

linked to Ag(1) *via* acetate groups [Ag(2)—O(2) 2.241 (8), Ag(2)—O(3) 2.260 (10) Å] in a similar fashion to that shown in (1) except that the O(2)—Ag—O(3) angle is only 97.9 (3)° and not 160° as found in the examples cited above. Ag(1) is also bonded to triphenylphosphine [Ag(1)—P(1) 2.354 (3) Å] and to two O atoms of acetates that bridge to Ag(2) [Ag(1)—O(1) 2.320 (7), Ag(1)—O(4) 2.226 (12) Å, O(1)—Ag—O(4) 99.8 (4)°]. In addition, Ag(1) is bonded to an O atom [Ag(1)—O(1<sup>1</sup>) 2.475 (7) Å] of a second dinuclear unit. There is a precedent for the O—Ag—O angles in the tetramer; in bis(silvertrifluoroacetate)benzene (Hunt, Lee & Amma, 1974) there are two independent bridges of type (1), one with an angle of 98.3 and the other of 161.6°.

The geometries of the Ag(1), Ag(2) environments can be considered to be trigonal planar and tetrahedral, respectively, with large distortions caused by the ring formation. The Ag—O distances (mean 2.24 Å) are as expected except for Ag(1)—O(1) and Ag(1)—O(1<sup>1</sup>), which are lengthened by bridge formation. The Ag—P distances can be compared with those found in Ag<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>X<sub>4</sub> (Teo & Calabrese, 1975, 1976) which are 2.372–2.386 (X = Cl), 2.429, 2.415 (X = Br) and 2.455, 2.466 Å (X = I). It was argued that these distances were different because of variations in steric crowding in the three molecules and therefore it is fitting that the Ag—P distances in the present uncrowded tetramer are comparable to those in the tetrachloride.

No report of the analogous Cu(O<sub>2</sub>CMe)(PPh<sub>3</sub>) complex has been found but Cu(O<sub>2</sub>CMe)(PPh<sub>3</sub>)<sub>2</sub> is a monomer with a bidentate acetate ligand in which the metal atom has a distorted tetrahedral environment (Drew, Othman, Edwards & Richards, 1975). We have also prepared Ag(O<sub>2</sub>CMe)(PPh<sub>3</sub>)<sub>2</sub>. Tetragonal silver(I)

ketenide (2 g, 0.008 mol) was refluxed for 15 h with PPh<sub>3</sub> (2.45 g, 0.009 mol) in toluene. The toluene phase was filtered from unreacted silver ketenide, evaporated to dryness and the resulting solid was recrystallized from toluene. Found C 66.0%, H 4.73%, P 8.12%, Ag 16.2%. Calculated for Ag(O<sub>2</sub>CMe)(PPh<sub>3</sub>)<sub>2</sub> C 66.0%, H 4.78%, P 8.97%, Ag 15.6%. Powder patterns show that the Ag and Cu compounds are not isomorphous.

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## 2,3,7,8,12,13,17,18-Octaethyl-5-[2,2-bis(ethoxycarbonyl)vinyl]-22H,24H-porphine

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**Abstract.** C<sub>44</sub>H<sub>56</sub>N<sub>4</sub>O<sub>4</sub>, triclinic,  $P\bar{1}$ ,  $a = 14.590$  (10),  $b = 15.439$  (7),  $c = 9.692$  (6) Å,  $\alpha = 92.61$  (3),  $\beta = 100.93$  (4),  $\gamma = 66.98$  (3)°,  $M_r = 737.0$ ,  $Z = 2$ ,  $D_x = 1.24$  g cm<sup>-3</sup>. The porphyrin skeleton is significantly ruffled, in particular in ring *A*, where atom deviations of  $-0.202$  and  $-0.171$  Å [C(2) and C(3)] from the N

atom least-squares plane are observed. Although individual bond lengths and angles in the macrocycle are similar to those in porphine the geometry of the central 'hole' is distinctly rhomboid (neighbouring N...N distances: 2.78, 3.06, 2.79, 3.06 Å) rather than rhombic as in the parent compound.

