respectively. The S(1)–C(1), C(1)–N(1) and C(1)–N(2) distances of 1·667 (6), 1·374 (7) and 1·320 (7) Å, respectively, for the imidazolidine ring indicate the effect of the thiourea resonance system.

There are three intermolecular hydrogen bonds: $O(3)–H\cdots O(4)(\frac{1}{2}+y,\frac{3}{2}-x,-\frac{1}{4}+z) = 2\cdot673$ (7), and $H\cdots O(4) = 1\cdot72$ (5) Å; $O(2)–H\cdots O(1)(\frac{3}{2}-x,\frac{1}{2}+y,\frac{5}{4}-z) = 2\cdot988$ (6) and $H\cdots O(1) = 1\cdot97$ (5) Å; $O(4)–H\cdots O(3)(\frac{3}{2}-x,-\frac{1}{2}+y,\frac{5}{4}-z) = 2\cdot697$ (7) and $H\cdots O(3) = 1\cdot63$ (5) Å. All other intermolecular contacts are van der Waals interactions. The molecular packing is shown in Fig. 2.

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Structure of 25-Ethoxycarbonyl-2,3,7,8,12,13,17,18-octaethyl-21,22-methano-21*H*,22*H*-porphyrin Hydrobromide, $C_{40}H_{51}N_4O_2^+.Br^-$. The First Example of a *cis-N,N*-Bridged Porphyrin

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Dedicated to Professor Dorothy Hodgkin on the occasion of her 75th birthday

Abstract. $M_r = 699\cdot79$, monoclinic, $C2/c$, $a = 20\cdot324$ (3), $b = 19\cdot947$ (3), $c = 18\cdot976$ (3) Å, $\beta = 98\cdot31$ (5)°, $V = 7612\cdot07$ Å³, $Z = 8$, $D_m = 1\cdot21_8$, $D_x = 1\cdot221$ Mg m⁻³, graphite-monochromatized Cu $K\alpha$ radiation, $\lambda = 1\cdot54178$ Å, μ(Mo $K\alpha$) = 10·51, μ(Cu $K\alpha$) = 16·23 mm⁻¹, $T = 295$ K, $F(000) = 2960$, $R = 0\cdot073$ for 1811 observed reflections. The porphyrin macroring is considerably folded as illustrated by the angles the pyrrole rings form with the mean N(21)–N(24) plane: −9·8, −3·9, 12·8 and 6·1° (e.s.d.'s *ca* 0·9°) respectively. The ethoxycarbonylmethylene group and Br are disordered. The H atom bonded to N(23) deviates −0·22 (9) Å from the plane of the macroring in the opposite direction from the side chain.

Introduction. Reactions of cobalt(II) octaethyl-porphyrin and corresponding cobalt(III) complexes with ethyl diazoacetate were investigated to ascertain the possibility that a cobalt carbene complex is an intermediate in the reactions of biochemical rearrangements controlled by cobalamin-containing enzymes (Batten, Hamilton, Johnson, Shelton & Ward, 1974; Johnson, Ward, Batten, Hamilton, Shelton & Elson, 1975). The title hyrobromide and a number of metalloporphyrins obtained in the course of this work

were the first examples of a *cis-N,N*-substituted porphyrin and of metalloporphyrins.

The present work was undertaken to investigate the geometry of the octaethylporphyrin (OEP) nucleus when the neighboring N atoms are bridged by ethoxy-carbonylmethylene. The introduction of a C atom between N(21) and N(22) completes a new six-membered ring within the porphyrin macrocycle. This was expected to cause considerable difference in the stereochemistry of the N atoms present in the structure. Additionally, the position of the inner proton was of interest. It was postulated (Johnson, 1976) that this proton should be at equal distances from the N atoms and deviate from the plane of these N atoms in the opposite direction from the bridging methine group. The crystals of the hydrobromide were kindly supplied by the late Professor A. W. Johnson of Sussex University, England.

