Tableau 2. *Distances interatomiques* (Å) *et angles* (°) *avec leurs écarts-type*

S(1)—O(1)	1,512 (5)	C(3a)—C(4)	1,370 (7)
S(1)—C(7a)	1,786 (5)	C(3a)—C(7a)	1,371 (7)
S(1)—C(2)	1,815 (6)	C(4)—C(5)	1,367 (8)
S(2)—C(3)	1,821 (5)	C(5)—C(6)	1,369 (10)
S(2)—C(1′)	1,827 (6)	C(6)—C(7)	1,352 (9)
O(2)—C(2′)	1,404 (7)	C(7)—C(7a)	1,379 (8)
C(2)—C(3)	1,537 (8)	C(1′)—C(2′)	1,471 (8)
C(3)—C(3a)	1,494 (7)		
⟨C—H⟩	0,97 (6)		
O(1)—S(1)—C(7a)	106,4 (2)	C(7a)—C(3a)—C(3)	115,2 (4)
O(1)—S(1)—C(2)	106,4 (3)	C(5)—C(4)—C(3a)	119,8 (5)
C(7a)—S(1)—C(2)	91,2 (3)	C(4)—C(5)—C(6)	120,8 (5)
C(3)—S(2)—C(1′)	103,3 (3)	C(7)—C(6)—C(5)	120,5 (6)
C(3)—C(2)—S(1)	109.7 (4)	C(3a)—C(7a)—C(7)	122,2 (5)
C(3a)—C(3)—S(2)	114,9 (3)	C(3a)—C(7a)—S(1)	113,8 (4)
C(2)—C(3)—S(2)	113,5 (4)	C(7)—C(7a)—S(1)	123,9 (4)
C(4)—C(3a)—C(7a)	118,4 (5)	C(2′)—C(1′)—S(2)	112,4 (4)
C(4)—C(3a)—C(3)	126,4 (5)	O(2)—C(2′)—C(1′)	112,3 (5)

angle de 29,4° avec le plan (001) (Fig. 2). Les liaisons S(1)—O(1) et C(3)—S(2) se trouvent du même côté par rapport aux cycles. Nous sommes en présence d'un diastéréoisomère racémique (R^*,S^*) pour les atomes S(1) et C(3) selon la 'règle des séquences' de Cahn, Ingold & Prelog (1956). Les molécules de même chiralité sont reliées entre-elles par des liaisons hydrogène en formant deux chaînes dans la maille. Les distances et les angles interatomiques avec leurs écarts-type sont donnés dans le Tableau 2. En ce qui concerne le groupement sulfoxyde, l'atome S(1) occupe le 'centre' d'un tétraèdre irrégulier dont la base est constituée par C(7a), O(1) et C(2) tandis que le quatrième sommet est occupé par le doublet libre. Alors que le cycle thiophène du 2-méthyl-1-benzothiophène est symétrique, avec un angle C—S—C de 92,4 (6)°, dans notre cas le cycle pentagonal est asymétrique mais l'angle C(7a)—S(1)—C(2) ne change pas sensiblement, il est égal à 91,2 (3)°. Si l'on compare cet angle avec celui d'autres sulfoxydes organiques, il est inférieur aux valeurs déjà trouvées qui varient de 96,1 à 98,8° (Svinning, Mo & Bruun, 1976; Ji & van der Helm, 1989) mais les distances C—S et les angles C—S—O se trouvent dans les limites des valeurs déjà observées.

C'est l'atome d'oxygène du groupement hydroxyle qui contribue probablement le plus à la cohésion cristalline par la liaison hydrogène qu'il forme. Nous trouvons les distances O(2)···O(1) de 2,672 (7), O(2)—H(O2)···O(1) de 1,75 (6) Å et l'angle O(2)—H(O2)···O(1) de 175° (6) pour une transformation de coordonnées $\frac{1}{2} - x$, $\frac{1}{2} + y$, $-z$.

Références

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Rapport ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, EU.

Cahn, R. S., Ingold, C. K. & Prelog, V. (1956). *Experientia*, **12**, 81–94.

Ji, X. & van der Helm, D. (1989). *Acta Cryst.* **B45**, 93–99.

Johnson, C. K. (1976). *ORTEP*II. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee, EU.

Mansuy, D., Valadon, P., Erdelmeier, I., Lopez-Garcia, P., Amar, C., Girault, J.-P. & Dansette, P. (1991). *J. Am. Chem. Soc.* **113**, 7825–7826.

Sheldrick, G. M. (1986). *SHELXS*86. Programme pour la détermination des structures cristallines. Univ. de Göttingen, Allemagne.

Sutherland, H. H. & Rawas, A. (1985). *Acta Cryst.* **C41**, 929–931.

Svinning, T., Mo, F. & Bruun, T. (1976). *Acta Cryst.* **B32**, 759–764.

