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Crystal and Molecular Structure of Anthracene and Biphenylene Pillared Cofacial Diporphyrins

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Abstract: The structures of two cofacial metalloporphyrins anchored by rigid pillaring spacer groups of anthracene and biphenylene have been determined by using X-ray crystallographic methods (DP-A and DP-B, respectively). The cobalt complexes of these two porphyrin hosts have demonstrated electrocatalytic activity of mediating the four-electron reduction of dioxygen to water. The structures reported here are as the dinickel (DP-A) and the dicopper (DP-B) complexes. The porphyrins of both molecules slip with respect to each other: 2.40 Å in DP-A giving a Ni–Ni distance of 4.566 Å and 1.60 Å in DP-B giving a Cu–Cu distance of 3.807 Å. The slip of the former leads to an average porphyrin plane-to-plane separation of 3.88 Å while that of the latter corresponds to about 3.45 Å. The larger distance of the DP-A is a consequence of the greater lack of planarity of the Ni porphyrin structure. The slip of the porphyrin rings appears to be an optimizational positioning of the rings with respect to van der Waals interactions and its extent is limited by the following: (1) repulsive interactions between pyrrole substituent methyl groups and atoms of the pillaring connector group and (2) the ruffling of the porphyrin rings by the metal. The structures of the pyrroles adjacent to the aromatic connector groups are different from the outer pyrroles while the structures of the connectors compare quantitatively with those of the isolated molecules. Interestingly, although both crystal structures are triclinic, the crystal packing of the two is very different. The results of these studies suggest indirectly that an exact metal–metal distance is not absolutely crucial for four-electron dioxygen reduction.

In recent years great interest has been shown in the use of metalloporphyrins for catalyzing dioxygen activation and reduction.[1,2] The ability of certain cofacial dicobalt porphyrins to catalyze the electroreduction of dioxygen at unusually positive potentials has made such complexes, supported on inexpensive graphite, promising alternatives to platinum as electrode material in air battery and fuel cell applications.[3–5] It has been shown, however, that the performance of these macrocycle catalysts is extremely sensitive to the porphyrin structure. To date, only three diporphyrins are capable of achieving the four-electron electroreduction of dioxygen to water without accumulating a substantial amount of hydrogen peroxide. Among these, the first compound consists of two stacked porphyrin rings doubly linked via short alkyl amide straps[3,4] while the other two are based on a design in which two porphyrins are anchored cofacially onto a rigid pillaring spacer group (e.g., anthracene or biphenylene).[5] The strapped system is, due to the synthetic approach employed, always composed of more than one stereoisomer[6] which undoubtedly has contributed to the difficulty of obtaining good quality crystals for X-ray diffraction studies. There are two published crystallographic diporphyrin structures[7,8] but neither is for the active (4-e process) catalyst and neither is very accurate due to disorder leading to relatively poor diffraction quality. The recently synthesized anthracene and biphenylene pillared dimers contain no stereoisomers and generally tend to crystallize easily. Most important of all, both diporphyrins as cobalt complexes are effective electrocatalysts.[5] We report here the X-ray crystal structures of dinickel anthryl diporphyrin and dicopper biphenylene diporphyrin. This is the first time that structural parameters which may be important for dioxygen reduction are observed for diporphyrins with demonstrated 4-e activities.

Experimental Section

A. Dinickel(II) Anthracene Diporphyrin (DP-A). The anthryl diporphyrin was synthesized as previously described.[9] Nickel insertion was accomplished by heating an acetic acid solution of the porphyrin with nickel(II) acetate. Crystals of DP-A suitable for X-ray analysis were obtained by slow evaporation of a methanol/methylene chloride solution.[10a] Pertinent crystal and associated data are summarized in Table I. Background measurements during intensity data collection were made at both ends of the scan for a time which was 0.2 of the total scan time. However, the background was averaged in shells of 2θ during data reduction (background was independent of the ϕ angle), and the average background was used to correct measured intensities. Such a procedure virtually eliminates error from the background correction. An empirical absorption correction was applied based on ϕ and layer-line height,[11] and standard corrections were applied for the Lorentz–polarization factor.

B. Dicopper(II) Biphenylene Diporphyrin (DP-B). The biphenylene diporphyrin was synthesized as previously described.[12,13] Copper insertion was accomplished by heating a chloroform solution of the porphyrin with copper(II) acetate. Crystals of DP-B were also grown by the slow evaporation of a methanol/methylene chloride solution.[10a] The intensity data collection[10b] and processing of DP-B was practically identical with that of DP-A; pertinent crystal and associated data of DP-B are also listed in Table I.

Structure Solution and Refinement. A. DP-A. The positions of the two Ni(II) atoms were determined from a three-dimensional Patterson function. The other non-hydrogen atoms were located from a three-dimensional-difference electron-density map by using phases based on the Ni(II) positions. Full-matrix least-squares refinement using isotropic thermal parameters gave $R = 0.15$ [$R = \sum||F_o| - |F_c||/\sum|F_o|$ for $|F_o| > 3 \times \sigma(|F_o|)$]. Introducing anisotropic thermal parameters reduced R to 0.090 in several cycles. All non-methyl hydrogen atoms were then included at the calculated positions; methyl hydrogens were either located in a difference map and idealized or their calculated positions were used. The hydrogen positions were not refined and were simply up-dated periodically during the refinement of the structure which converged to a final R of 0.053. The weighting scheme in the latter stages of the refinement was the following: $\omega^2 = 1/(1.0 + \sigma^2(|F_o|) + 0.0004|F_o|^2)$, where $\sigma^2(|F_o|)$ is the variance of $|F_o|$ based on counting statistics. The final individual parameter shifts of the atoms averaged 0.03 of their standard deviations, and a final difference map only showed significant density near a disordered ethyl group of the molecule ($\approx$0.5 eÅ^{-3}).

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Table I. Summary of Crystal Data and Experimental Details of X-ray Diffraction Measurements of DP-A and DP-B

A. Crystal Parameters

	DP-A	DP-B		DP-A	DP-B
a (Å)	14.437 (2)	12.322 (1)	space group	$P1$	$P1$
b (Å)	15.420 (3)	13.036 (1)	Z	2	2
c (Å)	16.866 (2)	21.519 (3)	ρ_c (gm cm^{-3})	1.297	1.336
α (deg)	102.45 (1)	77.35 (1)	empirical form.	$C_{78}H_{78}N_8Ni_2$	$C_{76}H_{76}N_8Cu_2$
β (deg)	100.06 (1)	80.38 (1)	mol	1244.3	1228.6
γ (deg)	114.47 (1)	65.33 (1)	μ (cm^{-1})	10.15	12.83
V (Å^3)	3186.4	3053.6			

B. Intensity Data Measurement Parameters[a]

	DP-A	DP-B
temp (°C)	16 ± 1	16 ± 1
2θ range (deg)	2–124	2–124
scan speed (deg min^{-1})	5.86	5.86
scan width	$2° + (2\theta_2 - 2\theta_1)$	$2° + (2\theta_2 - 2\theta_1)$
check reflectns	(10, 12, 0), (1, 15, 0), (1, 3, 16)	(6, 1, 10), (8, 3, 6), (1, 10, 1)
monitored every	4500 s	4500 s
behavior	random variation, no decay	random variation, no decay
cryst size (mm)	0.2 × 0.3 × 0.5	0.2 × 0.3 × 0.3
R_{symm}	0.025	0.013
unique reflectns	9983	9565

C. Refinement Data Parameters - Results

	DP-A	DP-B
no. of obsvatns, ($\lvert F_o\rvert > 3\sigma$)	8021	7639
R (final)	0.053	0.063
R (weighted)	0.067	0.089
σ of unit weight, obsvatn	1.901	1.998

[a] Instrument: Nicolet P3F. Radiation: CuKα (λ = 1.5418 Å) graphite monochromatized.