Experimental. Deep-purple prisms grown by slow evaporation from acetone–aqueous NaBr solution. D_m by flotation in aqueous KI. CAD-4 automated four-circle diffractometer. Crystal 0·10 × 0·18 × 1·30 mm; 15 reflections in the θ range 25–35° used for refinement of the unit-cell parameters; graphite-monochromatized

Mo $K\alpha$; no absorption correction; θ–2θ scanning mode; max. $\sin\theta/\lambda = 0\cdot572$ Å^{-1}; max. hkl −22 to 22,22,10; 2250 reflections measured. Second data set collected using Cu $K\alpha$ graphite-monochromatized radiation: approximately spherical crystal 0·3 mm in diameter; no absorption correction; θ–2θ scanning mode; max. $\sin\theta/\lambda = 0\cdot458$ Å^{-1}; max. hkl −18 to 18,18,17; 2008 reflections measured; 1811 reflections with $F_o > 2\sigma(F_o)$ used in the structure solution and refinement using program *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); solution obtained for space group Cc; positional parameters of all but a few terminal C atoms belonging to ethyl groups were found and later transformed to $C2/c$; refinement using F_o by blocked-full-matrix least-squares technique and difference electron density syntheses in isotropic (porphyrin core) and anisotropic (Br, eight outer ethyl groups and ethoxycarbonyl-methylene group) mode; all H atoms found in a weighted difference Fourier synthesis based on reflections with $\sin\theta/\lambda \leq 0\cdot3$ Å^{-1}, or calculated geometrically; positional and isotropic thermal parameters of H atoms taken as for their parent C atoms; H-atom parameters included in final calculations of the structure factors but not refined except for positional parameters of H(23); 307 parameters refined; ratio unique reflections/parameters = 5·9:1, $R = 0\cdot073$, $wR = 0\cdot078$, $w = 1\cdot264/[\sigma^2(F_o) + 0\cdot00227F_o{}^2]$; max. $\Delta/\sigma = 0\cdot32$ for atoms in the porphyrin core; max. height in final difference Fourier synthesis ca 0·3 e Å^{-3}; scattering factors and anomalous-dispersion parameters of *SHELX*76 (Sheldrick, 1976). No secondary-extinction correction. Attempts to use the slightly more extensive Mo data set in the refinement of the structure were unsuccessful, probably because of the highly disordered crystal used for the data collection. The final atomic coordinates used with the Mo data set gave $R = 0\cdot16$. All calculations performed with programs *SHELX*76 (Sheldrick, 1976), and *XANADU* (Roberts & Sheldrick, 1975).*

Discussion. Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2. The numbering scheme is shown in Fig. 1, and Fig. 2 shows deviations of atoms from the plane described by the four pyrrole N atoms. The crystal structure consists of discrete molecules of N(21),N(22)-bridged OEP. The Br atom is disordered and can be described as half-occupying two positions: one at the center of symmetry, the other general. The closest contacts made by these Br atoms are: Br(1)···H(252) = 2·84 and Br(2)···H(401) =

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* Lists of structure factors, anisotropic thermal parameters and positional parameters and isotropic U values for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39930 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates* $(\times10^4)$ *and isotropic thermal parameters* $(\text{Å}^2 \times 10^3)$