Acta Cryst. (1992). C48, 1810–1815

Structure and Conformation of Photosynthetic Pigments and Related Compounds. 4. Two Crystal Forms of a Chlorin – Rhodochlorin XV Dimethyl Ester

By Mathias O. Senge,* Karin Ruhlandt-Senge and Kevin M. Smith

Department of Chemistry, University of California, Davis, CA 95616, USA

(*Received* 25 *November* 1991; *accepted* 11 *February* 1992)

Abstract. Two different crystal forms of the title compound, (2*S*)-*trans*-methyl 8-ethenyl-13-ethyl-2,3-dihydro-18-methoxycarbonyl-3,7,12,17-tetramethyl-21*H*,23*H*-porphine-2-propionate, were found and investigated by single-crystal X-ray crystallography. Triclinic form: $C_{34}H_{38}N_4O_4.CH_2Cl_2$, $M_r = 647.6$, $P\bar{1}$, $a = 9.879$ (4), $b = 10.648$ (6), $c = 16.059$ (8) Å, $\alpha = 97.29$ (5), $\beta = 94.24$ (4), $\gamma = 96.97$ (4)°, $V = 1656.3$ (14) Å^3, $Z = 2$, $D_x = 1.300$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.237$ mm^{-1}, $F(000) = 680$, $T = 130$ K, $R = 0.075$ for 3496 reflections with $I > 2\sigma(I)$. This form crystallizes with one methylene chloride of solvation in antiparallel oriented layers, stacked by π–π interaction. The solvent molecules

---

* Author to whom correspondence should be addressed.

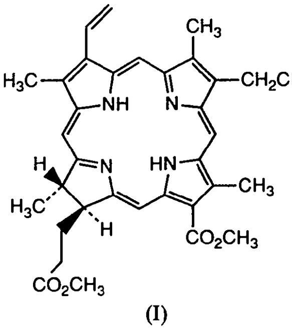
0108-2701/92/101810-06$06.00

© 1992 International Union of Crystallography

are situated between neighboring chlorin molecules in each layer. Orthorhombic form: $C_{34}H_{38}N_4O_4$, $M_r = 566.7$, $P2_12_12$, $a = 14.892$ (6), $b = 26.491$ (11), $c = 7.648$ (3) Å, $V = 3017$ (2) Å^3, $Z = 4$, $D_x = 1.250$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 0.077$ mm^{-1}, $F(000) = 1204$, $T = 130$ K, $R = 0.067$ for 3281 reflections with $I > 3\sigma(I)$. The molecules in the orthorhombic form are packed by forming dimeric structures held together by interaction of neighboring propionic ester groups. The molecular structures of both forms are slightly different. In the triclinic form the β-pyrrole atoms of ring IV deviate by approximately 0.4 Å from the plane of the N atoms, while in the orthorhombic form ring I is located 0.2 Å above, and ring IV 0.15 Å below the plane.

Introduction. Chlorins have been used for a long time as structural models for biologically important molecules such as chlorophylls (Hoppe, Will, Gassmann & Weichselgartner, 1969). Interest in the structure and conformation of these pigments stems from the fact that conformational flexibility of the macrocycle is believed to be important in modifying their physicochemical properties *in vivo* (Barkigia, Chantranupong, Smith & Fajer, 1988). Different chromophore conformations have been observed in the bacterial photosynthetic reaction center (Deisenhofer & Michel, 1988) and in a photosynthetic light-harvesting complex (Tronrud, Schmid & Matthews, 1985). Contemporary work on isolated tetrapyrroles indicates the flexibility of these chromophores, which can be induced by crystal packing, steric effects or insertion of different metals (Scheidt & Lee, 1987; Senge & Smith, 1991, 1992).

The majority of structural studies undertaken on tetrapyrrolic pigments have centered on the more easily available porphyrins (Scheidt & Lee, 1987). During studies aimed at a detailed analysis of the structure–function relationship in chlorins we have found that rhodochlorin XV dimethyl ester (I) crystallizes in two different crystal forms. This compound is a key intermediate in the degradative and synthetic chemical pathways of chlorophylls (Smith & Lewis, 1981; Hynninen, 1991; Smith, 1991).



(I)

Experimental. The compound was prepared by degradation of methyl pheophorbide a, as outlined in a previous paper (Smith & Lewis, 1981). The methyl pheophorbide a was in turn obtained by extraction from *Spirulina maxima* alga (Smith, Goff & Simpson, 1985).

Crystals of the triclinic form were obtained by liquid diffusion of *n*-hexane into a concentrated solution of the compound in methylene chloride. Blue parallelpipeds, 0.66 × 0.6 × 0.5 mm, were used for data collection on a Syntex $P2_1$ diffractometer using the ω-scan technique; scan rate 8.08° min^{-1} (in ω). 5821 intensities were recorded with graphite-monochromated Mo $K\alpha$ radiation; $2\theta_{max} = 50°$; $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $0 \leq l \leq 19$. Two check reflections measured every 198 reflections showed a 2% decrease in intensity. Of the 5821 independent reflections, 3496 with $I > 2.0\sigma(I)$ were used for all calculations (*SHELXTL-Plus*; Sheldrick, 1990). Cell constants were refined from 22 reflections in the range $14 < 2\theta < 18°$. An absorption correction was performed using the program *XABS* (Hope & Moezzi, 1987).