Table 1. *Positional parameters* ( $\times 10^4$ ) *for the nonhydrogen atoms*

|       | <i>x</i>  | <i>y</i>  | <i>z</i>  |        | <i>x</i>  | <i>y</i>  | <i>z</i>  |
|-------|-----------|-----------|-----------|--------|-----------|-----------|-----------|
| N(21) | 7857 (3)  | 772 (3)   | 10779 (4) | C(31)  | 10234 (4) | 767 (3)   | 13218 (5) |
| C(1)  | 8379 (4)  | -144 (4)  | 11223 (5) | C(32)  | 10950 (4) | 817 (4)   | 12261 (6) |
| C(2)  | 9306 (4)  | -274 (4)  | 12207 (5) | C(71)  | 7365 (5)  | 4508 (4)  | 10729 (6) |
| C(3)  | 9329 (4)  | 601 (4)   | 12374 (5) | C(72)  | 8280 (6)  | 4457 (5)  | 10188 (8) |
| C(4)  | 8404 (4)  | 1256 (4)  | 11481 (5) | C(81)  | 5489 (4)  | 5020 (4)  | 8278 (6)  |
| C(5)  | 8101 (4)  | 2239 (4)  | 11348 (5) | C(82)  | 5867 (5)  | 5170 (4)  | 7012 (7)  |
| N(22) | 6633 (3)  | 2513 (3)  | 9466 (5)  | C(121) | 3182 (5)  | 3443 (4)  | 5413 (6)  |
| C(6)  | 7270 (4)  | 2823 (4)  | 10378 (6) | C(122) | 2352 (6)  | 3943 (5)  | 6243 (8)  |
| C(7)  | 6923 (4)  | 3823 (4)  | 10064 (6) | C(131) | 3146 (4)  | 1374 (4)  | 5122 (6)  |
| C(8)  | 6096 (4)  | 4075 (4)  | 9004 (6)  | C(132) | 2357 (4)  | 1348 (4)  | 5936 (6)  |
| C(9)  | 5905 (4)  | 3242 (4)  | 8645 (6)  | C(171) | 5634 (4)  | -2052 (4) | 7767 (6)  |
| C(10) | 5113 (4)  | 3201 (4)  | 7633 (6)  | C(172) | 4844 (5)  | -2062 (5) | 8550 (7)  |
| N(23) | 5319 (3)  | 1569 (3)  | 7724 (4)  | C(181) | 7715 (5)  | -2720 (4) | 9982 (6)  |
| C(11) | 4809 (4)  | 2471 (4)  | 7199 (6)  | C(182) | 8604 (5)  | -3177 (4) | 9230 (8)  |
| C(12) | 3939 (4)  | 2544 (4)  | 6133 (6)  | C(51)  | 8713 (4)  | 2681 (3)  | 2332 (5)  |
| C(13) | 3916 (4)  | 1680 (4)  | 6019 (6)  | C(52)  | 8493 (4)  | 3036 (3)  | 3544 (6)  |
| C(14) | 4776 (4)  | 1078 (4)  | 7015 (6)  | C(53)  | 7567 (5)  | 3116 (5)  | 14064 (6) |
| C(15) | 5042 (4)  | 125 (4)   | 7252 (6)  | O(53)  | 6835 (3)  | 3817 (3)  | 14042 (5) |
| N(24) | 6546 (4)  | -173 (3)  | 9056 (5)  | O(54)  | 7666 (3)  | 2295 (3)  | 14573 (4) |
| C(16) | 5864 (5)  | -456 (4)  | 8204 (6)  | C(54)  | 6792 (5)  | 2283 (5)  | 15112 (7) |
| C(17) | 6190 (4)  | -1456 (4) | 8449 (6)  | C(55)  | 6943 (5)  | 1266 (5)  | 15135 (8) |
| C(18) | 7048 (4)  | -1732 (4) | 9444 (6)  | C(56)  | 9221 (5)  | 3388 (4)  | 14472 (8) |
| C(19) | 7283 (4)  | -916 (4)  | 9823 (6)  | O(56)  | 9949 (4)  | 3423 (3)  | 14092 (5) |
| C(20) | 8106 (4)  | -897 (3)  | 10774 (5) | O(57)  | 8988 (3)  | 3591 (3)  | 15723 (5) |
| C(21) | 10080 (4) | -1198 (3) | 12826 (5) | C(57)  | 9761 (6)  | 3766 (6)  | 16841 (9) |
| C(22) | 10796 (4) | -1742 (4) | 11865 (6) | C(58)  | 9470 (7)  | 4702 (6)  | 16959 (9) |