B. DP-B. The solution and refinement of DP-B was very similar to that of DP-A. Isotropic refinement gave $R = 0.17$ which reduced to 0.12 with anisotropy. Subsequent refinement with hydrogen atoms included gave a final $R = 0.063$. The final weighting scheme was the following: $\omega^2 = 1/(0.89 + \sigma^2(|F_o|) + 0.0005\,|F_o|^2)$. The final average shifts were the same as DP-A, and a final difference map also had residual density of about 0.5 eA^{-3} associated with a disordered ethyl group. The coordinates of both molecules are given in Table II; the thermal parameters of the molecules are listed in Table I of the supplementary material.

Results and Discussion

The numbering systems used to describe DP-A and DP-B are shown in Figure 1. The numbering of the aromatic connector atoms is straightforward while each atom of the porphyrin rings is additionally identified with the pyrrole ring (a, ..., d) and with the porphyrin ring (1 or 2) in which it occurs.

(i) Secondary Structure. Three approximately mutually perpendicular views of DP-A are shown in Figure 2 while those of DP-B are shown in Figure 3. From these it will be seen that the porphyrin rings are not stacked over one another but, rather, have slipped with respect to each other as previously noted with other cofacial porphyrin structures[7,8] and that the porphyrin rings of both DP-A and DP-B are markedly nonplanar with the nonplanarity being significantly less in the case of the Cu(II) complex. The lateral translation in both cases corresponds fairly closely to the methine–methine direction perpendicular to the aromatic connector (Figures 2 and 3) unlike that observed with cofacial dicopper hexyldiporphyrin-7 (Cu_2DP-7)[7] and Cu_2 (FTF6-3,2-NH diamide),[8] where it occurs close to the direction containing the connector groups. The former is a consequence of the inflexibility of the aromatic pillaring connector, except for a free rotation about the connector–porphyrin bond. The magnitude of the slip is 2.40 Å in DP-A so with a Ni–Ni distance of 4.566 Å this corresponds to a slip angle of 31.7°.[14] The corresponding values of DP-B are the following: 1.60 Å for slip, 3.807 Å for Cu–Cu distance, and 24.9° for slip angle. These angles are also closely related to the orientational angles of the porphyrin rings around the bond to the pillaring aromatic group (Figures 2b and 3b). The fact that these angles are about the same for each porphyrin ring in a given pillared molecule indicates that the rings shear with respect to one another and that the slip effect is not merely rotational, in which case the two angles could be different. The slip exhibited by DP-A leads to an average porphyrin plane-to-plane distance of 3.88 Å while that of DP-B practically corresponds to a van der

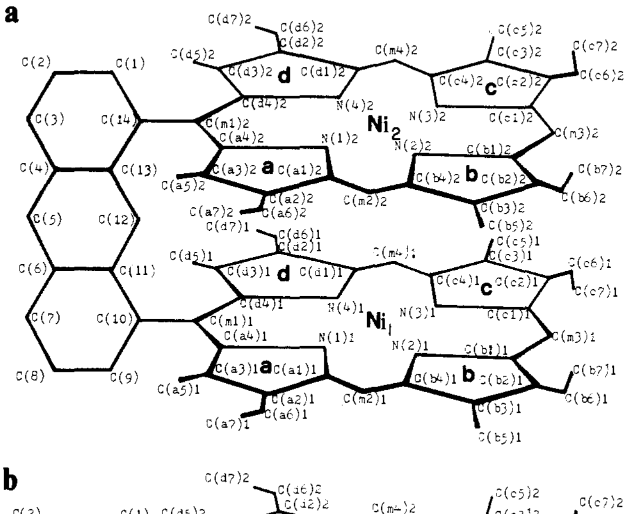

Figure 1. Numbering scheme used for DP-A (a) and DP-B (b).

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[14] Slip angle = sin^{-1} (magnitude of slip)/(metal–metal distance).

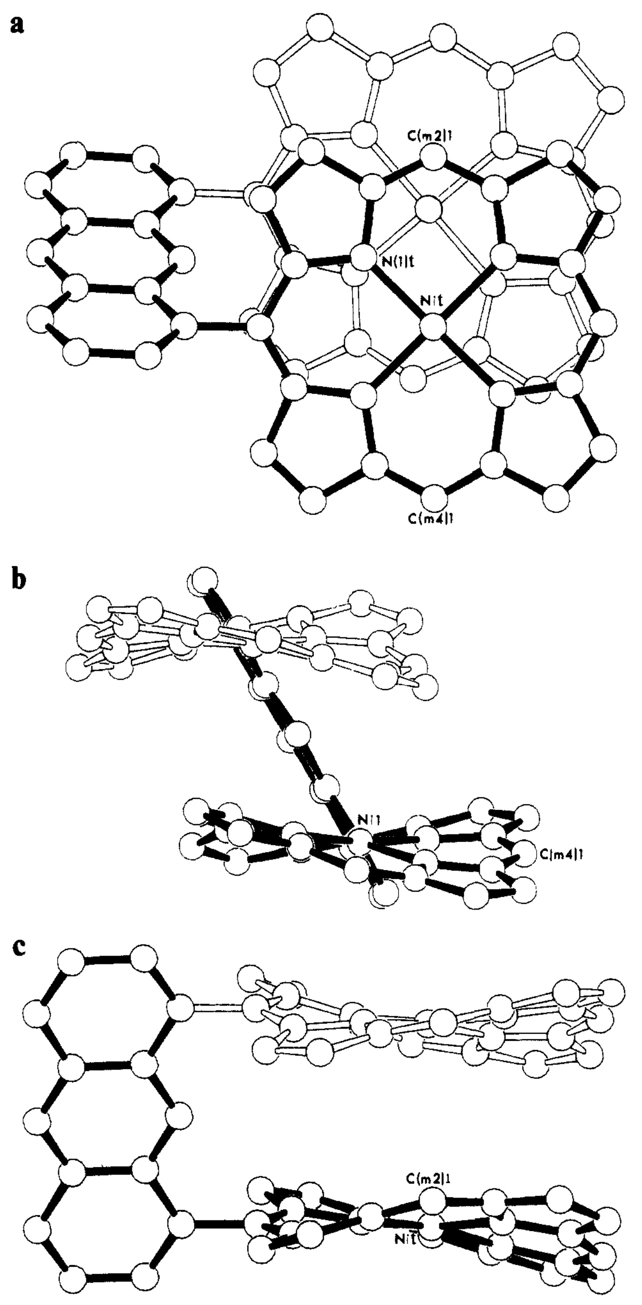

Figure 2. ORTEP drawings of DP-A excluding side groups. Views approximately mutually perpendicular: (a) nearly perpendicular to porphyrin planes; (b) parallel to C(m1)–C(m3) direction; (c) parallel to C(m2)–C(m4) direction; ring 1 shaded.

Waals contact at 3.45 Å. However, an examination of a space-filling representation of the structures with the interactive graphics program FRODO[15] shows that the "vacant" interplanar space of both molecules is strikingly similar in both magnitude and extent, indicating that the 3.88 Å interplanar separation of DP-A is only an apparent difference resulting from the greater degree of nonplanarity. A perspective stereoview of the molecules is shown in Figure 4.

