

Photoinduced Electron Transfer in Porphyrin-Quinone Cyclophanes, 8^[1]

Conformational Mobility and Crystal Structures of Porphyrin-Quinone Cyclophanes

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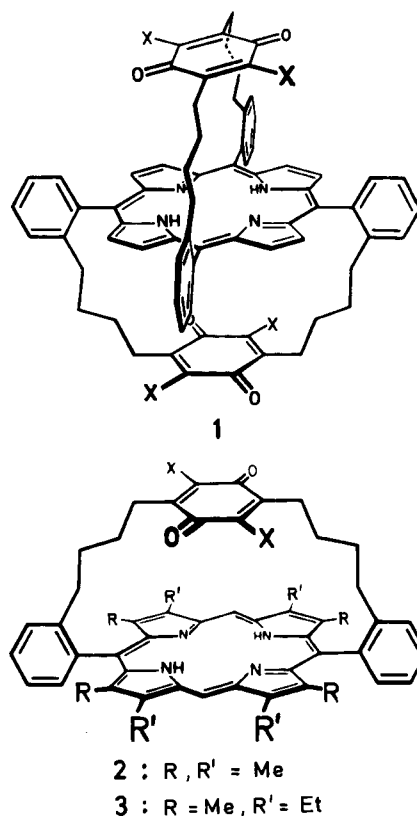
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In order to correlate photoinduced electron-transfer in porphyrin-quinone cyclophanes to specific molecular conformations, the internal mobility of single- and double-bridged porphyrin-quinone cyclophanes was studied by low-temperature ¹H-NMR measurements. The dynamic processes observed are discussed in terms of N-H/N tautomerisation, of the rotation of the rings in the bridges, and of a specific "swinging bridge" process back and forth between two equivalent unsymmetrical conformations with a tilted orientation of the porphyrin and quinone ring planes. For comparison with the conformational situation in solution the results of X-ray structure analyses

of **3** (**X** = **OMe**) and **6**, as representative examples of single-bridged quinone-porphyrin cyclophanes, and of the corresponding tetramethoxybenzene-bridged octamethylporphyrin cyclophane **4** (**X** = **OMe**) are reported and discussed. In contrast to the previously solved crystal structure of the quinone-porphyrin-quinone cyclophane **1** (**X** = **H**), all three X-ray structure analyses proved the existence of unsymmetrical, tilted-plane structures similar to those discussed as the stable conformations in the "swinging bridge" process.

In a series of preceding papers we reported on the syntheses of quinone-porphyrin-quinone cyclophanes **1** and of corresponding single-bridged quinone-porphyrin cyclophanes of type **2** and **3**^[1-3]. These intramolecular porphyrin-quinone systems were conceived to study the photoinduced electron transfer from the *S*₁ state of porphyrin to the quinone units since due to their rather well-defined and relatively rigid structural skeletons these vertically stacked porphyrin-quinone cyclophanes were expected to allow the controlled and selective variation of parameters on which electron transfer depends. For example, donor and acceptor strengths were modified by electron-withdrawing and electron-donating substituents^[2,3], and porphyrin-quinone distances were varied^[4] while keeping constant other parameters relevant to electron transfer. First results on electron-transfer rates obtained by short-time-resolved spectroscopy were recently published^[5,6]. For the interpretation of these data in terms of structure dependence of electron transfer, the mutual sterical orientations of the quinone and porphyrin units were to be determined as precisely as possible.

For **1** (**X** = **H**), the parent compound of the doubly quinone-bridged porphyrin cyclophanes, an X-ray analysis proved the presence of a highly symmetrical *S*₄ structure in the crystalline state: the quinone planes are parallel to each other and to the least-squares plane of the porphyrin unit, and the three ring-centers are exactly superimposed along the rotary inversion axis with center-to-center distances of 342 pm^[2,7]. ¹H-NMR data of **1** (**X** = **H**) were found to be well in agreement with this structure. On the basis of the close correspondence of ¹H-NMR spectra similar sterical



structures were assumed for the other members of the **1**-family, too^[3]. For single-bridged quinone-porphyrin cyclophanes of type **2** and **3** again the comparison of ¹H-NMR

spectra with **1** provided strong indications for the presence of structures basically analogous to that of **1** with regard to the porphyrin-quinone orientations.

