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3^1,3^2-Didehydrorhodochlorin-15-acetic Acid Trimethyl Ester

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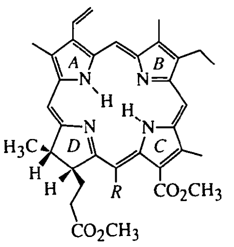
Abstract

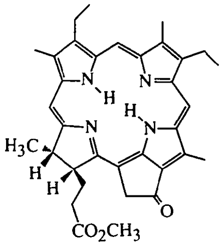
The structure of the title compound, methyl (2*S*,3*S*)-8-ethenyl-13-ethyl-2,3-dihydro-18-methoxycarbonyl-20-methoxycarbonylmethyl-3,7,12,17-tetramethylporphyrin-2-propionate, $C_{37}H_{42}N_4O_6$, containing no solvent molecules of crystallization, has been determined at 193 (2) K. The subrings *A*, *B* and *C* of the chlorin macrocycle are approximately in the least-squares plane defined by the four N atoms. The reduced ring *D* is distorted owing to the steric repulsion between the C17 and C15 substituents. The crystal packing is dominated by π–π interactions between subrings *A* and *C* of adjacent molecules in a slipped parallel orientation.

Comment

Chlorin e$_6$ trimethyl ester, (I), has played an important role in chlorophyll chemistry (Willstätter & Stoll, 1913; Fischer & Stern, 1940; Stoll & Wiedemann, 1952; Seely, 1966; Inhoffen, 1968; Woodward *et al.*, 1990; Smith, 1991; Hynninen, 1991*a*). It was the actual end product in Woodward's total synthesis of chlorophyll a (Woodward *et al.*, 1990). The three final steps (formation of the isocyclic ring, phytylation and Mg insertion) were considered by Woodward to proceed along 'well trodden paths', worked out earlier by Fischer (Fischer & Stern, 1940). The investigations of Inhoffen (1968) and his group concerned the electrochemical reduction of chlorin (I) and subsequent photo-oxygenation. These reactions rendered it possible to functionalize ring *B* and led finally to the invention of partial synthetic routes to bacteriochlorin derivatives and to chlorophyll b. Recently, the tetrasodium salt of mono-L-aspartyl chlorin e$_6$ was proposed as a promising photosensitizer for the photodynamic therapy of cancer (Aizawa *et al.*, 1987).



(I) $R = CH_2CO_2CH_3$
(II) $R = H$



(III)

Considering the important position of compound (I) among chlorophyll derivatives [two additional examples are given by structures (II) and (III)] and the fact that well formed crystals had been reported for free chlorin e$_6$ earlier this century (Willstätter & Stoll, 1913; Stoll & Wiedemann, 1952), it is surprising that no X-ray diffraction data have been available for it thus far. We have now succeeded in obtaining good crystals of (I) by allowing methanol to diffuse into a concentrated solution of (I) in acetone. Here, we describe the results from our X-ray crystallographic analysis of (I).

The subrings *A*, *B* and *C* of the chlorin macrocycle are approximately in the least-squares plane defined by the four N atoms. The reduced ring *D* is distorted as a result of steric repulsion between the C15 and C17 substituents. The C18 atom is situated below the plane composed of the N21, N22, N23 and N24 atoms by 0.19 (1) Å, C17 is raised out of the plane by 0.22 (1) Å, while the methoxycarbonylmethyl group at C15 is simultaneously oriented in the opposite direction to relieve steric strain. The torsion angle between the *trans* C17 and C18 H atoms is 107.7 (1)°. Regarding rotation about the C17^1—C17 bond, the most favoured conformational rotamer is the antiperiplanar form and, regarding rotation about the C17^2—C17^1 bond, the most populated rotamer is the *gauche*$^+$ form (for the Newman projections of the conformers, see Helaja, Hyvärinen, Heikkinen, Kilpeläinen & Hynninen, 1995). The predominant conformation for all three ester groups is *trans* (*Z*) (Eliel, Wilen & Mander, 1994).