The slip of the porphyrin rings exhibited by DP-A and DP-B appears to be an optimizational positioning of the rings with respect to van der Waals interactions. The effect is common among diporphyrin molecules and leads to a small range of interplanar separations approaching van der Waals contacts for a diversity of bridging groups between porphyrins.[13] The fact that DP-A does not attain as close a ring contact as DP-B suggests that either (a) further lateral translation to achieve this is offset by the loss of the total number of van der Waals contacts or (b) further rotation of the porphyrin rings about the connector bond leads to distortive repulsions between the aromatic connector and methyl groups of the porphyrin ring which contribute to the buckling of the porphyrin, since the porphyrin core is much more flexible than the aromatic connector; (c) the degree of nonplanarity can also be a factor by inhibiting further slippage to avoid the development of unfavorable contacts. As mentioned previously, the latter is supported by space-filling considerations which show that the contact space between the rings is quantitatively similar even though their average separations differ by about 0.4 Å. With planar porphyrin rings and no slip (i.e., stacked over each other), the porphyrin methyl–connector atom distances are about 3.25 Å. However, these decrease to about 3.0 Å in the slipped state with buckled porphyrin rings (Table III). Since the opposite methyl group–adjacent atom connector distances are somewhat greater (≈3.15 Å, Table III), the distances suggest that the extent of the slip is limited by (1) the methyl–connector atom repulsive interaction and (2) the ruffling of the porphyrin rings. Thus, the larger slip angle of DP-A is consistent with the larger size of the pillaring anthracene permitting more rotation before termination by repulsive and buckling effects. Option (a) above is not while option (c) is independently supported by the Cu_2DP-7 structure which has a considerably larger slip than DP-A and thus still has a sufficient number of contacts, but which also has more nearly planar porphyrin rings,[7] and Cu_2 (FTF6-3, 2-NH diamide), which also has a large slip but only attains a 3.9 Å average interplanar

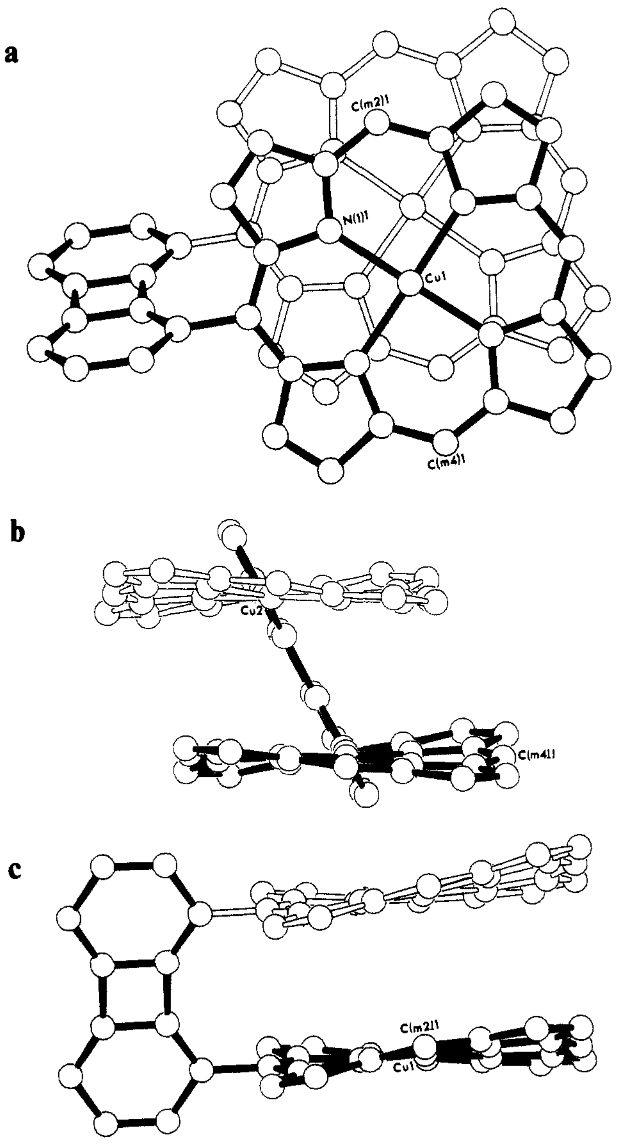

Figure 3. ORTEP drawings of DP-B excluding side groups. Otherwise as in Figure 2.

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Table II. Atomic Coordinates with Estimated Standard Deviations in Parentheses

