Structure and Conformation of Photosynthetic Pigments and Related Compounds. Part 6.[1] The First Crystal Structure of a Covalently-linked Chlorin Dimer: 20,20′-Ethylenebis(*trans*-2,3,7,8,12,13,17,18-octaethylchlorin)

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The crystal structure of the title compound **1** has been determined by X-ray diffraction methods to obtain structural information on covalently-linked chlorin dimers as biomimetic models for the photosynthetic reaction centre. The dimer crystallizes in two different crystal forms. Both forms show different macrocycle conformations which indicates the conformational flexibility of the chlorin macrocycle. This shows that not only the overall structural similarity but also conformational parameters have to be considered in the design of reaction centre models. Crystal data: Form **A**: $C_{74}H_{98}N_8{\cdot}CH_2Cl_2$, monoclinic, space group *C*2/*c* with $a = 32.610(9)$ Å, $b = 10.804(2)$ Å, $c = 21.185(5)$ Å, $\beta = 108.90(6)°$, and $V = 7063(3)$ Å^3, $Z = 4$. $R = 0.073$ (120 K). Form **B**: $C_{74}H_{98}N_8$, monoclinic, space group *C*2/*c* with $a = 24.068(14)$ Å, $b = 10.216(6)$ Å, $c = 26.44(3)$ Å, $\beta = 92.19(6)°$, $V = 6497(7)$ Å^3, $Z = 4$. $R = 0.063$ (130 K).

Structural investigations of chlorophyll derivatives have elicited wide interest due to the importance of these pigments in photosynthesis.[2] Recent studies have focused on the concept of the conformational flexibility in tetrapyrroles which implies that different conformations give rise to the different physicochemical properties of similar chromophores in different tetrapyrrole protein complexes *in vivo*.[3,4] One of the most interesting problems is that of preparing covalently-linked tetrapyrrole dimers as models for the photosynthetic reaction centre. Although a variety of different model systems have been prepared[5] only few structural investigations have been performed on dimeric systems.[6–10] Nevertheless, a detailed understanding of the geometrical arrangement of the subunits and their conformation is crucial for correctly interpreting the physicochemical properties of such dimers and to ascertain that the model synthesized has geometrical features comparable with those of the bacterial photosynthetic reaction centre.[11] The problem associated with the structures determined so far is that they all constitute porphyrin dimers, while the special pair in the photosynthetic reaction centre is comprised of two chlorins or bacteriochlorins. During studies aimed at the development of a synthetic strategy to build biomimetic models with geometric features more closely related to the photosynthetic reaction centre we have obtained crystals of two different forms of ethylene-bis(*trans*-2,3,7,8,12,13,17,18-octaethylchlorin) **1** and performed a X-ray structure determination. This work presents the first structural characterization of a *meso*-covalently-linked chlorin dimer.

Results and Discussion

The atomic coordinates for both modifications of the dimer are compiled in Tables 1 and 2.* Table 3 compares selected bond lengths and bond angles for the macrocycle atoms. Fig. 1 shows the molecular structure of the dimer **1** in both crystal forms. Both orientations have been drawn with the least-squares plane through all atoms. It is evident that no large structural

Table 1 Atomic coordinates [× 10^4] for form **A** of 20,20′-ethylenebis(*trans*-2,3,7,8,12,13,17,18-octaethylchlorin) **1**