Structure solution was by random-start multisolution direct methods. The solvent molecule (CH_2Cl_2) was found to be severely disordered and was refined with three split positions for each Cl atom (0.33 occupancy, each). H atoms were inserted at calculated positions with a riding model with C—H = 0.96, N—H 0.9 Å, and $U_{iso}(H) = 0.04$ Å^2. All non-H atoms were refined with anisotropic thermal parameters. The final cycle of refinement on $|F|$ included 457 variable parameters and converged with $R = 0.075$ (the high value of R results from the disorder), $wR = 0.091$ and $S = 1.89$. The function minimized was $\sum w(F_o - F_c)^2$. The weighting scheme was defined as $w^{-1} = \sigma^2(F) + 0.0008F^2$. The data to parameter ratio was 7.7:1. $(\Delta/\sigma)_{max} = 0.096$. In the final difference Fourier synthesis $-0.41 \leq \Delta\rho \leq 0.46$ e Å^{-3}. No extinction correction was applied. Atomic scattering factors were as supplied with *SHELXTL-Plus*. The final atomic coordinates and thermal parameters are given in Table 1.*

The orthorhombic form was crystallized by slow evaporation of a solution of the chlorin in methylene chloride/methanol, containing 1% imidazole. Dark-red cubes, 0.56 × 0.36 × 0.34 mm, were used for data collection on a Siemens $R3m/V$ diffractometer using the ω-scan technique; scan rate 8.08° min^{-1} (in ω), 4037 intensities were recorded with graphite-monochromated Mo $K\alpha$ radiation, $2\theta_{max} = 50°$; $0 \leq$

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55179 (44 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^3$) *for the triclinic form of rhodochlorin* XV *dimethyl ester*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N(21)	9345 (4)	8207 (3)	424 (2)	31 (1)
N(22)	6886 (4)	7120 (3)	−656 (2)	31 (1)
N(23)	5248 (4)	6913 (3)	794 (2)	30 (1)
N(24)	7733 (4)	8084 (3)	1896 (2)	34 (1)
C(1)	10322 (5)	8734 (4)	1055 (3)	33 (2)
C(2)	11588 (5)	9039 (4)	676 (3)	36 (2)
C(21)	12936 (5)	9580 (5)	1153 (3)	44 (2)
C(3)	11296 (5)	8732 (4)	−185 (3)	35 (2)
C(31)	12197 (5)	8859 (5)	−843 (3)	48 (2)
C(32)	13347 (6)	9570 (6)	−821 (4)	65 (3)
C(4)	9873 (5)	8195 (4)	−348 (3)	33 (2)
C(5)	9142 (5)	7771 (4)	−1112 (3)	35 (2)
C(6)	7738 (5)	7271 (4)	−1273 (3)	33 (2)
C(7)	7050 (5)	6865 (4)	−2101 (3)	34 (2)
C(71)	7665 (5)	6941 (5)	−2924 (3)	47 (2)
C(8)	5737 (5)	6436 (4)	−1985 (3)	36 (2)
C(81)	4547 (5)	5911 (5)	−2653 (3)	45 (2)
C(82)	3698 (6)	6928 (6)	−2884 (3)	62 (2)
C(9)	5651 (5)	6597 (4)	−1087 (3)	31 (2)
C(10)	4463 (5)	6269 (4)	−705 (3)	33 (2)
C(11)	4266 (5)	6392 (4)	139 (3)	31 (2)
C(12)	3036 (5)	6051 (4)	504 (3)	31 (2)
C(121)	1723 (5)	5454 (5)	12 (3)	41 (2)
C(13)	3315 (5)	6382 (4)	1374 (3)	31 (2)
C(131)	2358 (5)	6249 (4)	2028 (3)	36 (2)
C(132)	73 (5)	5597 (5)	2294 (3)	54 (2)
C(14)	4725 (5)	6929 (4)	1551 (3)	30 (2)
C(15)	5462 (5)	7422 (4)	2326 (3)	33 (2)
C(16)	6808 (5)	7957 (4)	2481 (3)	35 (2)
C(17)	7444 (5)	8484 (5)	3373 (3)	38 (2)
C(171)	7551 (6)	7440 (5)	3940 (3)	49 (2)
C(172)	8009 (6)	7989 (6)	4853 (3)	56 (2)
C(173)	6937 (7)	8637 (6)	5269 (3)	56 (2)
C(174)	6522 (8)	10288 (7)	6301 (4)	92 (3)
C(18)	8835 (5)	9177 (5)	3212 (3)	41 (2)
C(181)	8901 (6)	10627 (5)	3367 (4)	62 (2)
C(19)	8923 (5)	8711 (4)	2289 (3)	35 (2)
C(20)	10121 (5)	8968 (4)	1907 (3)	36 (2)
O(1)	1103 (3)	5725 (3)	1704 (2)	47 (1)
O(2)	2646 (4)	6586 (4)	2766 (2)	61 (2)
O(3)	5714 (5)	8361 (5)	5114 (3)	84 (2)
O(4)	7471 (4)	9607 (4)	5853 (3)	71 (2)
C(1*S*)	2936 (6)	6570 (7)	4722 (5)	85 (4)
Cl(1*A*)	4132 (15)	5489 (17)	4895 (16)	66 (5)
Cl(1*B*)	3758 (15)	5247 (13)	4960 (13)	86 (6)
Cl(1*C*)	2442 (20)	5083 (6)	5078 (5)	117 (7)
Cl(2*A*)	1516 (13)	7435 (17)	4624 (9)	135 (7)
Cl(2*B*)	1200 (7)	6098 (16)	4883 (16)	75 (6)
Cl(2*C*)	1450 (13)	5564 (17)	4906 (16)	88 (7)