atom	10^5x	10^5y	10^5z
		a. DP-A	
Ni1	55 143 (4)	27 479 (3)	36 676 (3)
Ni2	27 096 (4)	3 168 (3)	14 077 (3)
C(1)	−2 159 (28)	19 043 (28)	6 372 (21)
C(2)	−7 303 (29)	25 214 (32)	6 693 (24)
C(3)	−2 488 (30)	34 624 (32)	12 451 (24)
C(4)	7 882 (27)	38 582 (26)	18 348 (21)
C(5)	13 063 (29)	48 168 (26)	24 309 (22)
C(6)	23 076 (28)	51 870 (25)	30 049 (20)
C(7)	28 449 (34)	61 719 (26)	36 314 (24)
C(8)	38 109 (35)	64 986 (26)	41 819 (23)
C(9)	43 193 (30)	58 858 (26)	41 620 (21)
C(10)	38 454 (27)	49 345 (24)	35 898 (19)
C(11)	28 146 (25)	45 609 (23)	29 801 (19)
C(12)	22 993 (25)	36 000 (23)	23 831 (19)
C(13)	12 954 (25)	32 344 (24)	18 083 (19)
C(14)	7 593 (25)	22 335 (25)	11 928 (20)
N(1)1	41 504 (19)	26 511 (19)	37 171 (15)
C(a1)1	33 118 (26)	18 516 (25)	37 999 (21)
C(a2)1	25 714 (26)	21 541 (28)	40 734 (22)
C(a3)1	29 394 (26)	31 434 (26)	41 476 (20)
C(a4)1	38 812 (24)	34 275 (23)	38 561 (18)
C(a5)1	24 922 (31)	37 953 (31)	45 397 (25)
C(a6)1	16 156 (31)	14 895 (33)	42 898 (31)
C(a7)1	18 817 (46)	14 289 (51)	51 801 (41)
C(m1)1	43 554 (25)	42 680 (23)	35 964 (18)
N(2)1	50 762 (21)	14 065 (19)	37 569 (16)
C(b1)1	56 901 (29)	9 442 (25)	39 033 (21)
C(b2)1	50 473 (32)	−756 (26)	38 784 (23)
C(b3)1	40 234 (30)	−2 471 (25)	36 964 (21)
C(b4)1	40 537 (28)	6 960 (24)	36 569 (20)
C(b5)1	30 450 (34)	−11 770 (28)	36 214 (27)
C(b6)1	54 719 (36)	−7 901 (30)	40 581 (27)
C(b7)1	55 648 (58)	−13 851 (44)	32 780 (35)
C(m2)1	32 266 (27)	9 053 (26)	36 799 (22)
N(3)1	69 549 (21)	29 363 (21)	37 953 (17)
C(c1)1	73 732 (29)	23 391 (28)	40 266 (22)
C(c2)1	85 034 (31)	27 889 (32)	41 248 (26)
C(c3)1	87 702 (29)	36 452 (32)	39 292 (25)
C(c4)1	78 057 (28)	37 405 (28)	37 244 (23)
C(c5)1	98 313 (35)	43 571 (41)	38 784 (35)
C(c6)1	92 096 (34)	23 341 (38)	43 929 (35)
C(c7)1	95 541 (47)	25 486 (49)	53 400 (40)
C(m3)1	67 863 (31)	13 981 (28)	40 727 (24)
N(4)1	58 919 (21)	40 179 (19)	34 541 (16)
C(d1)1	68 030 (28)	45 706 (25)	32 693 (22)
C(d2)1	67 012 (31)	53 325 (27)	29 454 (23)
C(d3)1	57 430 (30)	52 596 (25)	29 514 (22)
C(d4)1	52 584 (26)	44 770 (23)	33 224 (19)
C(d5)1	52 761 (36)	58 524 (31)	25 851 (27)
C(d6)1	75 626 (35)	60 650 (33)	26 620 (31)
C(d7)1	75 942 (45)	56 171 (45)	17 950 (37)
C(m4)1	77 174 (29)	44 751 (28)	34 344 (24)
N(1)2	13 447 (20)	1 483 (19)	15 307 (16)
C(a1)2	6 615 (28)	−5 950 (28)	17 876 (26)
C(a2)2	−867 (32)	−3 189 (32)	20 763 (31)
C(a3)2	895 (27)	5 685 (28)	19 494 (25)
C(a4)2	9 582 (25)	8 369 (24)	15 680 (20)
C(a5)2	−4 480 (33)	11 798 (32)	22 474 (29)
C(a6)2	−8 113 (47)	−9 033 (52)	27 114 (72)
C(a7)2	−16 797 (114)	−13 399 (74)	20 921 (62)
C(m1)2	12 986 (24)	15 970 (23)	12 040 (18)
N(2)2	23 616 (20)	−10 285 (19)	14 434 (16)
C(b1)2	29 503 (28)	−15 289 (26)	13 323 (21)
C(b2)2	23 459 (30)	−25 678 (27)	12 758 (25)
C(b3)2	13 940 (30)	−26 889 (27)	13 738 (25)
C(b4)2	14 241 (27)	−17 228 (26)	14 976 (23)
C(b5)2	4 449 (36)	−36 261 (32)	13 391 (37)
C(b6)2	27 215 (36)	−33 534 (32)	11 323 (31)
C(b7)2	24 370 (52)	−39 147 (43)	2 236 (41)
C(m2)2	6 592 (30)	−15 000 (28)	17 205 (27)
N(3)2	41 460 (20)	5 723 (20)	14 445 (15)
C(c1)2	45 787 (26)	−667 (27)	14 583 (21)
C(c2)2	57 108 (27)	4 475 (30)	15 579 (21)
C(c3)2	59 550 (26)	14 037 (29)	15 853 (21)
C(c4)2	49 840 (25)	14 694 (26)	14 916 (21)
C(c5)2	70 170 (29)	22 262 (32)	16 313 (29)
C(c6)2	64 424 (30)	−231 (33)	15 657 (26)
C(c7)2	66 440 (42)	−2 601 (39)	7 167 (29)
C(m3)2	40 042 (29)	−10 776 (28)	13 618 (23)
N(4)2	29 656 (20)	15 558 (19)	11 826 (16)
C(d1)2	38 889 (26)	22 416 (24)	10 909 (22)
C(d2)2	36 987 (30)	29 323 (25)	7 210 (23)
C(d3)2	26 641 (30)	26 908 (25)	6 008 (21)
C(d4)2	22 196 (25)	18 750 (23)	9 509 (19)
C(d5)2	20 981 (34)	31 651 (31)	1 573 (26)
C(d6)2	45 294 (35)	37 320 (31)	4 787 (31)
C(d7)2	46 608 (45)	33 202 (42)	−3 676 (40)
C(m4)2	48 605 (28)	22 557 (26)	13 218 (24)
		b. DP-B	
Cu1	4 306 (5)	34 156 (4)	120 452 (2)
Cu2	4 009 (5)	52 199 (4)	132 250 (2)
C(1)	14 098 (44)	87 863 (37)	114 455 (21)
C(2)	16 657 (50)	95 405 (40)	109 501 (23)
C(3)	18 342 (48)	93 720 (38)	103 013 (23)
C(4)	17 355 (41)	84 085 (35)	102 083 (20)
C(5)	18 169 (40)	76 548 (34)	97 439 (20)
C(6)	19 832 (46)	74 870 (40)	91 278 (21)
C(7)	18 771 (47)	64 876 (42)	90 390 (22)
C(8)	16 424 (43)	57 325 (38)	95 384 (22)
C(9)	14 669 (36)	59 093 (33)	101 823 (20)
C(10)	15 626 (36)	68 846 (32)	102 623 (19)
C(11)	14 852 (37)	76 282 (32)	107 265 (19)
C(12)	12 945 (39)	77 872 (34)	113 485 (20)
N(1)1	−3 767 (29)	50 175 (26)	115 978 (16)
C(a1)1	−15 059 (38)	57 746 (35)	117 608 (23)
C(a2)1	−18 921 (39)	67 580 (34)	112 668 (24)
C(a3)1	−10 012 (39)	66 127 (31)	107 963 (23)
C(a4)1	−2 (37)	55 378 (32)	110 183 (20)
C(a5)1	−11 211 (41)	73 491 (37)	101 395 (24)
C(a6)1	−31 137 (42)	77 166 (40)	112 838 (27)
C(a7)1	−40 459 (49)	73 755 (52)	111 303 (35)
C(m1)1	11 661 (36)	51 211 (32)	107 335 (20)
N(2)1	−9 588 (33)	36 356 (31)	127 055 (17)
C(b1)1	−11 146 (49)	28 488 (45)	132 151 (23)
C(b2)1	−21 946 (56)	33 749 (53)	136 125 (26)
C(b3)1	−27 214 (52)	44 833 (49)	133 285 (27)
C(b4)1	−19 498 (43)	46 304 (41)	127 658 (23)
C(b5)1	−38 874 (59)	53 921 (54)	135 302 (31)
C(b6)1	−26 223 (76)	27 747 (61)	142 176 (34)
C(b7)1	−33 790 (80)	22 130 (78)	141 260 (42)
C(m2)1	−21 971 (40)	56 147 (38)	123 226 (24)
N(3)1	11 629 (32)	17 686 (29)	124 491 (16)
C(c1)1	6 857 (47)	11 996 (39)	129 603 (22)
C(c2)1	15 032 (49)	−129 (40)	130 862 (23)
C(c3)1	24 636 (46)	−1 427 (37)	126 558 (24)
C(c4)1	22 616 (42)	9 687 (37)	122 650 (21)
C(c5)1	35 803 (52)	−12 187 (41)	125 805 (28)
C(c6)1	12 745 (56)	−9 018 (44)	135 917 (24)
C(c7)1	6 089 (73)	−14 706 (58)	133 673 (29)
C(m3)1	−3 489 (53)	17 017 (46)	133 225 (23)
N(4)1	18 405 (29)	32 299 (26)	114 060 (16)
C(d1)1	28 981 (38)	22 683 (35)	114 193 (21)
C(d2)1	38 078 (39)	24 986 (37)	109 738 (24)
C(d3)1	33 052 (38)	36 021 (35)	106 819 (22)
C(d4)1	20 645 (36)	40 499 (33)	109 362 (20)
C(d5)1	40 008 (43)	42 172 (43)	102 172 (27)
C(d6)1	50 805 (44)	16 235 (44)	108 780 (29)
C(d7)1	51 456 (61)	8 280 (51)	104 548 (37)
C(m4)1	30 640 (40)	12 115 (36)	117 995 (22)
N(1)2	−4 681 (29)	68 168 (27)	127 867 (15)
C(a1)2	−16 039 (39)	75 354 (36)	129 745 (22)
C(a2)2	−20 243 (40)	85 421 (37)	124 963 (22)
C(a3)2	−11 500 (43)	84 408 (35)	120 210 (22)
C(a4)2	−1 408 (37)	73 737 (32)	122 110 (19)
C(a5)2	−12 931 (49)	92 921 (41)	114 068 (23)
C(a6)2	−32 319 (46)	95 287 (44)	125 606 (27)
C(a7)2	−31 403 (61)	104 460 (51)	128 449 (39)
C(m1)2	10 113 (38)	69 906 (32)	119 035 (18)
N(2)2	−8 750 (35)	54 313 (32)	139 531 (17)