Atom	*x*	*y*	*z*
N(21)	922(1)	−1653(4)	4092(2)
N(22)	1496(1)	445(4)	4918(2)
N(23)	1425(1)	1853(4)	3776(2)
N(24)	831(1)	−215(4)	2942(2)
C(1)	671(2)	−2502(5)	3652(3)
C(2)	612(2)	−3528(4)	4043(3)
C(21)	383(2)	−4765(3)	3856(3)
C(22)	675(2)	−5798(4)	3765(3)
C(3)	827(2)	−3257(5)	4704(3)
C(31)	854(2)	−4043(5)	5309(3)
C(32)	510(2)	−3689(6)	5618(3)
C(4)	1021(2)	−2066(5)	4742(3)
C(5)	1264(2)	−1465(5)	5322(3)
C(6)	1476(2)	−319(5)	5417(3)
C(7)	1719(2)	177(5)	6067(2)
C(71)	1769(2)	−432(5)	6734(2)
C(72)	2124(2)	−1405(5)	6916(3)
C(8)	1886(2)	1267(5)	5949(3)
C(81)	2147(2)	2206(4)	6452(3)
C(82)	1872(2)	3300(5)	6523(3)
C(9)	1743(2)	1417(5)	5234(3)
C(10)	1856(2)	2423(5)	4905(3)
C(11)	1709(2)	2625(5)	4232(3)
C(12)	1809(2)	3611(4)	3847(3)
C(121)	2090(2)	4714(4)	4159(3)
C(122)	1849(2)	5647(5)	4444(3)
C(13)	1584(2)	3404(5)	3191(3)
C(131)	1582(2)	4168(5)	2589(3)
C(132)	1185(2)	4992(5)	2339(3)
C(14)	1338(2)	2292(5)	3148(3)
C(15)	1049(2)	1760(5)	2563(3)
C(16)	823(2)	654(5)	2476(3)
C(17)	523(1)	302(5)	1792(3)
C(171)	97(1)	1010(5)	1590(2)
C(172)	−181(2)	799(6)	870(2)
C(18)	475(2)	−1108(5)	1870(3)
C(181)	778(2)	−1845(5)	1599(2)
C(182)	631(2)	−1912(6)	842(2)
C(19)	605(2)	−1228(5)	2627(3)
C(20)	520(2)	−2284(5)	2954(3)
C(201)	257(2)	−3296(5)	2517(3)
C(1S)	1912(2)	1007(5)	8699(4)
Cl(1S)	2382(1)	210(2)	8824(1)
Cl(2S)	1819(1)	2190(2)	8135(1)

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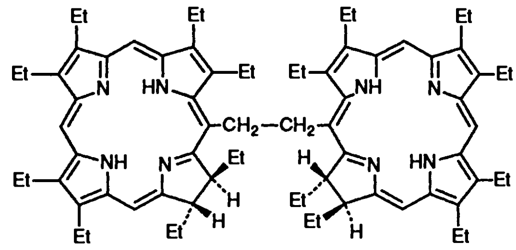
* Full lists of bond length and angles, hydrogen atom co-ordinates, thermal parameters, torsion angles and least-squares planes have been deposited at the Cambridge Crystallographic Data Centre. For details of the deposition scheme see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