	x	y	z	U_{iso}/U_{eq}
Br(1)†	0	0	0	151 (2)*
Br(2)†	3111 (2)	2062 (2)	4883 (2)	132 (2)*
N(21)	7377 (3)	1330 (3)	4253 (3)	48 (2)
N(22)	8133 (3)	2207 (3)	4160 (3)	46 (2)
N(23)	6892 (3)	3375 (3)	3948 (3)	54 (2)
H(23)	6672 (30)	2923 (30)	4121 (30)	53
N(24)	6074 (3)	2404 (3)	4056 (3)	56 (2)
C(1)	6779 (4)	983 (5)	4302 (5)	59 (3)
C(2)	6969 (5)	325 (5)	4547 (5)	65 (3)
C(3)	7656 (4)	255 (4)	4614 (4)	63 (3)
C(4)	7906 (4)	872 (4)	4415 (4)	54 (3)
C(5)	8547 (4)	1096 (4)	4399 (4)	54 (3)
C(6)	8663 (4)	1759 (4)	4280 (4)	53 (3)
C(7)	9271 (4)	2134 (4)	4276 (4)	54 (3)
C(8)	9110 (4)	2779 (5)	4146 (4)	49 (3)
C(9)	8393 (4)	2855 (4)	4052 (5)	49 (3)
C(10)	8080 (5)	3457 (4)	3899 (4)	52 (3)
C(11)	7440 (4)	3710 (4)	3809 (4)	52 (3)
C(12)	7242 (4)	4371 (4)	3549 (4)	58 (3)
C(13)	6575 (5)	4418 (5)	3540 (5)	69 (3)
C(14)	6338 (4)	3782 (5)	3772 (5)	62 (3)
C(15)	5714 (5)	3535 (5)	3794 (6)	65 (4)
C(16)	5571 (4)	2878 (4)	3919 (5)	65 (3)
C(17)	4935 (5)	2525 (5)	3866 (5)	65 (3)
C(18)	5055 (5)	1875 (4)	3967 (5)	64 (4)
C(19)	5788 (5)	1805 (4)	4074 (5)	58 (3)
C(20)	6111 (5)	1204 (5)	4206 (5)	64 (3)
C(21)	6488 (5)	−225 (5)	4720 (7)	87 (2)*
C(22)	6174 (6)	−567 (7)	4068 (8)	135 (4)*
C(23)	8068 (6)	−344 (7)	4873 (8)	83 (4)*
C(24)	8163 (7)	−808 (7)	4301 (8)	115 (6)*
C(25)	9953 (4)	1814 (4)	4390 (6)	74 (4)*
C(26)	10138 (6)	1534 (7)	3695 (6)	114 (5)*
C(27)	9580 (4)	3354 (4)	4097 (6)	70 (4)*
C(28)	9559 (6)	3492 (7)	3321 (6)	115 (5)*
C(29)	7705 (4)	4878 (4)	3315 (5)	75 (4)*
C(30)	7903 (6)	4704 (7)	2590 (6)	111 (5)*
C(31)	6119 (4)	4999 (5)	3272 (4)	90 (4)*
C(32)	5932 (6)	4987 (7)	2453 (6)	142 (6)*
C(33)	4261 (4)	2883 (4)	3696 (5)	89 (4)*
C(34)	4014 (7)	2917 (6)	2906 (6)	128 (7)*
C(35)	4579 (5)	1302 (5)	3982 (6)	97 (4)*
C(36)	4473 (7)	909 (5)	3294 (6)	145 (7)*
C(37)	7491 (4)	1922 (3)	3854 (3)	44 (5)*
H(37)	7120	2287	3970	60
C(38)	7481 (8)	1747 (7)	3060 (7)	70 (5)*
O(1)	7241 (8)	1256 (7)	2793 (7)	136 (15)*
O(2)	7766 (8)	2207 (7)	2736 (7)	106 (12)*
C(39)	7793 (9)	2122 (8)	1974 (6)	136 (23)*
C(40)	8292 (10)	2520 (11)	1764 (9)	306 (52)*

* U_{eq} values; $U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3(1-\cos^2\beta)$.
† Site-occupation factor 0·5.

2·57 Å. The only other known example of a hydro-bromide of a porphyrin-like structure is that of hexamethylcorrole hydrobromide (Anderson, Bartczak & Hodgkin, 1974). The ethoxycarbonylmethylene group is also disordered but no useful model for such disorder was found from difference electron density syntheses. The temperature factors of the atoms belonging to this group were constantly enlarged in the course of refinement and the bond lengths within this group were affected. Therefore, those bond lengths were constrained using values found for 21-ethoxycarbonyl-methyl-2,3,7,8,12,13,17,18-octamethylporphyrin (Mc-Laughlin, 1974). The terminal C atoms of all ethyl groups point in the same direction as the ethoxy-carbonylmethylene group. The H atom was found bonded to N(23) and deviates −0·22 (9) Å from the plane of the macroring described by the four pyrrole N atoms; *i.e.* in the opposite direction from the side chain.