The C_β—C_β bond length in ring *B* [1.346 (8) Å] is shorter than those in rings *A* [1.371 (8) Å] and *C* [1.412 (7) Å]. The C_α—C_β bond lengths in ring *B* are 1.476 (7) and 1.477 (7) Å. These values for ring *B* are consistent with the concept that the C7═C8 double

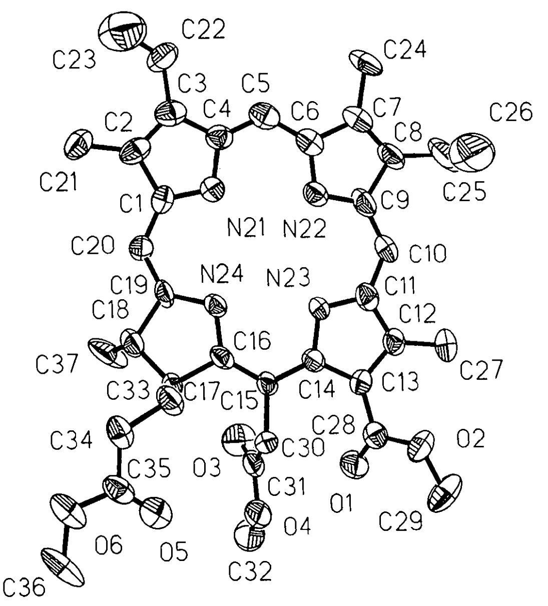


Fig. 1. The structure of (I) shown with 50% probability displacement ellipsoids.

bond is largely isolated from the delocalized π-system, an aromatic [18]diaza-annulene (Lötjönen & Hynninen, 1984). The C_α—C_β and C_β—C_β bond lengths in the reduced ring *D* are very close to the average value of C_{sp^3}—C_{sp^3} bonds (1.54 Å). The C_α—N—C_α angles in rings *A* and *C* have higher values [110.4 (4) and 110.7 (4)°, respectively] than the corresponding angles in rings *B* and *D* [105.3 (4) and 109.2 (4)°, respectively]. This shows that the four subrings are not equivalent in the metal-free chlorin. The higher C_α—N—C_α angle values are a manifestation of the localization of the two central H atoms on N21 and N23. The N21 and N23 atoms should be denoted as amino-type N atoms (not pyrrole-type) and the N22 and N24 atoms as pyridine-type (Hynninen, 1991*b*).

The crystal packing is dominated by π–π interactions between subrings *A* and *C* of adjacent molecules in a slipped parallel orientation. The shortest interatomic distance is 3.560 (8) Å betveen C3 of ring *A* and C11(*x*, *y*, 1 + *z*) of ring *C*.

The consequences of the steric crowding caused by the methoxycarbonylmethyl group at C15 of compound (I) can be further illustrated by comparing our structural data with those for $3^1,3^2$-didehydrorhodochlorin dimethyl ester [(II); Senge, Ruhlandt-Senge & Smith, 1992]. As a result of different packing forces, this compound was found to crystallize in two different forms possessing different macrocyclic conformations. The overall structural pattern indicated by bond angles and distances is, however, very similar for the two crystal forms. The angles C12—C13—C28 and C14—C13—C28 are significantly different in chlorins (I) and (II). For chlorin (I), the C12—C13—C28 angle is narrower by *ca* 7° and the C14—C13—C28 angle wider by *ca* 8° than the corresponding angles in chlorin (II). These angle changes occur to relieve Prelog's strain between the C13 and C15 substituents. Nevertheless, the flexibility of the chlorin macrocycle also plays an important role in relieving steric strain arising from steric crowding between the C13, C15 and C17 substituents. In addition to the sizeable distortion in ring *D*, the conformational flexibility of the chlorin macrocycle is indicated by several other significant deviations (Δ > 0.10 Å) from the mean plane: C7 0.14, C8 0.13, C13 −0.11 and C20 −0.12 (1) Å. Compared with chlorin (II), ring *D* of chlorin (I) has a more prominent zigzag conformation, the C17 and C18 atoms being situated *ca* 0.2 Å above and below the plane, respectively. To a lesser extent, this kind of deformation has also been found for methyl phytochlorin [(III); Senge & Smith, 1992], which probably experiences appreciably less steric repulsions (suggested by smaller deviations from the mean plane). For chlorin (I), these deviations are approximately double the values for chlorin (III). Finally, it should be noted that the comparison of our structural data with those for methyl pheophorbide a (Fischer, Templeton, Zalkin & Calvin, 1972) or methyl $3^1,3^2$-didehydrophyllochlorin (Hoppe, Will, Gassmann & Weichselgartner, 1969) is hindered by the fact that the X-ray data for the latter derivatives were measured at room temperature.