Even for these cyclophanes with relatively rigid molecular structures, though, it remains questionable to apply conformational details derived from crystal structures to the conformations of individual molecules in solution. Furthermore, drawing conclusions on molecular conformations from NMR data may be misleading if conformational interconversions occur rapidly in relation to the time scale of NMR. These are especially critical points when dealing with the structure dependence of electron-transfer processes the rates of which are orders of magnitude higher than the rates of conformational processes.

In an attempt to gain better insight into the residual conformational mobility of these quinone-porphyrin cyclophanes, we report in this paper primarily on low-temperature $^1\text{H-NMR}$ measurements on representative examples of the quinone-porphyrin cyclophanes **1**, **2** and **3**. To complement these conformational studies the non-quinoid compounds of the series **4** and **5** containing the same carbon skeleton as **2** and **3**, resp., were included as well as the qui-

none-bridged tetraphenylporphyrin **6** and its non-quinoid analog **7**.

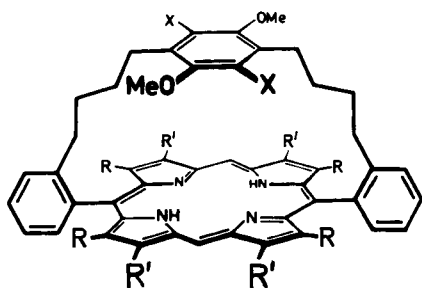
In the second part of this paper X-ray analyses of single-bridged porphyrin cyclophanes **3** ($\text{X} = \text{OMe}$) and **4** ($\text{X} = \text{OMe}$) are reported as well as the structure analysis of **6**. In a separate paper^[8] we describe the syntheses of porphyrin cyclophanes dealt with in these studies as far as they have not yet been reported in the preceding papers^[2,3].

Low-Temperature $^1\text{H-NMR}$ Studies on Intramolecular Dynamic Processes in Quinone-Porphyrin Cyclophanes

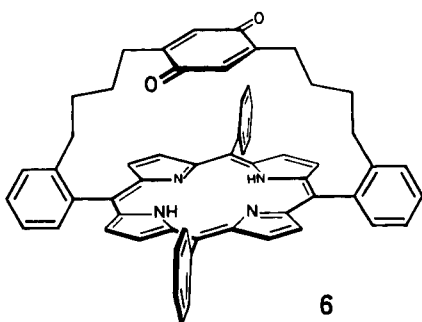
In contrast to more flexible quinone-porphyrin systems studied recently in other groups^[9], for the cyclophanes of types **1**, **2** and **3** due to the particular bridged structures the internal mobility was expected to be limited to only a few rather well-defined processes. A first fast dynamic process is, of course, the N-H/N tautomerism which is ubiquitous to porphyrins (except diprotonated or metallated species). A second obvious process is the rotation of the quinoid (or aromatic) rings in the central part of the bridges around the axis through the bridgehead atoms; this process should be strongly dependent on the sterical requirements of the substituents on these central rings. In addition to these evident processes the separation and identification of which are reported below, at rather low temperatures (coalescence temperatures $T_c \approx 140\text{--}190\text{ K}$) $^1\text{H-NMR}$ measurements revealed that there occurs a third conformational interconversion which originally was not anticipated. This process is specific to the porphyrin cyclophanes in question, and it certainly has to be considered in relation to photoinduced electron-transfer reactions.

N-H/N Tautomerism: For the otherwise unsubstituted 5,10,15,20-tetraphenylporphyrin a splitting of the signal of the 2,3,7,8,12,13,17,18-protons (" β -protons") was observed with coalescence temperatures of 220–225 K (100 MHz); for the underlying exchange process free activation enthalpies $\Delta G_{T_c}^\ddagger$ of 11.1–11.4 kcal/mol were estimated from the $\Delta\nu$ values^[10]. By the effect of N-deuteration on the coalescence temperature and exchange barrier this process was assigned to N-H/N tautomerism. Own measurements (CD_2Cl_2 , 500 MHz) yielded $T_c = 238\text{ K}$, $\Delta\nu = 103\text{ Hz}$ (at 223 K), and $\Delta G_{238\text{K}}^\ddagger = 11.3\text{ kcal/mol}$ in agreement with the earlier results. For these and the following data the approximated experimental errors are $\pm 5\text{ K}$ for T_c and $\pm 0.3\text{ kcal/mol}$ for $\Delta G_{T_c}^\ddagger$.