Table II (Continued)

atom	10^5x	10^5y	10^5z	atom	10^5x	10^5y	10^5z
C(b1)2	−8974 (57)	46707 (52)	145076 (27)	C(c5)2	37715 (55)	6800 (44)	137815 (29)
C(b2)2	−19413 (69)	51745 (64)	149250 (32)	C(c6)2	13713 (100)	7867 (86)	148796 (50)
C(b3)2	−25630 (57)	62451 (56)	146226 (30)	C(c7)2	19900 (107)	10039 (94)	152446 (70)
C(b4)2	−18925 (46)	63882 (43)	140135 (24)	C(m3)2	−627 (64)	35474 (54)	146120 (29)
C(b5)2	−37287 (64)	71477 (61)	148457 (35)	N(4)2	17610 (28)	50711 (26)	125545 (14)
C(b6)2	−21305 (84)	47094 (82)	156814 (43)	C(d1)2	28303 (36)	41330 (34)	125344 (19)
C(b7)2	−29686 (101)	43075 (97)	157014 (68)	C(d2)2	36977 (36)	43898 (37)	120748 (20)
C(m2)2	−22407 (41)	73516 (40)	135503 (25)	C(d3)2	31665 (38)	55097 (38)	118062 (20)
N(3)2	12506 (33)	36083 (30)	136456 (16)	C(d4)2	19310 (35)	59311 (33)	120857 (18)
C(c1)2	8927 (53)	30537 (47)	142094 (26)	C(d5)2	38158 (44)	61651 (46)	113588 (25)
C(c2)2	17704 (62)	18769 (49)	143304 (31)	C(d6)2	49792 (39)	35912 (43)	119555 (23)
C(c3)2	26293 (50)	17330 (41)	138614 (25)	C(d7)2	57560 (49)	36855 (56)	123992 (31)
C(c4)2	23334 (40)	28188 (36)	134333 (21)	C(m4)2	30546 (37)	30706 (35)	129196 (20)

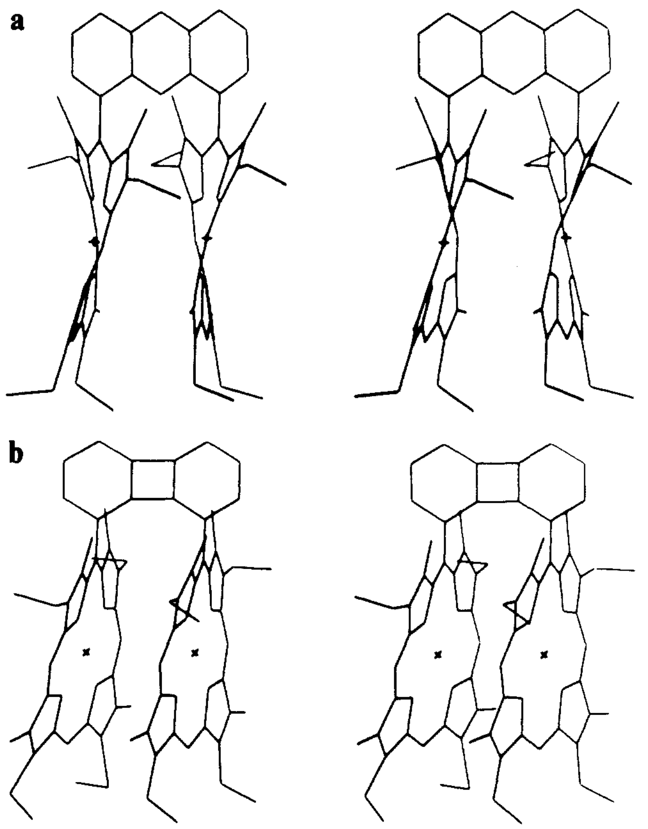

Figure 4. Perspective stereoview of DP-A (a) and DP-B (b).

Table III. Limiting Methyl–Connector Group Contacts

DP-A	Å	DP-B	Å
C(10)–C(d5)1	3.00	C(9)–C(a5)1	2.95
C(10)–C(a5)1	2.99	C(9)–C(d5)1	2.98
C(14)–C(a5)2	2.97	C(12)–C(d5)2	2.94
C(14)–C(d5)2	2.97	C(12)–C(a5)2	2.96
C(11)–C(a5)1	3.14	C(1)–C(a5)2	3.13
C(9)–C(d5)1	3.20	C(11)–C(d5)2	3.06
C(13)–C(d5)2	3.20	C(8)–C(d5)1	3.14
C(1)–C(a5)2	3.17	C(10)–C(a5)1	3.15

contact probably because of ruffled rings.[8] Although the approximate symmetry (D_{2d}) of the ruffling of DP-A is the same as that of Cu_2 (FTF6-3, 2-NH diamide), the ruffling of DP-A is about twice the magnitude with pyrroles tilted up–down about the C(1)–C(4) direction alternately above and below the mean plane of the porphyrin rings. Thus, the symmetry and exact nature of the buckling might also complicate and contribute to restricting the degree of slip. The structure determination of a Cu(II) anthracene bridged structure, which should be more planar than that of the Ni(II), or a structure with the crucial methyls absent could resolve some of these alternatives. Clearly, however, the actual situation will be at best complicated because of the number of factors competing with each other and their relative importance and extent of participation.

Another possibility to account for the slippage is that it could be intrinsic to stacked porphyrins and that the connecting structure dominates and limits the lateral shift.[13] This could be the case with DP-A and DP-B where the potential maximum porphyrin separation of DP-B (3.80 Å compared to 4.96 Å) and its slip (1.60 Å vs. 2.40 Å) is actually less. However, it would seem that the influence of the pillaring group in this case is only indirect and that the limitation in the slip derives from the onset of repulsive interactions which are associated with the porphyrin rings. Once again, this alternative can be differentiated through a structure determination of an anthracene-bridged structure with porphyrin rings that are more nearly planar. The slip angle should increase, and the interplanar separation should approach 3.5 Å.