Table 2. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^3$) *for the orthorhombic form of rhodochlorin* XV *dimethyl ester*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
N(21)	2384 (2)	7530 (1)	7560 (6)	21 (1)
N(22)	4049 (3)	6993 (1)	8267 (6)	19 (1)
N(23)	5165 (2)	7817 (1)	6915 (6)	18 (1)
N(24)	3469 (2)	8394 (1)	6351 (6)	18 (1)
C(1)	1718 (3)	7862 (2)	7083 (7)	21 (2)
C(2)	871 (3)	7604 (2)	7365 (7)	22 (2)
C(21)	−22 (3)	7825 (2)	6895 (7)	29 (2)
C(3)	1062 (3)	7135 (2)	7994 (7)	22 (2)
C(31)	434 (3)	6730 (2)	8478 (7)	22 (2)
C(32)	−368 (3)	6795 (2)	9206 (7)	26 (2)
C(4)	2020 (3)	7079 (2)	8129 (7)	21 (2)
C(5)	2508 (3)	6672 (2)	8692 (7)	23 (2)
C(6)	3450 (3)	6630 (2)	8772 (7)	19 (1)
C(7)	3902 (3)	6175 (2)	9382 (7)	22 (2)
C(71)	3447 (3)	5702 (2)	9990 (8)	32 (2)
C(8)	4799 (3)	6270 (2)	9225 (7)	24 (2)
C(81)	5573 (3)	5920 (2)	9592 (10)	45 (2)
C(82)	5864 (5)	5630 (2)	7984 (11)	90 (4)
C(9)	4873 (3)	6782 (2)	8515 (7)	20 (2)
C(10)	5682 (3)	7018 (2)	8120 (8)	22 (2)
C(11)	5837 (3)	7485 (2)	7399 (7)	20 (2)
C(12)	6664 (3)	7730 (2)	7038 (7)	21 (2)
C(121)	7572 (3)	7490 (2)	7317 (8)	26 (2)
C(13)	6472 (3)	8198 (2)	6342 (7)	19 (2)
C(131)	7091 (3)	8601 (2)	5744 (8)	20 (2)
C(132)	8603 (3)	8855 (2)	5469 (9)	38 (2)
C(14)	5513 (3)	8257 (2)	6309 (7)	15 (1)
C(15)	5005 (3)	8678 (2)	5817 (7)	20 (1)
C(16)	4089 (3)	8742 (2)	5857 (7)	20 (2)
C(17)	3670 (3)	9243 (2)	5285 (8)	21 (2)
C(171)	3927 (3)	9383 (2)	3432 (7)	24 (2)
C(172)	3562 (3)	9892 (2)	2849 (7)	25 (2)
C(173)	3757 (3)	9995 (2)	959 (7)	26 (2)
C(174)	4079 (4)	10610 (2)	−1162 (8)	48 (2)
C(18)	2658 (3)	9136 (2)	5496 (8)	23 (2)
C(181)	2158 (3)	9512 (2)	6645 (9)	47 (2)
C(19)	2640 (3)	8598 (2)	6172 (7)	21 (2)
C(20)	1845 (3)	8346 (2)	6485 (7)	25 (2)
O(1)	7944 (2)	8482 (1)	6031 (6)	31 (1)
O(2)	6874 (2)	8997 (1)	5101 (6)	38 (1)
O(3)	3958 (6)	9680 (3)	−148 (12)	32 (2)
O(3*A*)	3603 (6)	9672 (3)	−181 (14)	35 (3)
O(4)	3880 (3)	10477 (1)	640 (5)	38 (1)

$h \leq 9$, $0 \leq k \leq 17$, $0 \leq l \leq 32$. Two check reflections were measured every 198 reflections and showed 2.5% decrease in intensity. Of the 4037 reflections measured, 3281 with $I > 3.0\sigma(I)$ were used for all calculations. Cell constants were refined from 24 reflections in the range $19 < 2\theta < 23°$. An absorption correction was performed using the program *XABS*.

The structure was solved by direct methods. O(3) was found to be disordered and was refined over two split positions (occupancy 0.51:0.49). H atoms were inserted at calculated positions using the same riding model as described above. All non-H atoms, excluding O(3), were refined with anisotropic thermal parameters. The final cycle of refinement included 379 variable parameters and converged with $R = 0.067$, $wR = 0.071$ and $S = 2.13$. The function minimized was $\sum w(F_o - F_c)^2$. The weighting scheme was defined as $w^{-1} = \sigma^2(F) + 0.0002F^2$. The data to parameter ratio was 8.7:1. $(\Delta/\sigma)_{\max} = 0.005$. In the final difference Fourier synthesis $-0.54 \leq \Delta\rho \leq 0.50$ e Å^{-3}. No extinction correction was applied. The program system used was the same as described above. Final atomic coordinates and thermal parameters are listed in Table 2. Bond distances and bond lengths for both the triclinic and orthorhombic forms are compiled in Table 3.