Table 2 Atomic co-ordinates [× 10^4] for form **B** of 20,20′-ethylenebis(*trans*-2,3,7,8,12,13,17,18-octaethylchlorin) **1**

Atom	*x*	*y*	*z*
N(21)	905(1)	1270(3)	1400(1)
N(22)	1581(1)	3457(3)	914(1)
N(23)	1694(1)	4868(3)	1821(1)
N(24)	1033(1)	2680(3)	2316(1)
C(1)	646(2)	347(4)	1689(1)
C(2)	458(2)	−681(4)	1343(1)
C(21)	191(2)	−1989(4)	1446(1)
C(22)	618(2)	−3067(4)	1575(2)
C(3)	606(2)	−307(4)	862(1)
C(31)	504(2)	−1056(4)	377(2)
C(32)	985(2)	−1943(5)	239(2)
C(4)	895(2)	909(4)	898(1)
C(5)	1147(2)	1548(4)	502(1)
C(6)	1472(2)	2673(4)	504(1)
C(7)	1753(2)	3155(4)	60(1)
C(71)	1723(2)	2564(4)	−461(1)
C(72)	1221(2)	3020(6)	−782(2)
C(8)	2041(2)	4237(4)	213(1)
C(81)	2410(2)	5097(4)	−93(2)
C(82)	2100(2)	6230(5)	−345(2)
C(9)	1919(2)	4424(4)	745(1)
C(10)	2111(2)	5475(4)	1093(1)
C(11)	1997(2)	5707(4)	1536(1)
C(12)	2134(2)	6826(4)	1847(1)
C(121)	2421(2)	8032(4)	1668(1)
C(122)	2011(2)	8994(4)	1419(2)
C(13)	1906(2)	6635(4)	2308(1)
C(131)	1917(2)	7560(4)	2751(1)
C(132)	2354(2)	7200(5)	3160(2)
C(14)	1631(2)	5375(4)	2293(1)
C(15)	1353(2)	4769(4)	2685(1)
C(16)	1104(2)	3548(4)	2699(1)
C(17)	866(2)	3075(4)	3187(1)
C(171)	325(2)	3790(4)	3307(2)
C(172)	139(2)	3507(5)	3840(2)
C(18)	794(2)	1593(4)	3081(1)
C(181)	1276(2)	788(4)	3308(1)
C(182)	1279(2)	701(5)	3878(2)
C(19)	793(1)	1560(4)	2502(1)
C(20)	599(1)	487(4)	2220(1)
C(201)	322(1)	−597(3)	2509(1)



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deviations exist between the two forms. While some differences occur in the orientation of the side-chain ethyl groups the main arrangement of the two macrocycles to each other is very similar.

