.

⁵ D. Dolphin, A. W. Johnson, J. Leng, and P. van den Broek, *J. Chem. Soc. (C)*, 1966, 880.

⁶ D. Dolphin, R. L. N. Harris, A. W. Johnson, and I. T. Kay, *J. Chem. Soc. (C)*, 1966, 98.

⁷ G. Struckmeier, U. Thewalt, and J. Engel, *J.C.S. Chem. Comm.*, 1976, 963.

⁸ G. Struckmeier and J. Engel, unpublished results.

⁹ W. S. Sheldrick, A. Borkenstein, G. Struckmeier, and J. Engel, submitted for publication.

¹⁰ Program system XDRED, XREF, XTAN and XMAP, G. M. Sheldrick, University of Cambridge.

¹¹ W. S. Sheldrick, *J.C.S. Perkin II*, 1976, 1457.

¹² J. Engel and H. H. Inhoffen, *Annalen*, 1977, 767.