**Introduction.** Cell dimensions were determined by a least-squares fit to settings for 15 reflexions ( $\pm hkl$ ) on a Syntex  $P2_1$  four-circle diffractometer (Mo  $K\alpha$ ,  $\lambda = 0.71069$  Å). Intensity measurements were carried out in the  $\theta$ - $2\theta$  mode ( $3.0 \leq 2\theta \leq 50.0^\circ$ ) with graphite-monochromated Mo  $K\alpha$  radiation, at scan speeds varying linearly between  $3.91^\circ \text{ min}^{-1}$  (150 counts  $\text{s}^{-1}$  and below) and  $19.53^\circ \text{ min}^{-1}$  (5000 counts  $\text{s}^{-1}$  and above). Scan and background times were equal. Lorentz and polarization corrections were applied but none for absorption [ $\mu(\text{Mo } K\alpha) = 0.42 \text{ cm}^{-1}$ ]. After application of the acceptance criterion  $I \geq 2.5\sigma(I)$ , 2573 unique reflexions were retained for use in the structure analysis. The structure was solved by direct methods (*SHELX-75* by G. M. Sheldrick) and refined by blocked full-matrix least squares with anisotropic temperature factors for all the non-hydrogen atoms. The positions of all but one [on C(122)] of the 56 H atoms were located in difference syntheses and freely refined with group isotropic temperature factors (Table 2). The terminal value of  $R_G = (\sum w\Delta^2 / \sum wF_o^2)^{1/2}$  was 0.055, with  $R_w = (\sum w^{1/2}\Delta / \sum w^{1/2}|F_o|)$  = 0.055 and  $R = 0.069$ . The weights were given by  $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$  where  $k$  and  $g$  refined to 3.0818 and 0.000167 respectively.\* Complex neutral-atom scattering factors were employed (Cromer & Waber, 1965; Cromer &

Liberman, 1970). The atomic positional parameters are listed in Tables 1 and 2.

**Discussion.** Porphyrins with eight  $\beta$ -pyrrolic and one or more methine-bridge substituents have been termed 'highly substituted' (Fuhrhop, Witte & Sheldrick, 1976). The X-ray analyses of two such porphyrins, namely the title compound (I) and 2,3,7,8,12,13,17,

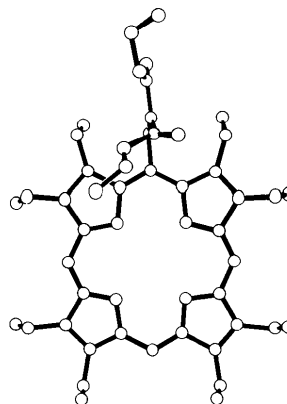


Fig. 1. The molecule of (I) in perspective. The standard porphyrin numbering system was used with side chains numbered according to the substituent position, e.g. C(21), C(22) for the ethyl group on C(2).

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32972 (19 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 ( $\times 10^3$ ) and isotropic temperature factors ( $\times 10^3$ )