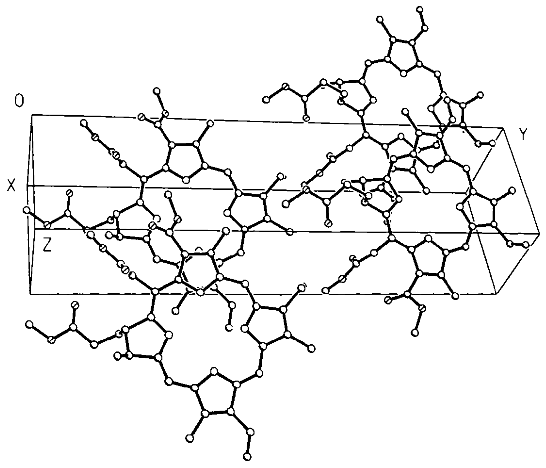


Fig. 2. A view of the molecular packing.

Experimental

The title compound (I) was prepared from methyl pheophorbide a according to the method of Lötjönen & Hynninen (1980). To completely avoid the formation of free carboxylic acid groups, the 0.5% KOH in methanol was replaced with 0.5% $KOCH_3$ in methanol. For crystallization, 20 mg of solid (I) was dissolved in 4 ml of acetone (pro anal., E. Merck, Darmstadt, Germany). The solution was placed into one flask of the diffusion apparatus and allowed to equilibrate against 20 ml of methanol (pro anal., J. T. Baker, UK, dried on

3Å molecular sieves) in the other flask of the apparatus. Two different forms of crystals were obtained, namely, long hair-thin needles and dark blue prisms. The latter were used for the structure analysis [m.p.: found 480.3–481.4 K; literature 480.5–482.0 K (Woodward *et al.*, 1990)].

Crystal data

$C_{37}H_{42}N_4O_6$
$M_r = 638.75$
Monoclinic
$P2_1$
$a = 7.4890\,(10)$ Å
$b = 27.829\,(6)$ Å
$c = 8.257\,(2)$ Å
$\beta = 102.05\,(3)°$
$V = 1682.9\,(6)$ Å^3
$Z = 2$
$D_x = 1.260$ Mg m^{-3}
$D_m = 1.24\,(3)$ Mg m^{-3}
D_m measured by flotation in KI solution

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15–20°$
$\mu = 0.086$ mm^{-1}
$T = 193\,(2)$ K
Prism
0.35 × 0.30 × 0.25 mm
Dark blue

Data collection

Rigaku AFC-7*S* diffractometer
$2\theta/\omega$ scans
Absorption correction: none
3560 measured reflections
3560 independent reflections
2006 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 26.50°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 34$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 200 reflections
intensity decay: 1.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0819$
$wR(F^2) = 0.2474$
$S = 0.939$
3560 reflections
425 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1232P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.842$

$\Delta\rho_{\max} = 0.512$ e Å^{-3}
$\Delta\rho_{\min} = -0.275$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: assigned to agree with the known chirality at C17