Except for the configurations of the substituent ethyl groups, the DP-A and DP-B molecules exhibit an approximate twofold symmetry element which passes through the center of the aromatic bridging groups and between the porphyrin rings. The methyls of the ethyl groups of porphyrin ring 2 of DP-A are oriented away from the interplanar space of the molecule; the same occurs with ring 1 of DP-B. The substituents of the two deviate from the approximate symmetry in slightly different ways: in DP-A, C(d7)1 and C(b7)1 are oriented toward the interplanar space while only C(b7)2 does so in DP-B (Figure 4). These apparent symmetry departures are probably due to van der Waals interactions of the ethyl groups. Although abnormally short contacts are not generated as a result, it appears that more contacts are developed with C(b7)1, which fits snugly between pyrrole rings b2 and c2 in DP-A, while in DP-B, C(b6)2–C(b7)2 is close and parallel to C(b6)1–C(b7)1. However, in this case the source of the deviation appears to be repulsive since C(b6)2 makes a close 3.46 Å contact with N(3)2 of another molecule; if the ethyl group were oriented in the opposite direction, C(b7)2 would come within 2.0 Å of the adjacent molecule. The approximate symmetry of the ruffling shown by the porphyrin rings [Figures 2 (b,c) and 3 (b,c)] even conforms roughly to the twofold symmetry. This can be seen more clearly from Figure 5 which shows the alternating tilt of the pyrrole rings about C(1)–C(4) tending toward a tetrahedral buckling. The out-of-plane deviations of DP-A go up to ±0.75 Å while those of the Cu(II) complex are considerably smaller at about ±0.4 Å (Table II, supplementary material). In both cases the effect of the pillaring group on the lack of planarity can be seen by the much larger tilt of pyrrole rings (a) and (d) (Figure 5). The interplanar angle between the least-squares planes of the porphyrins is 3.9° in DP-A and 1.7° in DP-B. Lastly, the pyrrole rings of DP-B are planar within the error of their determination (±0.01 Å) as are the outer pyrroles of DP-A; the inner pyrroles of DP-A show a greater fluctuation (±0.04 Å).

(ii) **Primary Structure.** (a) **Porphyrins.** The pyrrole groups of DP-A and DP-B closest to the aromatic connectors have a slightly but significantly different geometry from the outer pyrroles. Thus, they approximate a C_{2v} symmetry arrangement. However, the structures of these two classes of pyrroles are sufficiently similar in the individual porphyrin rings so that they can be fourfold averaged in both molecules (Figure 6).[16] Fur-

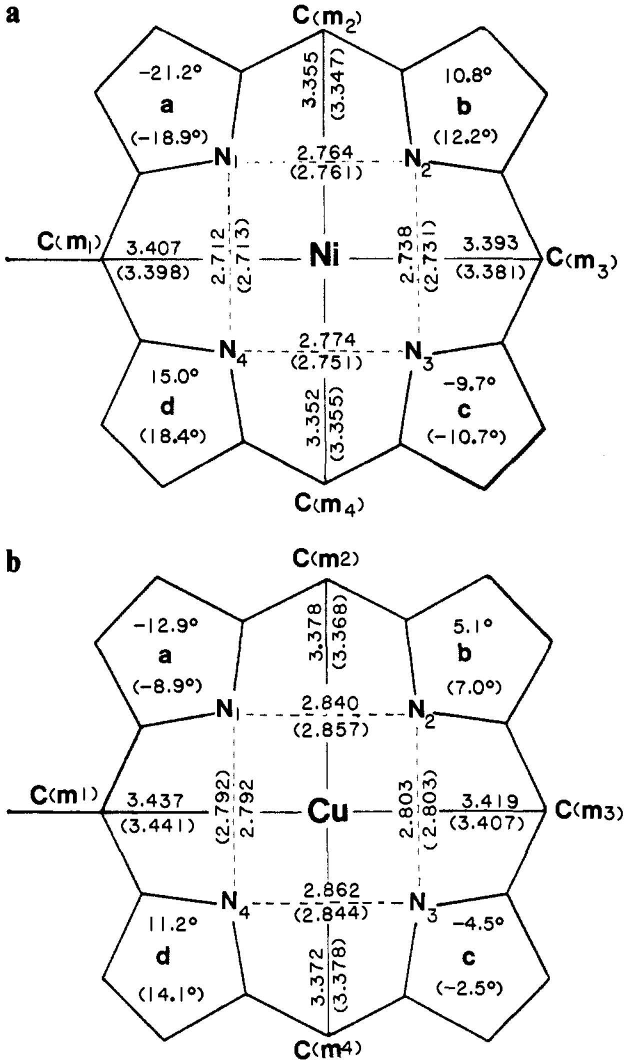

Figure 5. Out-of-plane tilt of pyrrole rings of DP-A (a) and DP-B (b) with respect to best plane of nitrogen atoms and geometry of inner core and methine bridges. Tilt angles in degrees approximately perpendicular to C(1)–C(4); ring 2 in parentheses; esd of DP-A is 0.004 Å; esd of DP-B is 0.007 Å.

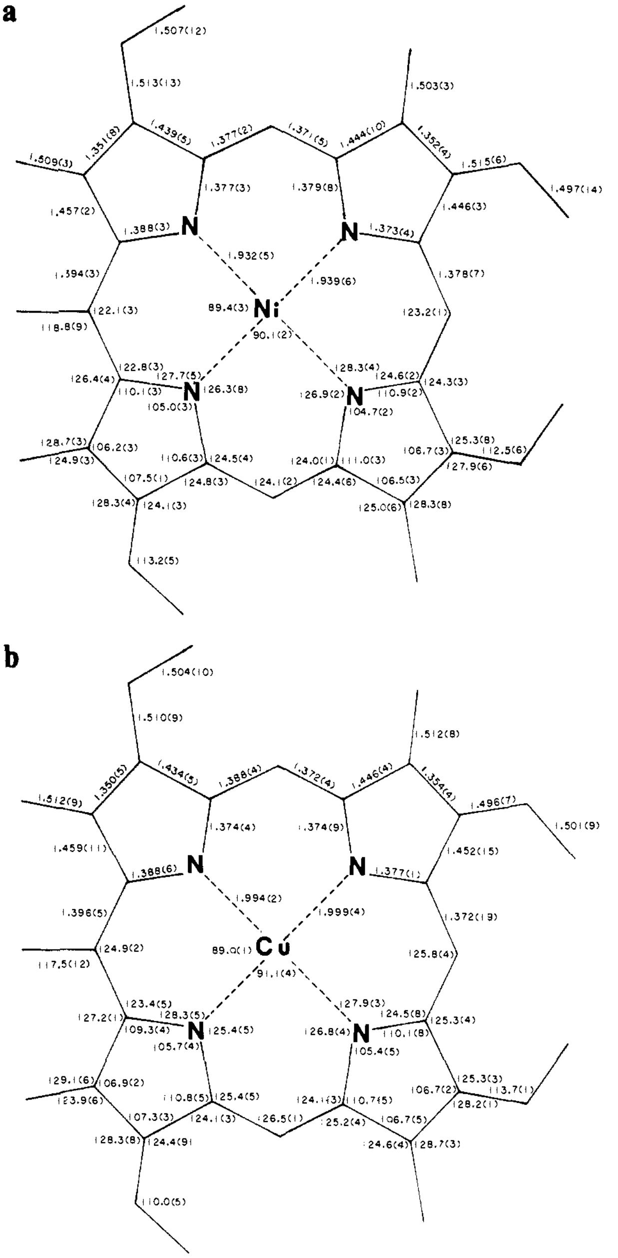

Figure 6. Average bond lengths and bond angles of DP-A (a) and DP-B (b). Inner and outer pyrroles of porphyrins averaged separately; distances (Å), angles (deg); esd from average in parentheses.

thermore, a comparison of the pyrrole classes in the two molecules shows that for practical purposes they can be considered identical and that the principal deviations between the two appear to be a consequence of the connector groups. This can be seen best from the smaller bond angles of N–C(4)–C(3) and N–C(4)–C(m1) with respect to their corresponding mates and noting that the outer pyrrole groups are symmetrical. The decrease in the angles appears to be due to the repulsion of the inner methyl groups by the aromatic connector: C(4)–C(3)–C(5) is about 3.7° greater in DP-A and 4.5° in DP-B while the corresponding angles around C(3) of the outer pyrroles show opposite deviations (repulsion between methyl–ethyl, Figure 6). The former repulsion also causes 2.0° increases in C(m1)–C(4)–C(3). Another manifestation of the effect might be the increase of the C(m1)–C(4) bond length to about 1.395 Å.