|        | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> (Å <sup>2</sup> ) |        | <i>x</i> | <i>y</i> | <i>z</i>  | <i>U</i> (Å <sup>2</sup> ) |
|--------|----------|----------|----------|----------------------------|--------|----------|----------|-----------|----------------------------|
| H(10)  | 852 (2)  | -148 (2) | 1133 (3) | 17 (10)                    | H(173) | 491 (4)  | -200 (4) | 952 (6)   | 125 (5)                    |
| H(15)  | 466 (3)  | -17 (2)  | 663 (4)  | 32 (11)                    | H(174) | 428 (4)  | -133 (4) | 857 (6)   | 125 (5)                    |
| H(20)  | 468 (2)  | 378 (2)  | 725 (3)  | 16 (9)                     | H(175) | 455 (4)  | -247 (4) | 815 (6)   | 125 (5)                    |
| H(131) | 273 (3)  | 181 (3)  | 453 (4)  | 58 (3)                     | H(183) | 904 (4)  | -281 (4) | 940 (6)   | 125 (5)                    |
| H(132) | 344 (3)  | 77 (3)   | 470 (4)  | 59 (3)                     | H(184) | 825 (4)  | -325 (4) | 811 (6)   | 125 (5)                    |
| H(182) | 795 (3)  | -270 (3) | 1091 (4) | 59 (3)                     | H(185) | 909 (4)  | -377 (4) | 968 (6)   | 125 (5)                    |
| H(181) | 740 (3)  | -310 (3) | 979 (4)  | 59 (3)                     | H(713) | 820 (4)  | 442 (4)  | 922 (6)   | 125 (5)                    |
| H(211) | 973 (3)  | -162 (3) | 1312 (4) | 59 (3)                     | H(714) | 847 (4)  | 484 (4)  | 1045 (6)  | 125 (5)                    |
| H(212) | 1046 (3) | -112 (3) | 1363 (4) | 59 (3)                     | H(715) | 892 (4)  | 379 (4)  | 1023 (6)  | 125 (5)                    |
| H(311) | 1064 (3) | 19 (3)   | 1388 (4) | 59 (3)                     | H(813) | 657 (4)  | 505 (4)  | 734 (6)   | 125 (5)                    |
| H(312) | 995 (3)  | 132 (3)  | 1377 (4) | 59 (3)                     | H(814) | 543 (4)  | 577 (4)  | 646 (6)   | 125 (5)                    |
| H(711) | 682 (3)  | 516 (3)  | 1049 (4) | 59 (3)                     | H(815) | 597 (4)  | 468 (4)  | 626 (6)   | 125 (5)                    |
| H(712) | 752 (3)  | 445 (3)  | 1181 (4) | 59 (3)                     | H(123) | 204 (4)  | 441 (4)  | 594 (6)   | 125 (5)                    |
| H(811) | 473 (3)  | 512 (3)  | 791 (4)  | 59 (3)                     | H(125) | 259 (4)  | 399 (4)  | 683 (6)   | 125 (5)                    |
| H(812) | 556 (3)  | 542 (3)  | 897 (4)  | 59 (3)                     | H(22)  | 670 (3)  | 191 (3)  | 952 (4)   | 77 (15)                    |
| H(121) | 285 (3)  | 328 (3)  | 456 (4)  | 59 (3)                     | H(24)  | 645 (4)  | 47 (4)   | 902 (5)   | 118 (20)                   |
| H(122) | 347 (3)  | 389 (3)  | 523 (4)  | 59 (3)                     | H(51)  | 935 (3)  | 270 (3)  | 1199 (5)  | 95 (18)                    |
| H(171) | 612 (3)  | -271 (3) | 780 (4)  | 59 (3)                     | H(541) | 689 (5)  | 247 (5)  | 1606 (8)  | 194 (22)                   |
| H(172) | 528 (3)  | -179 (3) | 681 (4)  | 59 (3)                     | H(542) | 612 (5)  | 282 (5)  | 1469 (8)  | 194 (22)                   |
| H(213) | 1137 (4) | -233 (4) | 1222 (6) | 125 (5)                    | H(551) | 756 (7)  | 94 (7)   | 1578 (11) | 275 (27)                   |
| H(214) | 1112 (4) | -138 (4) | 1162 (6) | 125 (5)                    | H(552) | 642 (7)  | 113 (6)  | 1563 (10) | 275 (27)                   |
| H(215) | 1044 (4) | -192 (4) | 1092 (6) | 125 (5)                    | H(553) | 705 (7)  | 106 (6)  | 1413 (10) | 275 (27)                   |
| H(313) | 1124 (4) | 30 (4)   | 1188 (6) | 125 (5)                    | H(571) | 963 (9)  | 372 (8)  | 1800 (11) | 293 (37)                   |
| H(314) | 1050 (4) | 139 (4)  | 1167 (6) | 125 (5)                    | H(572) | 1049 (8) | 334 (8)  | 1684 (11) | 293 (37)                   |
| H(315) | 1159 (4) | 82 (4)   | 1278 (6) | 125 (5)                    | H(581) | 857 (9)  | 496 (8)  | 1707 (12) | 343 (34)                   |
| H(133) | 273 (4)  | 82 (4)   | 674 (6)  | 125 (5)                    | H(582) | 949 (9)  | 478 (8)  | 1590 (12) | 343 (34)                   |
| H(134) | 187 (4)  | 117 (4)  | 524 (6)  | 125 (5)                    | H(583) | 1019 (9) | 475 (8)  | 1783 (12) | 343 (34)                   |
| H(135) | 197 (4)  | 197 (4)  | 620 (6)  | 125 (5)                    |        |          |          |           |                            |