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.2130 (5)	0.22945 (14)	−0.1618 (5)	0.0627 (11)
O2	0.3371 (5)	0.2866 (2)	−0.2946 (4)	0.0636 (11)
O3	0.2448 (6)	0.1707 (2)	0.1956 (5)	0.0781 (12)
O4	0.3124 (6)	0.13240 (13)	−0.0226 (5)	0.0685 (12)
O5	0.7925 (6)	0.0846 (2)	0.1977 (5)	0.0774 (13)
O6	0.9574 (6)	0.03864 (14)	0.3957 (6)	0.0845 (14)
N21	0.7288 (5)	0.34192 (14)	0.7574 (5)	0.0462 (10)
N22	0.5681 (5)	0.40365 (14)	0.5007 (5)	0.0487 (11)
N23	0.4952 (5)	0.32198 (13)	0.2452 (4)	0.0405 (10)
N24	0.6697 (5)	0.25966 (13)	0.5006 (4)	0.0432 (10)
C1	0.7984 (6)	0.3037 (2)	0.8523 (6)	0.0468 (13)
C2	0.8703 (7)	0.3211 (2)	1.0172 (6)	0.0545 (14)
C3	0.8418 (7)	0.3698 (2)	1.0154 (7)	0.059 (2)
C4	0.7504 (7)	0.3833 (2)	0.8504 (6)	0.0497 (13)
C5	0.6963 (7)	0.4273 (2)	0.7898 (7)	0.0576 (14)
C6	0.6107 (7)	0.4376 (2)	0.6242 (7)	0.0532 (14)
C7	0.5533 (8)	0.4857 (2)	0.5572 (7)	0.060 (2)
C8	0.4781 (8)	0.4804 (2)	0.3953 (8)	0.065 (2)
C9	0.4881 (7)	0.4283 (2)	0.3637 (7)	0.0561 (15)
C10	0.4222 (8)	0.4084 (2)	0.2102 (7)	0.0562 (15)
C11	0.4235 (7)	0.3606 (2)	0.1535 (6)	0.0498 (13)
C12	0.3514 (7)	0.3449 (2)	−0.0079 (6)	0.0477 (13)
C13	0.3793 (6)	0.2947 (2)	−0.0108 (5)	0.0426 (12)
C14	0.4705 (6)	0.2809 (2)	0.1515 (5)	0.0403 (11)
C15	0.5459 (6)	0.2356 (2)	0.2149 (5)	0.0377 (11)
C16	0.6385 (7)	0.2265 (2)	0.3749 (5)	0.0429 (11)
C17	0.7220 (7)	0.1778 (2)	0.4326 (5)	0.0443 (12)
C18	0.7522 (9)	0.1823 (2)	0.6200 (7)	0.064 (2)
C19	0.7408 (7)	0.2370 (2)	0.6462 (6)	0.0494 (13)
C20	0.7974 (7)	0.2560 (2)	0.8001 (6)	0.0496 (13)
C21	0.9675 (8)	0.2916 (2)	1.1593 (6)	0.063 (2)
C22	0.8880 (9)	0.4050 (3)	1.1511 (7)	0.076 (2)
C23	0.9629 (20)	0.3963 (5)	1.3011 (13)	0.177 (6)
C24	0.5888 (10)	0.5316 (2)	0.6555 (9)	0.077 (2)
C25	0.3790 (18)	0.5170 (2)	0.2682 (11)	0.146 (5)
C26	0.5151 (17)	0.5322 (4)	0.1827 (13)	0.157 (5)
C27	0.2522 (8)	0.3754 (2)	−0.1469 (7)	0.062 (2)
C28	0.3011 (7)	0.2656 (2)	−0.1567 (6)	0.0462 (13)
C29	0.2374 (9)	0.2683 (3)	−0.4503 (7)	0.087 (2)
C30	0.5134 (7)	0.1930 (2)	0.0956 (6)	0.0476 (13)
C31	0.3428 (8)	0.1663 (2)	0.0959 (6)	0.0526 (14)
C32	0.1441 (10)	0.1060 (2)	−0.0380 (9)	0.085 (2)
C33	0.9058 (8)	0.1706 (2)	0.3778 (7)	0.0580 (15)
C34	0.9905 (8)	0.1222 (2)	0.4243 (7)	0.059 (2)
C35	0.8972 (8)	0.0808 (2)	0.3239 (7)	0.0599 (15)
C36	0.8893 (10)	−0.0041 (2)	0.3029 (11)	0.098 (3)
C37	0.6127 (13)	0.1553 (2)	0.6895 (8)	0.128 (3)