Discussion. The present structure determination is part of the increasing number of structural analyses on aggregation and conformation of photosynthetic pigments and related compounds (Hoppe, Will, Gassmann & Weichselgartner, 1969; Fischer, Templeton, Zalkin & Calvin, 1972; Kratky & Dunitz, 1977; Barkigia, Chantranupong, Smith & Fajer, 1988; Senge & Smith, 1991, 1992).

The structure of the title compound (Fig. 1) consists of the tetrapyrrole macrocycle with peripheral substituents attatched to the β-pyrrole positions. The stereochemistry at ring IV and the *trans* arrangement of the C(17) and C(18) substituents are the same as

Table 3. *Bond lengths* (Å) *and angles* (°) *in the two crystal forms of rhodochlorin* XV *dimethyl ester*

	Triclinic form	Orthorhombic form
N(21)—C(1)	1.361 (5)	1.373 (6)
N(21)—C(4)	1.380 (5)	1.383 (6)
N(22)—C(6)	1.359 (6)	1.367 (6)
N(22)—C(9)	1.375 (5)	1.362 (6)
N(23)—C(11)	1.388 (5)	1.382 (5)
N(23)—C(14)	1.354 (6)	1.356 (5)
N(24)—C(16)	1.366 (6)	1.359 (6)
N(24)—C(19)	1.348 (5)	1.355 (6)
C(1)—C(2)	1.451 (7)	1.450 (7)
C(1)—C(20)	1.392 (7)	1.376 (7)
C(2)—C(21)	1.498 (6)	1.496 (7)
C(2)—C(3)	1.381 (6)	1.364 (7)
C(3)—C(31)	1.440 (7)	1.471 (7)
C(3)—C(4)	1.443 (6)	1.438 (7)
C(31)—C(32)	1.281 (8)	1.330 (7)
C(4)—C(5)	1.372 (6)	1.369 (7)
C(5)—C(6)	1.417 (6)	1.408 (6)
C(6)—C(7)	1.437 (6)	1.459 (6)
C(7)—C(71)	1.502 (7)	1.496 (7)
C(7)—C(8)	1.356 (7)	1.365 (7)
C(8)—C(81)	1.532 (6)	1.504 (7)
C(8)—C(9)	1.441 (6)	1.465 (6)
C(81)—C(82)	1.514 (8)	1.514 (10)
C(9)—C(10)	1.391 (7)	1.392 (7)
C(10)—C(11)	1.377 (6)	1.375 (7)
C(11)—C(12)	1.415 (6)	1.420 (6)
C(12)—C(121)	1.493 (6)	1.510 (6)
C(12)—C(13)	1.396 (6)	1.378 (7)
C(13)—C(131)	1.472 (7)	1.485 (7)
C(13)—C(14)	1.435 (6)	1.437 (6)
C(131)—O(1)	1.335 (5)	1.327 (5)
C(131)—O(2)	1.197 (6)	1.202 (6)
C(132)—O(1)	1.446 (6)	1.457 (6)
C(14)—C(15)	1.401 (6)	1.400 (6)
C(15)—C(16)	1.373 (6)	1.374 (7)
C(16)—C(17)	1.530 (6)	1.530 (6)
C(17)—C(171)	1.531 (7)	1.514 (8)
C(17)—C(18)	1.534 (7)	1.543 (6)
C(171)—C(172)	1.522 (7)	1.520 (7)
C(172)—C(173)	1.486 (9)	1.499 (8)
C(173)—O(3)	1.207 (8)	1.225 (10)
C(173)—O(4)	1.332 (6)	1.314 (6)
C(174)—O(4)	1.433 (9)	1.453 (7)
C(18)—C(181)	1.525 (7)	1.521 (8)
C(18)—C(19)	1.516 (6)	1.515 (6)
C(19)—C(20)	1.386 (7)	1.379 (7)
C(1)—N(21)—C(4)	110.4 (4)	110.7 (4)
C(6)—N(22)—C(9)	104.0 (3)	105.0 (4)
C(11)—N(23)—C(14)	111.4 (4)	111.2 (4)
C(16)—N(24)—C(19)	108.5 (4)	108.7 (4)
N(21)—C(1)—C(2)	107.7 (4)	106.8 (4)
N(21)—C(1)—C(20)	125.7 (4)	125.8 (4)
C(2)—C(1)—C(20)	126.6 (4)	127.5 (4)
C(1)—C(2)—C(21)	125.1 (4)	123.7 (4)
C(1)—C(2)—C(3)	106.9 (4)	107.4 (4)
C(21)—C(2)—C(3)	128.0 (4)	128.8 (4)
C(2)—C(3)—C(31)	128.9 (4)	128.4 (4)
C(2)—C(3)—C(4)	108.1 (4)	109.1 (4)
C(31)—C(3)—C(4)	123.0 (4)	122.5 (4)
C(3)—C(31)—C(32)	129.1 (5)	125.7 (5)
N(21)—C(4)—C(3)	106.8 (4)	106.0 (4)
N(21)—C(4)—C(5)	125.1 (4)	124.9 (4)
C(3)—C(4)—C(5)	128.1 (4)	129.1 (4)
C(4)—C(5)—C(6)	128.1 (4)	127.2 (4)
N(22)—C(6)—C(5)	123.5 (4)	125.6 (4)
N(22)—C(6)—C(7)	112.3 (4)	111.8 (4)
C(5)—C(6)—C(7)	124.2 (4)	122.6 (4)
C(6)—C(7)—C(71)	126.4 (4)	125.6 (4)
C(6)—C(7)—C(8)	106.1 (4)	105.7 (4)
C(71)—C(7)—C(8)	127.5 (4)	128.7 (4)
C(7)—C(8)—C(81)	128.4 (4)	128.3 (4)
C(7)—C(8)—C(9)	106.1 (4)	106.1 (4)
C(81)—C(8)—C(9)	125.4 (4)	125.5 (4)
C(8)—C(81)—C(82)	112.8 (4)	112.4 (5)
N(22)—C(9)—C(8)	111.5 (4)	111.4 (4)
N(22)—C(9)—C(10)	124.3 (4)	124.4 (4)
C(8)—C(9)—C(10)	124.1 (4)	124.1 (4)
C(9)—C(10)—C(11)	128.8 (4)	129.5 (4)
N(23)—C(11)—C(10)	125.6 (4)	124.0 (4)
N(23)—C(11)—C(12)	107.2 (4)	106.6 (4)
C(10)—C(11)—C(12)	127.2 (4)	129.4 (4)
C(11)—C(12)—C(121)	124.3 (4)	123.9 (4)
C(11)—C(12)—C(13)	106.8 (4)	107.7 (4)
C(121)—C(12)—C(13)	128.9 (4)	128.3 (4)
C(12)—C(13)—C(131)	127.7 (4)	129.5 (4)
C(12)—C(13)—C(14)	108.7 (4)	108.2 (4)
C(131)—C(13)—C(14)	123.6 (4)	122.3 (4)
C(13)—C(131)—O(1)	112.3 (4)	111.9 (4)
C(13)—C(131)—O(2)	124.8 (4)	125.8 (4)
O(1)—C(131)—O(2)	122.9 (5)	122.3 (4)
N(23)—C(14)—C(13)	106.0 (3)	106.3 (4)
N(23)—C(14)—C(15)	124.5 (4)	124.8 (4)
C(13)—C(14)—C(15)	129.5 (4)	128.9 (4)
C(14)—C(15)—C(16)	128.6 (4)	128.9 (4)
N(24)—C(16)—C(15)	126.4 (4)	126.7 (4)
N(24)—C(16)—C(17)	111.9 (4)	113.0 (4)
C(15)—C(16)—C(17)	121.7 (4)	120.3 (4)
C(16)—C(17)—C(171)	112.8 (4)	112.1 (4)
C(16)—C(17)—C(18)	102.5 (4)	102.1 (3)
C(171)—C(17)—C(18)	113.7 (4)	112.9 (4)
C(17)—C(171)—C(172)	112.3 (4)	113.7 (4)
C(171)—C(172)—C(173)	112.3 (5)	112.0 (4)
C(172)—C(173)—O(3)	126.2 (5)	126.2 (6)
C(172)—C(173)—O(4)	112.1 (5)	112.5 (4)
O(3)—C(173)—O(4)	121.6 (6)	119.9 (6)
C(17)—C(18)—C(181)	112.8 (4)	114.7 (4)
C(17)—C(18)—C(19)	102.1 (3)	103.0 (3)
C(181)—C(18)—C(19)	111.0 (4)	114.2 (5)
N(24)—C(19)—C(18)	113.4 (4)	113.2 (4)
N(24)—C(19)—C(20)	125.3 (4)	124.8 (4)
C(18)—C(19)—C(20)	121.3 (4)	122.0 (4)
C(1)—C(20)—C(19)	128.1 (4)	128.9 (4)
C(131)—O(1)—C(132)	116.5 (4)	115.7 (4)
C(173)—O(4)—C(174)	116.6 (5)	116.1 (4)