Both crystal modifications crystallize in the monoclinic space group *C*2/*c* and the asymmetric unit contains half of the dimer molecule, *i.e.* an octaethylchlorin moiety with a CH_2-group at position 20. Thus the macrocycle conformation and structural parameters in the 'monomeric' subunits of the dimer are identical in both forms. The bridging unit of the dimer is clearly a CH_2–CH_2 group, as evidenced by a C–C bond length of 1.55 Å and bond angles of 113.3(5)° (form **A**) and 116.4(3)° (form **B**) for the C(20)–CH_2–CH_2 bond angles. Interestingly the conformation about this connecting ethyl-bridge is not antiperiplanar with respect to the orientation of the two chlorin macrocycles.

Table 3 Selected bond lengths (Å) and bond angles (°) for the macrocycle atoms in the two crystal forms of **1**

	Form **A**	Form **B**
N(21)–C(1)	1.373(6)	1.377(5)
N(21)–C(4)	1.383(7)	1.378(5)
N(22)–C(6)	1.359(8)	1.365(5)
N(22)–C(9)	1.361(7)	1.366(5)
N(23)–C(11)	1.382(6)	1.370(5)
N(23)–C(14)	1.354(7)	1.365(5)
N(24)–C(16)	1.356(7)	1.352(5)
N(24)–C(19)	1.368(6)	1.379(5)
C(1)–C(2)	1.434(8)	1.453(6)
C(1)–C(20)	1.420(8)	1.422(5)
C(2)–C(3)	1.380(7)	1.390(5)
C(3)–C(4)	1.425(8)	1.425(6)
C(4)–C(5)	1.390(7)	1.393(5)
C(5)–C(6)	1.400(8)	1.390(6)
C(6)–C(7)	1.452(7)	1.463(5)
C(7)–C(8)	1.354(8)	1.358(6)
C(8)–C(9)	1.442(8)	1.461(5)
C(9)–C(10)	1.403(9)	1.394(6)
C(10)–C(11)	1.368(8)	1.374(5)
C(11)–C(12)	1.441(8)	1.438(6)
C(12)–C(13)	1.364(7)	1.370(5)
C(13)–C(14)	1.431(8)	1.447(5)
C(14)–C(15)	1.413(7)	1.400(5)
C(15)–C(16)	1.386(7)	1.386(5)
C(16)–C(17)	1.512(7)	1.509(5)
C(17)–C(18)	1.545(7)	1.548(6)
C(18)–C(19)	1.527(8)	1.532(5)
C(19)–C(20)	1.407(8)	1.396(5)
C(20)–C(201)	1.508(7)	1.514(5)
C(1)–N(21)–C(4)	110.9(4)	111.0(3)
C(6)–N(22)–C(9)	104.8(4)	105.3(3)
C(11)–N(23)–C(14)	110.8(5)	110.3(3)
C(16)–N(24)–C(19)	108.6(4)	108.6(3)
N(21)–C(1)–C(2)	106.7(5)	106.5(3)
N(21)–C(1)–C(20)	121.7(5)	122.3(3)
C(2)–C(1)–C(20)	131.6(5)	131.2(3)
C(1)–C(2)–C(3)	107.6(4)	107.0(3)
C(2)–C(3)–C(4)	108.7(5)	108.6(3)
N(21)–C(4)–C(3)	106.2(4)	106.8(3)
N(21)–C(4)–C(5)	127.8(5)	127.4(3)
C(3)–C(4)–C(5)	126.0(5)	125.6(3)
C(4)–C(5)–C(6)	130.8(6)	130.2(3)
N(22)–C(6)–C(5)	124.9(5)	125.4(3)
N(22)–C(6)–C(7)	111.5(5)	111.0(3)
C(5)–C(6)–C(7)	123.7(5)	123.6(3)
C(6)–C(7)–C(8)	105.9(5)	106.3(3)
C(7)–C(8)–C(9)	106.3(4)	105.9(3)
N(22)–C(9)–C(8)	111.6(5)	111.3(3)
N(22)–C(9)–C(10)	124.2(5)	124.4(3)
C(8)–C(9)–C(10)	124.2(5)	124.2(4)
C(9)–C(10)–C(11)	125.6(5)	126.3(4)
N(23)–C(11)–C(10)	124.2(5)	123.3(3)
N(23)–C(11)–C(12)	105.9(5)	107.3(4)
C(10)–C(11)–C(12)	129.9(5)	129.3(4)
C(11)–C(12)–C(13)	108.1(4)	107.7(3)
C(12)–C(13)–C(14)	108.0(5)	107.5(3)
N(23)–C(14)–C(13)	107.2(4)	107.1(3)
N(23)–C(14)–C(15)	126.0(5)	125.7(3)
C(13)–C(14)–C(15)	126.7(5)	127.2(3)
C(14)–C(15)–C(16)	129.9(6)	129.6(3)
N(24)–C(16)–C(15)	128.1(5)	127.8(3)
N(24)–C(16)–C(17)	112.2(4)	112.9(3)
C(15)–C(16)–C(17)	119.7(5)	119.3(3)
C(16)–C(17)–C(18)	101.7(4)	101.7(3)
C(17)–C(18)–C(19)	101.1(4)	101.4(3)
N(24)–C(19)–C(18)	111.5(5)	110.7(3)
N(24)–C(19)–C(20)	124.7(5)	126.7(3)
C(18)–C(19)–C(20)	123.7(4)	122.5(3)
C(1)–C(20)–C(19)	126.2(5)	124.6(3)
C(1)–C(20)–C(201)	117.1(5)	118.5(3)
C(19)–C(20)–C(201)	116.7(5)	116.8(3)