Table 2. *Selected geometric parameters (Å, °)*

O1—C28	1.198 (6)	C7—C8	1.346 (8)
O2—C28	1.357 (6)	C7—C24	1.507 (8)
O2—C29	1.438 (7)	C8—C9	1.477 (7)
O3—C31	1.218 (7)	C8—C25	1.538 (10)
O4—C31	1.345 (6)	C9—C10	1.377 (7)
O4—C32	1.441 (8)	C10—C11	1.412 (7)
O5—C35	1.171 (7)	C11—C12	1.399 (7)
O6—C35	1.348 (7)	C12—C13	1.412 (7)
O6—C36	1.450 (8)	C12—C27	1.495 (7)
N21—C1	1.359 (6)	C13—C14	1.425 (6)
N21—C4	1.375 (6)	C13—C28	1.469 (7)
N22—C9	1.351 (6)	C14—C15	1.436 (6)
N22—C6	1.379 (6)	C15—C16	1.381 (6)
N23—C11	1.359 (6)	C15—C30	1.526 (6)
N23—C14	1.371 (6)	C16—C17	1.527 (6)
N24—C19	1.363 (6)	C17—C18	1.522 (7)
N24—C16	1.372 (6)	C17—C33	1.549 (8)
C1—C20	1.395 (7)	C18—C37	1.495 (10)
C1—C2	1.440 (7)	C18—C19	1.542 (7)
C2—C3	1.371 (8)	C19—C20	1.360 (7)
C2—C21	1.492 (7)	C22—C23	1.271 (12)
C3—C4	1.441 (7)	C25—C26	1.42 (2)
C3—C22	1.475 (8)	C30—C31	1.478 (8)
C4—C5	1.352 (7)	C33—C34	1.506 (7)
C5—C6	1.413 (7)	C34—C35	1.503 (8)
C6—C7	1.476 (7)		
C28—O2—C29	116.2 (5)	C13—C12—C27	126.9 (4)
C31—O4—C32	115.7 (5)	C12—C13—C14	107.2 (4)
C35—O6—C36	115.7 (5)	C12—C13—C28	121.7 (4)
C1—N21—C4	110.4 (4)	C14—C13—C28	130.7 (4)
C9—N22—C6	105.3 (4)	N23—C14—C13	106.7 (4)
C11—N23—C14	110.7 (4)	N23—C14—C15	122.1 (4)
C19—N24—C16	109.2 (4)	C13—C14—C15	130.9 (4)
N21—C1—C20	126.2 (4)	C16—C15—C14	126.1 (4)
N21—C1—C2	107.7 (4)	C16—C15—C30	117.2 (4)
C20—C1—C2	126.1 (5)	C14—C15—C30	116.7 (4)
C3—C2—C1	107.2 (5)	N24—C16—C15	125.0 (4)
C3—C2—C21	127.0 (5)	N24—C16—C17	111.5 (4)

C1—C2—C21	125.7 (5)	C15—C16—C17	123.4 (4)
C2—C3—C4	108.1 (5)	C18—C17—C16	102.0 (4)
C2—C3—C22	129.6 (5)	C18—C17—C33	110.8 (4)
C4—C3—C22	122.3 (5)	C16—C17—C33	110.8 (4)
C5—C4—N21	124.1 (5)	C37—C18—C17	112.4 (5)
C5—C4—C3	129.3 (5)	C37—C18—C19	112.3 (5)
N21—C4—C3	106.6 (4)	C17—C18—C19	102.9 (4)
C4—C5—C6	125.6 (5)	C20—C19—N24	129.2 (4)
N22—C6—C5	124.4 (5)	C20—C19—C18	119.9 (4)
N22—C6—C7	109.8 (4)	N24—C19—C18	110.9 (4)
C5—C6—C7	125.8 (5)	C19—C20—C1	129.7 (5)
C8—C7—C6	107.6 (4)	C23—C22—C3	126.8 (9)
C8—C7—C24	128.1 (5)	C26—C25—C8	104.1 (9)
C6—C7—C24	124.1 (5)	O1—C28—O2	122.5 (5)
C7—C8—C9	104.8 (5)	O1—C28—C13	127.9 (5)
C7—C8—C25	130.4 (5)	O2—C28—C13	109.6 (4)
C9—C8—C25	124.4 (5)	C31—C30—C15	114.2 (4)
N22—C9—C10	125.3 (5)	O3—C31—O4	121.8 (5)
N22—C9—C8	112.4 (5)	O3—C31—C30	126.5 (5)
C10—C9—C8	122.3 (5)	O4—C31—C30	111.5 (5)
C9—C10—C11	131.1 (5)	C34—C33—C17	113.2 (5)
N23—C11—C12	108.2 (4)	C35—C34—C33	115.0 (5)
N23—C11—C10	126.2 (4)	O5—C35—O6	124.9 (5)
C12—C11—C10	125.6 (5)	O5—C35—C34	124.6 (5)
C11—C12—C13	107.2 (4)	O6—C35—C34	110.5 (5)
C11—C12—C27	125.8 (5)		

H atoms were placed at expected positions, riding, with $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}$ for NH, CH and CH_2, and $U(\mathrm{H}) = 1.5U_{\mathrm{eq}}$ for CH_3.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: JZ1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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