$$C_{40}H_{51}N_4O_2^+.Br^-$$

Table 2. Bond lengths (Å) and angles (°) (e.s.d.'s for angles ca 0·7–1·0°)

N(21)–C(1)	1·41 (1)	N(21)–C(4)	1·41 (1)
N(21)–C(37)	1·440 (9)	N(22)–C(37)	1·464 (9)
N(22)–C(6)	1·393 (9)	N(22)–C(9)	1·42 (1)
N(23)–C(11)	1·36 (1)	N(23)–C(14)	1·39 (1)
N(23)–H(23)	1·08	N(24)–C(16)	1·39 (1)
N(24)–C(19)	1·33 (1)	C(37)–C(38)	1·54 (1)
C(37)–H(37)	1·09	C(38)–O(1)	1·18 (1)
C(38)–O(2)	1·29 (1)	O(2)–C(39)	1·47 (1)
C(39)–C(40)	1·39 (3)	C(1)–C(2)	1·43 (1)
C(4)–C(3)	1·40 (1)	C(6)–C(7)	1·45 (1)
C(9)–C(8)	1·45 (1)	C(11)–C(12)	1·44 (1)
C(14)–C(13)	1·45 (1)	C(16)–C(17)	1·46 (1)
C(19)–C(18)	1·48 (2)	C(2)–C(3)	1·39 (1)
C(7)–C(8)	1·34 (1)	C(12)–C(13)	1·36 (1)
C(17)–C(18)	1·33 (2)	C(4)–C(5)	1·38 (1)
C(5)–C(6)	1·37 (1)	C(9)–C(10)	1·37 (1)
C(10)–C(11)	1·38 (2)	C(14)–C(15)	1·37 (1)
C(15)–C(16)	1·37 (1)	C(19)–C(20)	1·37 (1)
C(20)–C(1)	1·42 (1)	C(2)–C(21)	1·53 (1)
C(3)–C(23)	1·50 (2)	C(7)–C(25)	1·51 (1)
C(8)–C(27)	1·51 (2)	C(12)–C(29)	1·49 (1)
C(13)–C(31)	1·52 (3)	C(17)–C(33)	1·54 (2)
C(18)–C(35)	1·50 (2)	C(21)–C(22)	1·47 (2)
C(23)–C(24)	1·46 (3)	C(25)–C(26)	1·53 (3)
C(27)–C(28)	1·52 (3)	C(29)–C(30)	1·53 (3)
C(31)–C(32)	1·55 (3)	C(33)–C(34)	1·51 (3)
C(35)–C(36)	1·51 (3)		