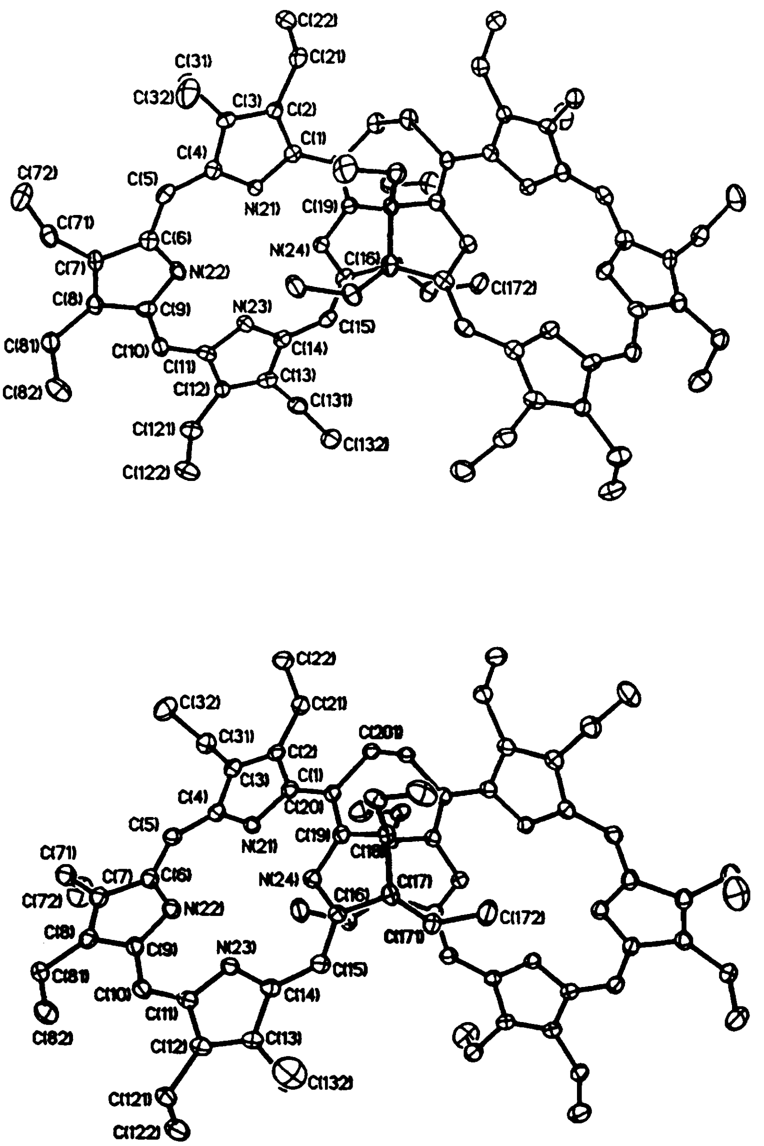

Fig. 1 View of the molecular structure of the chlorin dimer (top) Form **A**; (bottom) Form **B**. Ellipsoids are drawn to enclose 50% occupancy. Hydrogen atoms have been omitted for clarity. Both molecules have been drawn with the paper plane being the least-squares plane through all atoms.

Fig. 2 shows clearly that both macrocycles are twisted against each other and are not in a coplanar arrangement away from each other, which might have been expected for steric reasons. Rather, in form **A** the two macrocycle planes are twisted by 54.4° and the two nitrogen planes by 53.6°. The torsion angle of the C(20)–CH_2–CH_2– C(20A) unit is 75.8°. Thus the arrangement of the macrocycles resembles more a synclinal conformation. In the second modification, form **B**, the two macrocycles are twisted by 57.3° with respect to the mean planes of the macrocycle atoms and 59.1° with respect to the nitrogen planes. The torsion angle is $-70.4°$ for the C(20)–CH_2–CH_2–C(20A) unit. Thus the overall arrangement of the two macrocycles in both dimers is about the same.

Most of the known porphyrin dimeric structures have either parallel porphyrin rings or have forced the porphyrin macrocycle into a coplanar arrangement *via* a fixed bridging unit. Examples are anthracene and biphenylene pillared cofacial dimers[7] or porphyrins strapped together by two substituents at the 5- and 15-positions.[6a] The porphyrin dimer structurally closest to the chlorin dimer **1** is 20,20′-ethylenebis(octaethylporphyrinato)nickel(II).[6b] This molecule has the same bridging unit and the same side-chain substituents. However, this molecule has the porphyrin rings arranged parallel to each other and the torsion angle at the C_m–CH_2–CH_2–C_m unit is 180°. Obviously the present dimer structure is not closely related to the one found in the photosynthetic reaction centre.[11] However, the fact that, with the exception of dimers with a rigid bridging unit, in all known cases different arrangements of the ring subunits to each other have been found, indicates how crucial knowledge of the subunit arrangement is for studies on dimer properties.

Both crystal forms show typical bond lengths and bond angles as observed for other chlorins.[12] The chlorin character is clearly shown by the reduced character of ring IV. Bond lengths of 1.545(7) Å and 1.548(6) Å in forms **A** and **B** for the C(17)–C(18) indicate single bond character and the bond angles for the C(17)–C(18)–ethyl angle are on average 113.3°. Significant differences in bond lengths of equivalent groups in both forms >0.2 Å are not observed. The largest difference in bond angles is observed for the N(24)–C(19)–C(20) angle where the angle in form **B** with 126.7(3)° is 2° larger than in form **A**.

The main macroscopic difference between both crystal forms lies in the fact that form **A** crystallizes with one molecule of solvation (dichloromethane) per dimer, while form **B** contains only chlorin-dimer molecules. Fig. 3 shows a view of the packing in the unit cell of form **A**. The dimer molecules form parallel layers of molecules with the dichloromethane molecules situated in the space between neighbouring layers. Form **B**