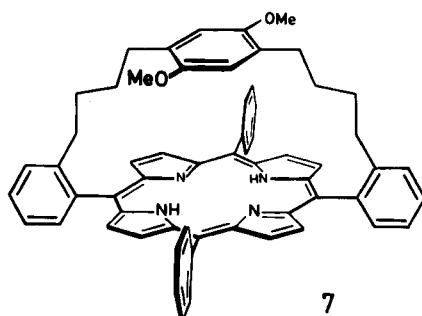
The doubly-bridged quinone-porphyrine-quinone cyclophane **1** ($\text{X} = \text{H}$) under the same conditions shows a coalescence of the β -proton signals at $T_c = 250\text{ K}$; with $\Delta\nu = 122\text{ Hz}$ (at 204 K) $\Delta G_{250\text{K}}^\ddagger = 11.8\text{ kcal/mol}$ results as the barrier. The effect of N-deuteration [$T_c = 292\text{ K}$, $\Delta\nu = 125\text{ Hz}$ (at 204 K), $\Delta G_{292\text{K}}^\ddagger = 13.8\text{ kcal/mol}$] clearly demonstrates that this dynamic process is due to N-H/N tautomerism. For **1** ($\text{X} = \text{Me}$) and **1** ($\text{X} = \text{OMe}$) closely similar values were obtained [$T_c = 250\text{ K}$, $\Delta\nu = 122\text{ Hz}$ (at 213 K), $\Delta G_{250\text{K}}^\ddagger = 11.8\text{ kcal/mol}$, and $T_c = 250\text{ K}$, $\Delta\nu = 115\text{ Hz}$ (at 224 K), $\Delta G_{250\text{K}}^\ddagger = 11.8\text{ kcal/mol}$, respectively]. The independence of the interconversion of the N-H/N tautomer-



4 : $\text{R}, \text{R}' = \text{Me}$
5 : $\text{R} = \text{Me}, \text{R}' = \text{Et}$



6



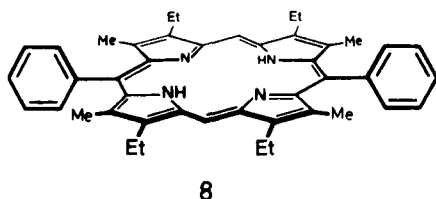
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isation of the structure of the cyclophane bridges is also demonstrated by the non-quinoid cyclophane with the carbon-skeleton of **1** ($X = H$) containing two dimethoxybenzene rings in place of the quinone units^[2]: $T_c = 250$ K, $\Delta\nu = 107$ Hz (at 190 K), $\Delta G_{250K}^\ddagger = 11.8$ kcal/mol.

For the single-bridged porphyrin-quinone cyclophane **6**, due to the lower molecular symmetry, for the β -protons of the five-membered rings, two doublets ($\delta = 8.69$ and 8.80 , $^3J = 4.7$ Hz) are observed at room temperature each of which on cooling is split further [$T_c = 256$ K; $\Delta\nu = 99$ and 121 Hz (at 201 K), respectively] yielding $\Delta G_{256K}^\ddagger = 12.2$ and 12.1 kcal/mol. Again, measurements on the *N*-deuterated **6** were carried out the results of which undoubtedly prove the observed process being due to *N*-H/*N* tautomerism [$T_c = 296$ K, $\Delta\nu = 100$ and 124 Hz (at 185 K), $\Delta G_{296K}^\ddagger = 14.1$ and 14.0 kcal/mol]. For the non-quinoid system **7** with the corresponding cyclophane structure analogous results were obtained [$T_c = 250$ K, $\Delta\nu = 107$ and 119 Hz (at 212 K), $\Delta G_{250K}^\ddagger = 11.8$ kcal/mol]. Increasing the sterical requirement by introducing two bromo substituents into **7** did not change the situation [$T_c = 256$ K, $\Delta\nu = 107$ and 115 Hz (at 204 K), $\Delta G_{256K}^\ddagger = 12.1$ kcal/mol]; *N*-deuteration in this case increased the coalescence temperature to 290 K and led, on the basis of $\Delta\nu = 108$ and 111 Hz (at 237 K), respectively, to $\Delta G_{290K}^\ddagger = 13.8$ kcal/mol.