As in other metalloporphyrins,[7,8,17-21] the Ni–N distances of DP-A of 1.93 Å are significantly smaller than their Cu(II) counterpart, which is 2.00 Å in DP-B. Both are significantly less than the Ct–N distance of 2.05 Å of the free base so that the contraction of the central core leads to nonplanarity of the porphyrin rings.[22] However, both metals lie in the plane of the nitrogen atoms, and the coordination of the metals is square. The pyrrole nitrogens of DP-B are somewhat more coplanar (±0.06 Å) than those of DP-A (±0.12 Å) with similar effects pervading the porphyrin rings. The small Ni–N distance of 1.93 Å in NiOEP leads to ±0.25-Å deviations from planarity[19] so that more than half of the buckling of DP-A (Table IIa, supplementary material) can be considered to be due to close methyl–connector contacts and their consequences. This is also consistent with only a small contribution to the nonplanarity from the Cu(II) ion in DP-B (Table IIIb, supplementary material) so that here the principal source of the porphyrin ruffling is the result of close pillar contacts.

The central core region defined by the nitrogens and that by the methine carbon atoms both deviate significantly from a square (Figure 5): the N–N and methine–methine separations are both

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(16) All the individual distances and angles are listed in Table III (supplementary material).

(17) Fleischer, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 146–148.

(18) Hamor, T. A.; Caughey, W. S.; Hoard, J. L. *J. Am. Chem. Soc.* **1965**, *87*, 2305–2321.

(19) Meyer, E. F., Jr. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 2162–2167.

(20) Fleischer, E. B.; Miller, C. K.; Webb, L. E. *J. Am. Chem. Soc.* **1964**, *86*, 2342–2347.

(21) Moustakali, I.; Tulinsky, A. *J. Am. Chem. Soc.* **1973**, *95*, 6811–6815.

(22) Hoard, J. L. In "Structural Chemistry and Molecular Biology"; Rich, A., Davidson, N., Eds.; W. H. Freeman and Co.: San Francisco 1968; 572–593.

elongated along the pillar connector bond direction. The bond angles between the nitrogen atoms are 90.0 ± 0.5°, so that the distortion in both molecules is rectangular. This is not the case with the methine atoms which show a significant angular contraction along the connector direction (≈1.2°) and a slight increase at right angles to it (≈0.7°) leading to an arrangement based on a rectangular parallelogram. Since Cu(II) *n*-propylporphine does not show such deviations,[21] this small distortion must also be an effect of the connector groups.

(b) **Anthracene.** The bonds from the porphyrin rings to the anthracene pillar in DP-A are about 1.49 Å and comparable to those of tetraphenylporphyrins,[20,23] indicating some π overlap even though the two rings are not coplanar. The geometry of the anthracene molecule closely approximates *mmm* symmetry (Figure 7a). The only significant departures from the symmetry are the bond angles involving the connector atoms of anthracene. It will be seen that these are about 1.2° smaller than their counterparts, suggesting that they are drawn toward the porphyrin moieties and are compatible with the small increases in the C(10)–C(11) and C(13)–C(14) bond distances. Comparing the angles of DP-A with those determined for the anthracene molecule at 290 K[24] shows that the angles of C(3) to C(7) have expanded. Except for this anomoly, there is a fairly quantitative agreement between the structure of anthracene and the aromatic pillar so that the angular discrepencies appear to be significant. However, the full significance of this observation is presently not clear. A discrepancy also seems to occur between the C(4)–(13)–C(14) and C(3)–C-(4)–(13) angles of the connector but this might simply be an error (Figure 7). Lastly, the anthracene pillar is coplanar within the error of its determination (±0.01 Å) with only small departures; the largest is shown by the connecting methine carbon atoms of the porphyrins (≈0.05–0.08 Å).

(c) **Biphenylene.** The biphenylene pillar connector bonds of DP-B also show π overlap, the group approximates *mmm* symmetry (Figure 7b), but not as well as the anthracene connector, and the pillar compares quantitatively with the structure determined for biphenylene.[25] The only possibly significant difference between biphenylene and the pillar in DP-B is that in the latter the connecting square between the phenyl rings is slightly distorted to a parallelogram. A severe distortion also occurs in two of the bond angles of the connector atoms: C(m1)1–C(9)–C(8) increases by about 2.5° which would cause the bonds to the porphyrin rings not to be quite parallel, but since C(m1)2–C(12)–C(11) also increases similarly, the nonparallel effect is negligible. In the case of the anthracene pillar, distortions also occur at these atoms but in an opposite sense, directing the connector bonds toward each other (Figure 7a). The differences in the behavior at these connector positions of DP-A and DP-B are probably due to the intrinsic difference in the distances between the atoms in the free molecules which are 4.96 and 3.80 Å, respectively. Finally, the biphenylene pillar is also coplanar within the error of its determination (±0.01 Å).

(iii) **Disordered Ethyl Groups.** In both molecules, there exists one poorly ordered ethyl group. In DP-A the disordered ethyl group is on pyrrole (a) of ring 2. This is apparent from bond lengths [C(a2)2-C(a6)2 = 1.755 (9) Å and C(a6)2-C(a7)2 = 1.287 (14) Å] and the bond angle [C(a2)2-C(a6)2-C(a7)2 = 90.9 (3)°]. Inspection of the electron density in this region suggested that C(a6)2 may occupy two positions. However, attempts to model and refine atom C(a6)2 at two sites with occupancy of 0.5 and isotropic or anisotropic temperature factors failed and resulted in both sites merging to form one position. It may be also noted that no second position for C(a7)2 could be found. Therefore, the final refinement of these two atoms was simply carried out in a normal fashion with anisotropic temperature factors.

A similar disorder was also noted in DP-B around atom C(c6)2. The corresponding bond lengths and angle are the following: C(c2)2–C(c6)2 = 1.820 (18) Å, C(c6)2–C(c7)2 = 1.330 (19) Å, and C(c2)2–C(c6)2–C(c7)2 = 79.4 (6)°, respectively. Once again the nature of the disorder could not be resolved by modeling.