N(21)–C(37)–N(22)	108	N(21)–C(37)–H(37)	106
N(22)–C(37)–H(37)	105	H(37)–C(37)–C(38)	116
N(21)–C(37)–C(38)	110	N(22)–C(37)–C(38)	111
C(37)–C(38)–O(1)	124	C(37)–C(38)–O(2)	111
O(1)–C(38)–O(2)	125	C(38)–O(2)–C(39)	118
O(2)–C(39)–C(40)	110	C(1)–N(21)–C(4)	107·7
C(1)–N(21)–C(37)	130	C(9)–N(22)–C(37)	128·6
C(6)–N(22)–C(9)	108·2	C(11)–N(23)–C(14)	109
C(37)–N(21)–C(4)	118	C(37)–N(22)–C(6)	116
C(11)–N(23)–H(23)	149	C(14)–N(23)–H(23)	102
C(9)–N(22)–C(37)	129	C(16)–N(24)–C(19)	108
C(20)–C(1)–N(21)	131·0	N(21)–C(1)–C(2)	106·2
N(21)–C(1)–C(20)	131	N(21)–C(4)–C(3)	109·4
N(21)–C(4)–C(5)	119	N(22)–C(6)–C(5)	120
N(22)–C(9)–C(8)	106	N(22)–C(6)–C(7)	108
N(23)–C(11)–C(10)	126	N(22)–C(9)–C(10)	131
N(23)–C(14)–C(13)	107	N(23)–C(11)–C(12)	109
N(24)–C(16)–C(15)	121	N(23)–C(14)–C(15)	120
N(24)–C(19)–C(18)	110	N(24)–C(16)–C(17)	108
C(1)–C(2)–C(21)	125·2	N(24)–C(19)–C(20)	126
C(2)–C(3)–C(23)	128	C(1)–C(2)–C(3)	110
C(23)–C(3)–C(4)	126	C(2)–C(3)–C(4)	107
C(4)–C(5)–C(6)	120	C(3)–C(4)–C(5)	132
C(6)–C(7)–C(25)	123·1	C(5)–C(6)–C(7)	132·0
C(25)–C(7)–C(8)	129	C(6)–C(7)–C(8)	108
C(7)–C(8)–C(9)	110	C(7)–C(8)–C(27)	127
C(8)–C(9)–C(10)	123	C(27)–C(8)–C(9)	123
C(10)–C(11)–C(12)	126	C(9)–C(10)–C(11)	138
C(11)–C(12)–C(13)	107	C(11)–C(12)–C(29)	124
C(12)–C(13)–C(31)	128	C(29)–C(12)–C(13)	128
C(31)–C(13)–C(14)	124	C(12)–C(13)–C(14)	108
C(14)–C(15)–C(16)	125	C(13)–C(14)–C(15)	133
C(16)–C(17)–C(33)	123	C(15)–C(16)–C(17)	131
C(33)–C(17)–C(18)	129	C(16)–C(17)–C(18)	109
C(17)–C(18)–C(19)	106	C(17)–C(18)–C(35)	130
C(18)–C(19)–C(20)	124	C(35)–C(18)–C(19)	124
C(20)–C(1)–C(2)	122·6	C(19)–C(20)–C(1)	136
C(3)–C(23)–C(24)	113	C(2)–C(21)–C(22)	111
C(8)–C(27)–C(28)	112	C(7)–C(25)–C(26)	111·5
C(13)–C(31)–C(32)	112	C(12)–C(29)–C(30)	112
C(18)–C(35)–C(36)	113	C(17)–C(33)–C(34)	113

Introduction of the C atom C(37) between N(21) and N(22) completes a new six-membered ring in the structure (Fig. 1). The resulting structure is relatively free from strain and considerably folded (Fig. 2). There are three different types of pyrrole rings in the structure: the two N-substituted rings, and one ring with an H atom bonded to N, and one without.

Single N-substitution in a non-metallo-OEP has been shown to have a significant effect on the normal planarity of the macrocycle (McLaughlin, 1974), as well as on the structure of a Co–OEP complex (Goldberg & Thomas, 1976) and on the N-substituted Cu corrole (Grigg, King & Shelton, 1970; Grigg, Shelton, Sweeney & Johnson, 1972). As Fig. 2 shows, the bridging of N(21) and N(22) results in a bending of the macrocycle roughly along the line passing through the C(10) and C(20) methine C atoms. The N(21) and N(22) pyrrole rings are bent downwards from the mean plane described by the four pyrrole N atoms, whereas the N(23) and N(24) pyrrole rings are above this plane (Fig. 2). There is additional twist of the macroring involving the C_β–C_β bonds of the N(21) and N(23) pyrroles deviating most from the mean plane. The angles between the pyrrole-ring planes and the mean N(21)–N(24) plane are −9·8, −3·9, 12·8 and 6·1° respectively (e.s.d.'s ca 0·9°). The pyrrole rings are not planar. The appropriate angles formed by the C_α–N–C_α' planes with the mean N(21)–N(24) plane are 3·0, 3·1, 14·3 and 7·2° (e.s.d.'s ca 0·9°) respectively for pyrrole rings N(21) through N(24). These deviations from planarity are in contrast to the situation found in OEP where pyrrole rings are essentially planar (Lauher & Ibers, 1976).
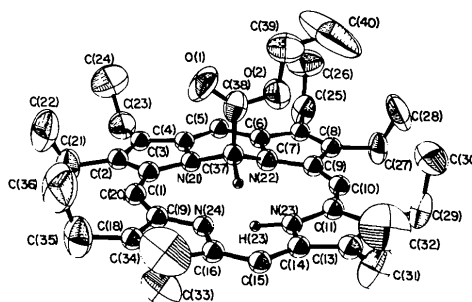