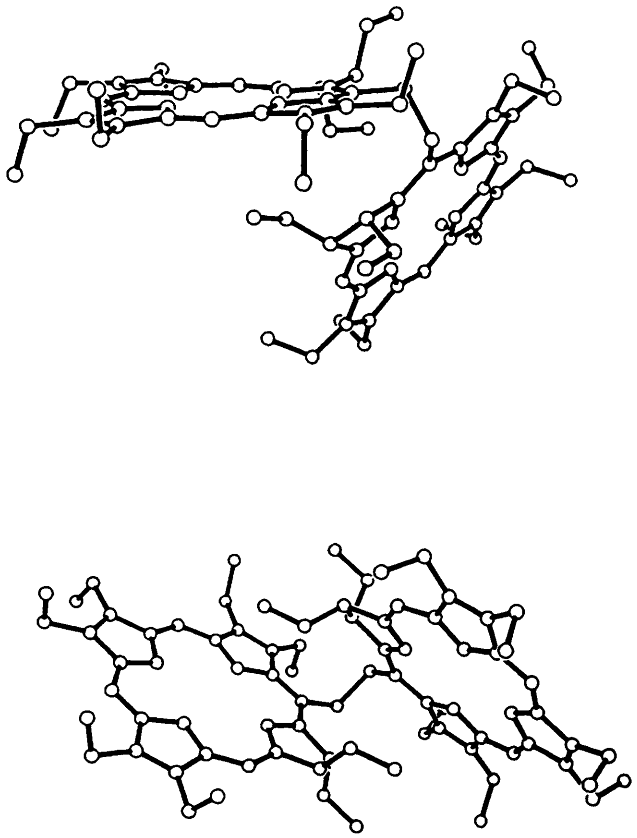

Fig. 2 Two different side views of the molecular structure of **1**, form **A**

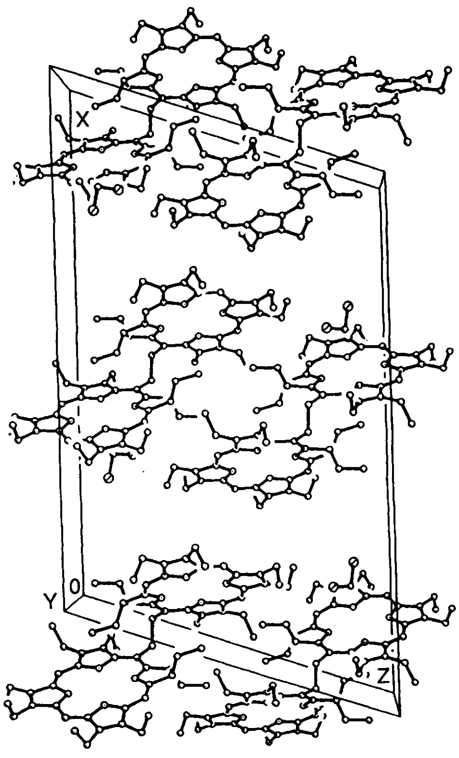

Fig. 3 View along the *y*-axis of the molecular arrangement in the unit cell of form **A**

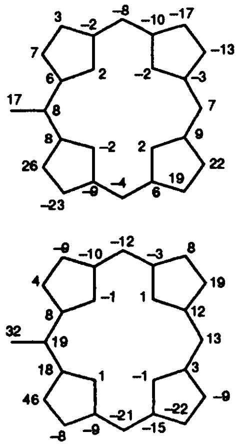

Fig. 4 Deviations from the least-square plane of the four nitrogen atoms (Å × 10^2) in the asymmetric unit of **1**; (top) form **A**, (bottom) form **B**

crystallizes in a rather similar fashion (not shown), only the solvent molecules are absent. Since the unit cell volume of form **A** is only about 8% larger than that of form **B** by overall similar molecular structure this is not too surprising. In both crystal forms the layers on top of each other are spaced roughly 10.5 Å apart. Thus, there is no evidence for π-stacking in the crystal.

Several other cases of multiple crystal phases have been described for porphyrins.[12,13] Examples of chlorins with different modifications include 8-isobutyl-12-ethyl methyl bacteriopheophorbide d[3a] and 3^1,3^2-didehydrorhodochlorin dimethyl ester[1,2] (rhodochlorin XV dimethylester in the older Fischer nomenclature).[14] The increasing evidence for multiple crystal forms of chlorins and different conformations of chemically very similar compounds points to the conformational flexibility inherent to the hydroporphyrins.