observed in other compounds chemically derived from chlorophyll a (Hoppe, Will, Gassmann & Weichselgartner, 1969).

The main difference between the crystal forms is that the triclinic modification crystallizes with one molecule of solvation, methylene chloride, per asymmetric unit. The packing in the triclinic unit cell (Fig. 2) is thus charcterized by antiparallel layers of chlorin molecules, stacked by π–π interactions between chromophores in the layer above and below. The solvent molecules are situated between neighboring chlorin molecules in each layer, thus preventing any interaction between the ester groups of neighboring molecules.

Major differences are found in the packing in the orthorhombic unit cell (Fig. 3). In this modification the molecules form closely packed layers in which dimeric structures can be observed. Neighboring layers are related by π overlap of the pyrrole rings I and III in different molecules. The dimers are formed by close interaction of the propionic side chain at C(17) and the carbonyl group of the ester group in a neighboring molecule. The closest contact is 2.89 Å between the carbonyl O atom O(3) and C(174), indicating weak bonding of the methyl-group H atoms to the carbonyl O atoms. This type of packing has recently been found in other chlorophyll derivatives such as methyl mesopyropheophorbide a (Senge & Smith, 1992) and *meso*-C(20)-substituted pheophorbides (Senge & Smith, unpublished results). These molecules have in common that all functional groups normally involved in hydrogen bonding have been removed. Chlorophyll derivatives normally form highly ordered aggregates in the crystalline state by hydrogen bonds between water coordinated to the central metal and the carbonyl group of ring V (Kratky & Dunitz, 1977), or in the case of the bacteriopheophorbides d, between the C(3^1)-hydroxy group and the ring-V keto group (Smith, Goff, Fajer & Barkigia, 1982).