18-octaethyl-5-formyl-10-[2,2-bis(benzyloxycarbonyl)-vinyl]porphinatocopper(II) (II), which were briefly discussed in the same article, have demonstrated that the porphyrin macrocycle is much more flexible than was previously supposed. In (II) the methine-bridge C atoms are placed alternately 0.41–0.53 Å above and below the N atom least-squares plane and large deviations of up to 0.41 Å are observed for the  $\alpha$  and  $\beta$ -pyrrolic C atoms in the rings neighbouring the substituted methine bridges. The fact that the aromatic character of the macrocycle is retained in (II) despite these very considerable distortions suggests that the porphyrin skeleton is intrinsically flexible enough to accommodate bulky substituents at the methine bridges and the  $\beta$ -pyrrolic positions. The detailed results of the X-ray analysis of (I) are reported here and compared with the structure of an analogous highly substituted porphyrin 2,3,7,8,12,13,17,18-octaethyl-5-benzyloxy-porphine (III) (Hursthouse & Neidle, 1972) and with those of the free-base porphyrins, porphine (Chen & Tulinsky, 1972), triclinic  $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine (Silvers & Tulinsky, 1967),  $\alpha,\beta,\gamma,\delta$ -tetra-*n*-propylporphine (Coddling & Tulinsky, 1972) and 2,3,7,8,12,13,17,18-octaethylporphine (Lauher & Ibers, 1973).

The salient features of the molecular structure of (I) (Fig. 1) may be summarized as follows:

(1) The porphyrin skeleton is ruffled in the neighbourhood of the substituted methine bridge. C(2) and C(3)

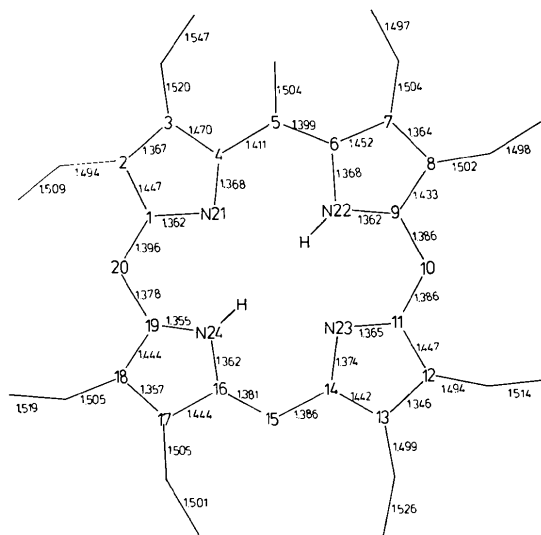


Fig. 2. Bond lengths in (I). Standard deviations are 0.006–0.010 Å for the macrocycle and 0.008–0.012 Å for the ethyl substituents.

are displaced  $-0.202$  and  $-0.171$  Å, the bridging atoms C(5) and C(20)  $0.078$  and  $-0.104$  Å, from the N atom plane. This may be accounted for by the fact that the ethyl C atom, C(55), of the  $\alpha$ -substituent is situated above the A ring of the macrocycle [C(55)···N(23)

4.61, C(55)···C(3) 4.56, C(55)···C(4) 4.46, C(54)···C(4) 4.49 Å]. Rings *A* and *B* are inclined at angles of 5.1 and 2.2° to this plane and at 6.6° to one another. These angles are somewhat smaller than the corresponding values of 6.4, 3.9 and 9.9° in (III), for which a larger distortion would be expected on account of the bulkier  $\alpha$ -substituent. Rings *C* and *D* in (I) are respectively inclined at 0.4 and 1.8° to the N atom plane, at 1.8° to one another, and at 2.6 and 3.3° to the *B* and *A* rings.