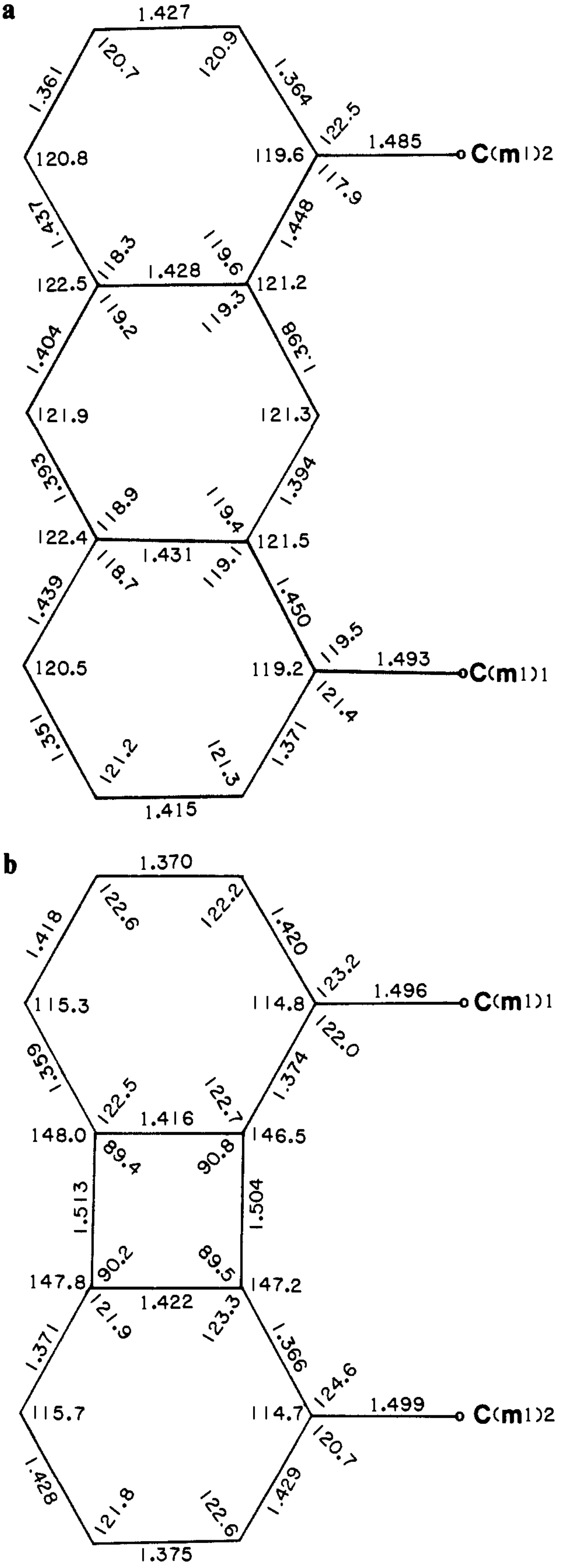

Figure 7. Bond lengths and bond angles of anthracene connector of DP-A (a) and biphenylene connector of DP-B (b), esd's range from 0.003–0.005 Å and 0.2–0.4° in DP-A and 0.008–0.010 Å and 0.4–0.6° in DP-B.

(iv) **Crystal Packing.** The three-dimensional packing of the two porphyrin systems is different (Figures 8 and 9). In DP-A,

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(23) Silvers, S. J.; Tulinsky, A. *J. Am. Chem. Soc.* **1967**, 3331–3337.
(24) Mason, R. *Acta Crystallogr.* **1964**, *17*, 547–555.
(25) Fawcett, J. K.; Trotter, J. *Acta Crystallogr.* **1966**, *20*, 87–93.

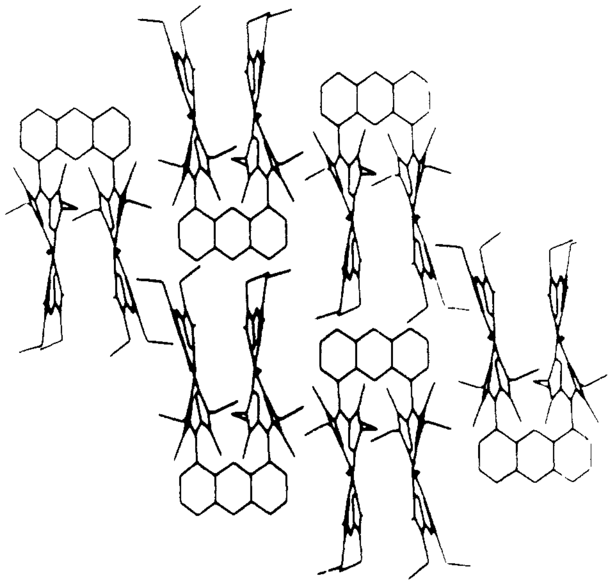

Figure 8. Crystal packing of DP-A molecules viewed down [110] direction.

centrosymmetric pairs stack on one another, with the anthracene ring located over the central core of the other molecule (Figure 8). The normals to the porphyrin planes of these pairs form columns running approximately along the [101] face diagonal of the unit cell so that the environment of each porphyrin moiety is very similar. For DP-B, the environment of each porphyrin is different: a pair of biphenylene moieties from symmetry related molecules are above methine carbons C(m2)1 and C(m4)1 and pyrroles (b)2 and (c)2 overlap the same pyrroles from another molecule (Figure 9). Therefore, ring 1 has two biphenylene moieties overlapping above it, while ring 2 only has a porphyrin ring below it. Once again, the molecules pack to form columns but the columns run approximately along the body diagonal.

Concluding Remarks

The difference in metal-to-metal distance between the two diporphyins is noteworthy. Prior to our study of these two compounds it was thought that the metal–metal distance is the most crucial factor that dictates whether or not the cobalt dimer can serve as an effective 4-e electrocatalyst for dioxygen reduction. This is borne out by the fact that among the ten or so amide-chain linked diporphyrins that have been synthesized, only one compound with diametrical $CH_2CONHCH_2$ connecting straps has been shown to be active.[3,4,26] Increase or decrease in the number of methylene units or transposition of the individual constituents in the above chain would lead to near total loss of activity. This is not the case with DP-A and DP-B. As indicated above, the metal separations in the two dimers differ by 0.76 Å yet it does not seem to have much of an effect on their electrocatalytic performance. Although the use of such a distance obtained from noncobalt complexes to discuss the behavior of the cobalt catalyst on a graphite surface is admittedly not direct, on the other hand, there is no evidence to prove that other metallodiporphyrins would adopt a grossly different structural configuration in another environment. In fact, our recent study on the EPR spectroscopy[13] of six dicopper diporphyrin complexes in frozen solution showed that both the metal–metal separation and ring-to-ring distance obtained by the EPR method agree well to, although systematically higher than (but small compared to the above 0.76 Å difference), three reported crystallographic structures. The present study, again, seems to reiterate the conclusion about the lack of a clear connection between inter-ring separation and a preference for 4-e vs. 2-e O_2 reduction pathways. Further structural studies as well as the synthesis of other diporphyrins are obviously needed to clarify in more detail the structure–function relationship of this important class of catalysts.

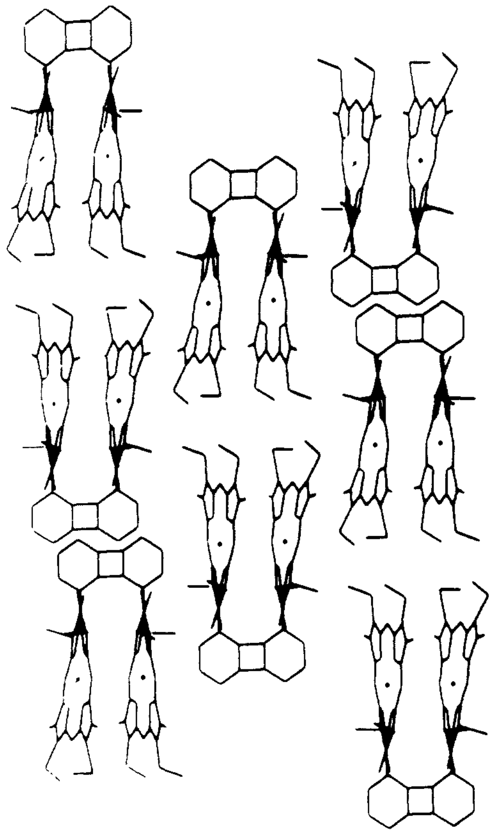

Figure 9. Crystal packing of DP-B molecules viewed down [110] direction.

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Supplementary Material Available: Anisotropic thermal parameters, out-of-plane distances, bond lengths, and bond angles for DP-A and DP-B (12 pages). Ordering information is given on any current masthead page.

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[26] Collman, J. P.; Bencosme, C. S.; Barnes, C. E.; Miller, B. D. *J. Am. Chem. Soc.* **1983**, *105*, 2704–2709.