A major point of interest in the structural analysis of chlorins is the conformational flexibility of the macrocycle. While the bond lengths and bond angles in both crystal forms are almost identical (Table 3) some differences are observed in the conformation of the macrocycle (Fig. 4). In the triclinic modification only the reduced ring is oriented out of the mean plane of the molecule. The β-pyrrole atoms of this ring are displaced up to 0.4 Å out of the plane of the four N atoms. The rest of the core is essentially planar. This can also be seen in the angle between the pyrrole rings and the mean N-atom plane: ring I 0.1, ring II 1.9, ring III 0.9 and ring IV 8°. In the orthorhombic form the β-pyrrole atoms of ring I are displaced by about 0.2 Å above the N-atom plane, while those in ring IV are displaced below the plane. These deviations are somewhat smaller than those observed in other chlorophyll derivatives which bear the five-membered cyclopentanone ring. This points to the influence of ring V, which should play a crucial role in photosynthesis, on stabilizing defined chromophore conformations. When more structural data on rhodochlorins and chlorins become available a comparison of the ring deformation in these compounds with those bearing the isocyclic cyclopentanone ring V should provide more information on the influence of ring V on the macrocycle conformation.

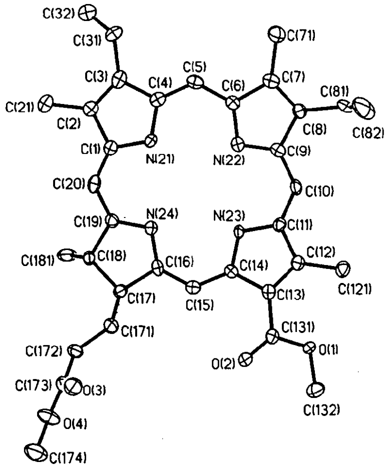


Fig. 1. The rhodochlorin XV dimethyl ester molecule with thermal vibration ellipsoids (50% probability).

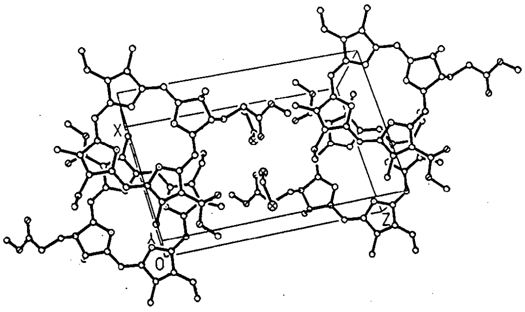


Fig. 2. View of the unit cell of the triclinic form of rhodochlorin XV dimethyl ester.

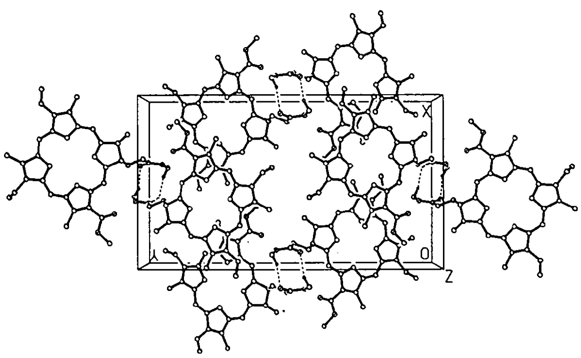


Fig. 3. View of the molecular packing (along the z axis) in the unit cell of the orthorhombic form of rhodochlorin XV dimethyl ester. Dashed lines indicate close contacts between neighboring propionic acid ester groups.

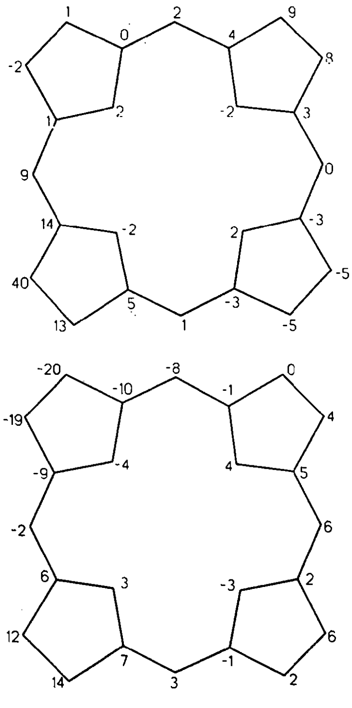


Fig. 4. Deviations from the least-squares plane of the four N atoms (Å × 10^2) in the triclinic (upper part) and orthorhombic (lower part) form or rhodochlorin XV dimethyl ester.