(2) The central 'hole' of the macrocycle in (I) is distinctly rhomboid [N(21)···N(22) 2.78, N(22)···N(23) 3.06, N(23)···N(24) 2.79, N(24)···N(21) 3.06, N(21)···N(23) 4.08, N(22)···N(24) 4.20 Å] rather than essentially rhombic as in the symmetrically substituted free-base porphyrins, e.g. neighbouring N···N distances of 2.916–2.917 Å in octaethylporphine, 2.91, 2.92 Å in tetraphenylporphine. The N(21)···N(23) and N(22)···N(24) distances are, however, very similar to those of 4.052 and 4.195 Å in octaethylporphine. A rhomboid porphyrin 'bite', albeit less pronounced, is also observed in other asymmetrically substituted porphyrins, e.g. average neighbouring N···N distances of 2.83 and 2.96 Å in (III) and 2.81 and 2.86 Å in mesoporphyrin IX dimethyl ester (Little & Ibers, 1975).

(3) Bond lengths and angles in (I) (Figs. 2 and 3) are quite similar to those of the common structure for the porphyrin macrocycle proposed by Coddling & Tulinsky (1972). The  $\alpha$ -methine bridge bonds are significantly longer than those of the unsubstituted bridges and are close to the average value of 1.398 (4) Å found for tetraphenylporphine. The difference of 0.019 Å between the averaged substituted and unsubstituted methine bridge bonds in (I) is similar to that of 0.018 Å

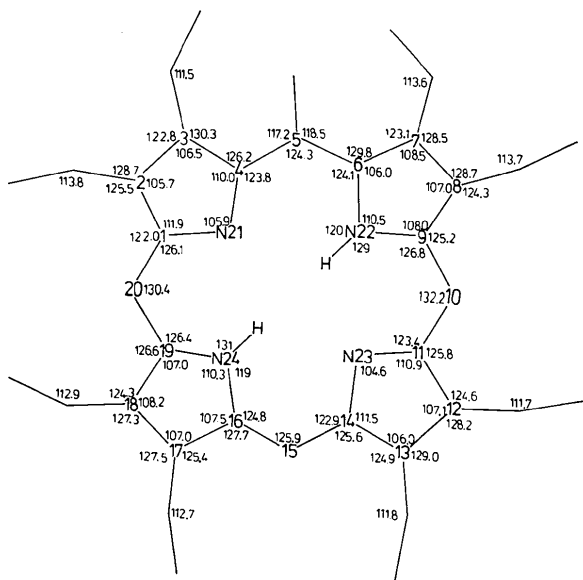


Fig. 3. Bond angles in (I). Standard deviations are 0.4–0.6°.

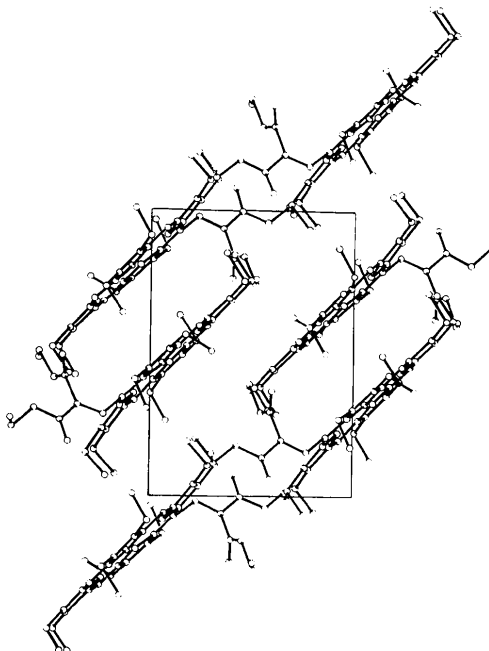


Fig. 4. The unit-cell contents of (I) viewed perpendicular to [010].

observed for other free-base porphyrins (Lauher & Ibers, 1973).

(4) The porphyrin macrocycles pack parallel to one another in the crystal lattice at the van der Waals distance of 3.5–4.0 Å (Fig. 4) as is observed for other porphyrins.

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