The largest differences between both crystal forms can be found in their macrocycle conformations. Fig. 4 displays the deviations of the macrocycle atoms in the asymmetric unit from the mean plane of the 24 core atoms. While form **A** exhibits an average deviation from planarity of 0.08 Å, form **B** shows a slightly higher degree of non-planarity with a mean deviation of 0.11 Å. The four nitrogen atoms are planar in both cases with 0.02 Å and 0.01 Å deviation from planarity for forms **A** and **B**, respectively. Larger differences are observed for the plane through the four *meso*-carbon atoms. The macrocycle atoms in form **A** show an average deviation from planarity of 0.07 Å, while the *meso*-carbons in form **B** deviate by *ca.* 0.16 Å from their least-squares plane. The individual pyrrole rings I, II and III are all planar, while ring IV, as a manifestation of its reduced character shows deviations from planarity of the order of 0.07 Å in form **B** and 0.09 Å in form **A**. In form **A** rings II, III and IV deviate from the mean plane of the molecule. Their β-pyrrole atoms are displaced by about 0.2 Å and the individual rings I, II, III, IV have angles with the mean plane of 2.1, 3, 4.9 and 9.3°. In form **B** much larger distortions are observed in ring IV, which has C(18) displaced from the 4N-plane by almost 0.5 Å. Rings, I, II, III and IV have angles of 4.8, 11.7, 6 and 6.1° with the mean plane of the macrocycle atoms. Thus, although both forms have overall a very similar molecular structure, they exhibit considerable differences in their core conformation. A similar flexibility of the chlorin system has been noted in several chlorophyll derivatives and synthetic chlorins.[2,3,4b,14] This clearly points to the flexibility of the tetrapyrrole conformation and its importance for modulating the properties of photosynthetic chromophores.[3]

Dimer **1** represents formally a mono-*meso*-substituted chlorin, the substituent in this case being an ethylene–chlorin moiety. This makes the compound similar to the bacteriochlorophylls c and e, which bear a C(20)-methyl group.[15] The *meso*-substituent has been inferred to induce steric strain in the molecule and thus be responsible for the easier photochemical ring-opening and different spectroscopic properties compared to the non-*meso*-methylated bacteriochlorophylls d.[16] While in nickel(II) complexes of porphyrins a single *meso*-substituent induces noticeable steric strain leading to conformational distortion,[1,6b,17] the situation in the present free-base is somewhat ambiguous. Form **A** shows no significant distortion of the macrocycle near the C(20) position while in form **B** considerable distortion is observed for the C(19) and C(20) atoms (Fig. 4). Thus, on the basis of the present free-base chlorin structures, no decisive argument can be made in favour of, or opposition to, the above hypothesis. The displacements of the CH_2-group at C(20) by 0.2 Å (form **A**) and 0.3 Å (form **B**) from the nitrogen plane of the molecule are, however, in agreement with the results of Fajer *et al.*[18] who observed a considerably smaller spin density for the methyl group in the anion radical of bacteriochlorophyll c, than predicted by molecular orbital calculations. This indicates that the methyl group in bacteriochlorophyll c and e may lie out of the chlorin plane to minimize steric interactions with ring I and IV substituents. A similar result was recently obtained with 15,20-dimethyloctaethylchlorin;[4b] however a di-*meso*-substituted chlorin is prone to have more conformational distortion than a mono-substituted one. All attempts to obtain crystal structures of bacteriochlorophyllides c or e have failed so far.[1]

Since it has been shown that the conformation of tetrapyrroles closely correlates with their physicochemical properties[3] the present study indicates the importance of knowing the macrocycle conformation when performing photophysical studies on reaction centre models. The data obtained may not be so much the result of a given dimer but of a specific macrocycle conformation. Overall structural similarity is a necessary but not a sufficient criterion for a compound to be a suitable reaction centre model. Knowledge of both the relative geometry of the subunits and the conformation are necessary for development of suitable reaction centre models.

Experimental

The dimer **1** was prepared by formylation of octaethylchlorin, reduction of the formyl group to the alcohol and acid-catalysed dimerization as described earlier.[19]

Crystals of form **A** were grown by slow diffusion of hexane into a solution of **1** in dichloromethane. Crystals of form **B** were obtained by slow diffusion of methanol into a solution of **1** in dichloromethane. The crystals were immersed in a hydrocarbon oil, a single crystal selected, mounted on a glass fibre and placed in the low-temperature N_2 stream.[20]

Crystal Data, Form **A**.—$C_{74}H_{98}N_8{\cdot}CH_2Cl_2$, $M = 1184.5$. Monoclinic, $a = 32.610(9)$ Å, $b = 10.804(2)$ Å, $c = 21.185(5)$ Å, $\beta = 108.90(6)°$, $V = 7063(3)$ Å^3, (by least-squares refinement on diffractometer angles for 21 automatically centred reflections in the range $42° \leqslant 2\theta \leqslant 59°$, Cu-K$\alpha$ radiation, $\lambda = 1.541\,78$ Å), space group $C2/c$, $Z = 4$, $D_x = 1.106$ Mg cm^{-3}. Green parallelpipeds. Crystal dimensions: $0.14 \times 0.035 \times 0.02$ mm, $\mu = 1.164$ mm^{-1}.