Fig. 1. ORTEP diagram (Johnson, 1965) showing the molecular structure and labeling scheme omitting all the H atoms except for those belonging to the bridging C(37) and N(23) atoms (50% probability contours for all atoms; the atoms belonging to the macroring were refined isotropically).
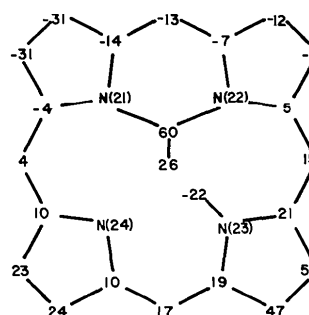

Fig. 2. The deviations of atoms (Å × 10²) from the mean plane defined by N(21), N(22), N(23) and N(24).

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Electrocrystallization and Structures of Perylene Radical Salts: Hexaperylene Perchlorate, $(C_{20}H_{12})_6^+ClO_4^-$, Triperylene Perchlorate, $(C_{20}H_{12})_3^+ClO_4^-$, and Diperylene Hexafluorophosphate–Tetrahydrofuran (3/2), $(C_{20}H_{12})_2^+PF_6^-.\frac{2}{3}\,C_4H_8O$

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Abstract. Crystals grown by electrocrystallization, species obtained depending on perylene concentration. Room-temperature data collections, Mo $K\alpha$, $\lambda = 0.71069$ Å. 6:1 salt: $M_r = 1613.3$, triclinic, $P\bar{1}$, $a = 12.571$ (7), $b = 13.699$ (5), $c = 13.835$ (11) Å, $\alpha = 110.43$ (4), $\beta = 107.13$ (7), $\gamma = 107.09$ (4)°, $V = 1913$ Å³, $Z = 1$, $D_x = 1.40$ g cm⁻³, $\mu = 1.1$ cm⁻¹, $F(000) = 841$, final $R = 0.077$ for 3171 observed reflections. The structure contains three independent perylene π dimers arranged nearly perpendicularly to each other. The anions are severely disordered or freely rotating. 3:1 salt: $M_r = 856.4$, triclinic, $P\bar{1}$, $a = 13.009$ (8), $b = 13.821$ (10), $c = 13.850$ (15) Å, $\alpha = 66.05$ (7), $\beta = 83.36$ (8), $\gamma = 63.51$ (6)°, $V = 2030$ Å³, $Z = 2$, $D_x = 1.40$ g cm⁻³, $\mu = 1.5$ cm⁻¹, $F(000) = 890$, final $R = 0.138$ for 3523 observed reflections. Tetrameric perylene stacks are surrounded on four sides by single perylene species, having their planes nearly perpendicular to the molecular planes in the stacks. 2:1 salt: $M_r = 697.7$, monoclinic, $P2/m$, $a = 13.04$ (1), $b = 14.12$ (1), $c = 13.75$ (1) Å, $\beta = 110.80$ (2)°, $V = 2367$ Å³, $Z = 3$, $D_x = 1.47$ g cm⁻³, $\mu = 1.5$ cm⁻¹, $F(000) = 1079$, final $R = 0.121$ for 1737 observed reflections. Nearly regular perylene stacks are surrounded by single perylene species in a way similar to the 3:1 salt. The thf solvent and one of the perylene molecules are disordered over two orientations.

Introduction. Electrochemically prepared organic metals of simple hydrocarbons (radical cation salts) have aroused considerable interest, owing to their simple preparation and their electronic and magnetic properties (Keller, Nöthe, Pritzkow, Wehe, Werner, Koch & Schweitzer, 1980; Kröhnke, Enkelmann & Wegner, 1980; Eichele, Schwoerer, Kröhnke & Wegner, 1981; Koch, Schweitzer, Harms, Keller, Schäfer,