The two different crystal forms of rhodochlorin XV dimethyl ester described here present an example of homoeotypes of a chlorin. Other cases of multiple crystal forms of tetrapyrroles include Ni^{II} octaethylporphyrin. This porphyrin has been found in two triclinic and one tetragonal form (Meyer, 1972; Cullen & Meyer, 1974; Brennan, Scheidt & Shelnutt, 1988). An example of a chlorin with two crystal forms is 8-isobutyl-12-ethyl methyl bacteriopheophorbide d, which has been described by Barkigia, Chantranupong, Smith & Fajer (1988). The observation of two crystalline phases for chlorins points to the conformational flexibility inherent to this type of molecule. It also shows that a given conformation, observed in the crystal, might not necessarily be the only one possible, and can be influenced by packing effects.

Financial support by the Deutsche Forschungsgemeinschaft (Se543/1-1) and the National Science Foundation (NSF CHE-90-01381) is gratefully acknowledged.

References

Barkigia, K. M., Chantranupong, L., Smith, K. M. & Fajer, J. (1988). *J. Am. Chem. Soc.* **110**, 7599–7582.
Brennan, T. D., Scheidt, W. R. & Shelnutt, J. A. (1988). *J. Am. Chem. Soc.* **110**, 3919–3924.
Cullen, D. L. & Meyer, E. F. Jr (1974). *J. Am. Chem. Soc.* **96**, 2095–2102.
Deisenhofer, J. & Michel, H. (1988). *Angew. Chem. Int. Ed. Engl.* **28**, 829–847.
Fischer, M. S., Templeton, D. H., Zalkin, A. & Calvin, M. (1972). *J. Am. Chem. Soc.* **94**, 3613–3619.
Hope, H. & Moezzi, B. (1987). *XABS*. Univ. of California, Davis, USA.
Hoppe, W., Will, G., Gassmann, J. & Weichselgartner, H. (1969). *Z. Kristallogr.* **128**, 18–35.
Hynninen, P. H. (1991). *Chlorophylls*, edited by H. Scheer, pp. 145–209. Boca Raton: CRC Press.
Kratky, C. & Dunitz, J. D. (1977). *J. Mol. Biol.* **113**, 431–442.
Meyer, E. F. Jr (1972). *Acta Cryst.* **B28**, 2162–2167.
Scheidt, W. R. & Lee, Y. J. (1987). *Struct. Bonding*, **64**, 1–70.
Senge, M. O. & Smith, K. M. (1991). *Photochem. Photobiol.* **54**, 841–846.
Senge, M. O. & Smith, K. M. (1992). *Z. Kristallogr.* **199**, 239–248.
Sheldrick, G. M. (1990). *SHELXTL-Plus*. Program for crystal structure solution. Univ. of Göttingen, Germany.
Smith, K. M. (1991). *Chlorophylls*, edited by H. Scheer, pp. 115–143. Boca Raton: CRC Press.
Smith, K. M., Goff, D. A., Fajer, J. & Barkigia, K. M. (1982). *J. Am. Chem. Soc.* **104**, 3747–3749.
Smith, K. M., Goff, D. A. & Simpson, D. J. (1985). *J. Am. Chem. Soc.* **107**, 4946–4954.
Smith, K. M. & Lewis, W. M. (1981). *Tetrahedron*, **37** (Suppl. 1), 399–403.
Tronrud, D. E., Schmid, M. F. & Matthews, B. W. (1985). *J. Mol. Biol.* **188**, 443–545.

Acta Cryst. (1992). C**48**, 1815–1818

Structure of *sp*-9-Hydroxy-9-pivaloylfluorene, Product of Base-Catalyzed Autoxidation of *ap*-9-Pivaloylfluorene

By Cal Y. Meyers* and Jennifer L. Tunnell

Department of Chemistry, Southern Illinois University, Carbondale, Illinois 62901, *USA*

Paul D. Robinson*

Department of Geology, Southern Illinois University, Carbondale, Illinois 62901, *USA*

and Duy H. Hua and Shankar Saha

Department of Chemistry, Kansas State University, Manhattan, Kansas 66506, *USA*

(*Received* 2 *October* 1991; *accepted* 11 *February* 1992)

Abstract. 1-(9-Hydroxyfluoren-9-yl)-2,2-dimethyl-1-propanone, $C_{18}H_{18}O_2$, $M_r = 266.34$, orthorhombic, *Pbcn*, $a = 18.917\,(10)$, $b = 11.843\,(8)$, $c = 13.177\,(7)$ Å, $V = 2952\,(5)$ Å^3, $Z = 8$, $D_x = 1.198$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.72$ cm^{-1}, $F(000) = 1136$, $T = 296$ K, $R = 0.044$ for 1042 unique observed reflections. Conversion of *ap*-9-pivaloylfluorene, *ap*-(I), into lithiated (I)-9-anion followed by the addition of MeOH, then H_2O, led to unexpected hydroxylation to provide 20–40% of *sp*-9-hydroxy-9-pivaloylfluorene, *sp*-(II), and 60–80% recovery of *ap*-(I). The singular *sp* conformation of (II) in solution suggested by NMR was confirmed in the crystalline state by X-ray diffraction which showed the O(1)—C(9)—C(10)—O(2) torsion angle

---

* Correspondence relating to the crystallography should be sent to PDR; that relating to the chemistry, to CYM.

0108-2701/92/101815-04$06.00 © 1992 International Union of Crystallography