Data Collection and Processing, Form **A**.—Data were collected on a Siemens P4/R4 (rotating anode) diffractometer equipped with a Siemens LT device using the $\theta - 2\theta$ scan technique with a scan speed 8.08° min^{-1} and a scan range of 2° plus Kα separation. 4767 reflections measured ($0 \leqslant 2\theta \leqslant 108.5°$, index range $-34 \leqslant h \leqslant 32$, $0 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 22$), 4318 unique reflections giving 2901 with $I > 3.0\sigma(I)$. Two standard reflections were measured every 198 reflections and showed only statistical changes in intensity (< 1% intensity loss). The intensities are corrected for Lorentz and polarization effects. An absorption correction was applied using the Program *XABS*,[21] extinction was disregarded.

Structure Analysis and Refinement, Form **A**.—Structure solution by Direct Methods using the SHELXTL PLUS program system.[22] The refinement was carried out by full-matrix least-squares on $|F|$ using the same program system. The function minimized was $\Sigma w(F_o - F_c)^2$. All hydrogen atoms were placed in calculated positions (the *meso* and pyrrole-N hydrogen atoms were also located in difference maps) using a riding model (C–H = 0.96 Å, N–H = 0.9 Å; $U_{iso} = 0.04$). All non-hydrogen atoms were refined with anisotropic thermal parameters. Calculations were carried out on a Vaxstation 3200. The final cycle of refinement on $|F|$ included 400 variable parameters and converged with $R = 0.073$, $wR = 0.074$, and $S = 1.62$. Weighting scheme defined as $w^{-1} = \sigma^2(F) + 0.0005F^2$, $(\Delta/\sigma)_{max}$ 0.026, final difference Fourier synthesis: $-0.54 \leqslant \Delta\rho \leqslant 0.40$ eÅ^{-3}. Atomic scattering factors as supplied with SHELXTL-PLUS.

Crystal Data, Form **B**.—$C_{74}H_{98}N_8$, $M = 1099.6$. Monoclinic, $a = 24.068(14)$ Å, $b = 10.216(6)$ Å, $c = 26.44(3)$ Å, $\beta = 92.19(6)°$, $V = 6497(7)$ Å^3, (by least-squares refinement on diffractometer angles for 19 automatically centred reflections in the range $21° \leqslant 2\theta \leqslant 24°$, Mo-K$\alpha$ radiation $\lambda = 0.710\,73$ Å), space group $C2/c$, $Z = 4$, $D_x = 1.124$ Mg cm^{-3}. Red parallelpipeds. Crystal dimensions: $0.41 \times 0.28 \times 0.11$ mm, $\mu = 0.132$ mm^{-1}.

Data Collection and Processing, Form **B**.—Data collection on a Siemens R3m/V diffractometer equipped with a Siemens LT device, ω-scan technique with a scan speed of 8.08° min^{-1} in ω and a scan range of 2.5°, graphite monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å); 8384 reflections measured ($0 \leqslant 2\theta \leqslant 55°$, index range $-31 \leqslant h \leqslant 31$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 34$), 7449 unique reflections giving 3744 with $I > 2.5\sigma(I)$. Two standard reflections were measured every 198 reflections and showed only statistical changes in intensity (< 1% intensity loss). The intensities are corrected for Lorentz, polarization and absorption effects,[21] extinction was disregarded.

Structure Analysis and Refinement, Form **B**.—Structure solution, refinement and treatment of hydrogen atoms as described for form **A**. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final cycle of refinement on $|F|$ included 370 variable parameters and converged with $R = 0.063$, w$R = 0.082$ and $S = 1.38$. Weighting scheme defined as $w^{-1} = \sigma^2(F) + 0.0011F^2$, data to parameter ratio 10.1:1 $(\Delta/\sigma)_{max}$ 0.001, final difference Fourier synthesis: $-0.89 \leqslant \Delta\rho \leqslant 0.26$ eÅ^{-3}.

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