Summarizing, it can be stated that the *N*-H/*N* tautomerism of the porphyrins is only scarcely influenced by the incorporation of the porphyrin units into cyclophane skeletons. As a result of the deuteration experiments the *N*-H/*N* tautomerism can unambiguously be distinguished from the rotation of the central rings in the cyclophane bridges which, in principle, would have a corresponding effect with regard to the symmetry-change involved.

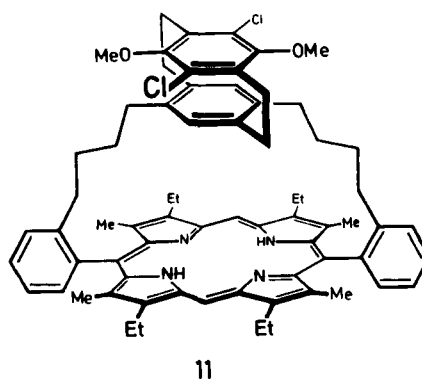
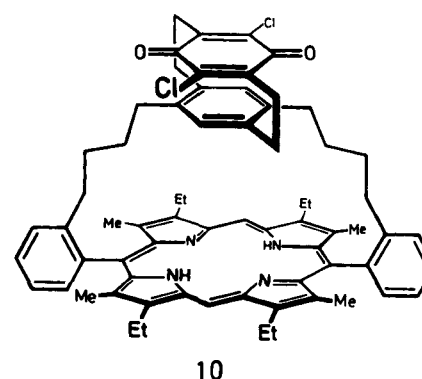
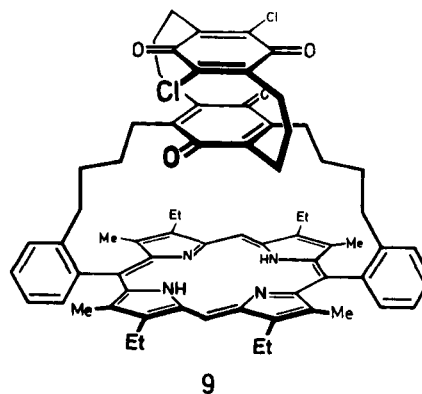
For completely alkylated porphyrins like **2** and **3** the freezing-in of the tautomerisation cannot be determined since obviously this process affects the periphery of the porphyrins not sufficiently in order to be measurable by ¹H-NMR of the protons of β -alkyl groups. This assumption is supported by the observation that, for example, the completely β -alkylated 5,15-diphenylporphyrin **8** does not show any splitting of the methyl singlets down to 175 K although at this low temperature the tautomerisation is certainly frozen-in.



Ring Rotation in the Cyclophane Bridges: Low-temperature ¹H-NMR (CD₂Cl₂, 500 MHz) of the dimethoxy-*p*-benzoquinone-bridged octamethylporphyrin (**2**, $X = OMe$) led to a splitting of the two β -methyl singlets at $\delta = 2.45$ (3,7,13,17-CH₃) and 3.49 (2,8,12,18-CH₃) with coalescence temperature $T_c = 192$ K. On the basis of $\Delta\nu = 45$ Hz for 3-Me and of $\Delta\nu = 40$ Hz for 2-Me (at 184 K), $\Delta G_{192K}^\ddagger = 9.3$ and 9.4 kcal/mol, resp., were obtained. The temperature

dependence of the two types of methyl signals suggests an identical process the slowing down of which results in reducing the apparent molecular symmetry C_{2v} to C_2 . That the observed splitting of the methyl signals is definitely not due to *N*-H/*N* tautomerism was shown by *N*-deuteration which did not change T_c and $\Delta G_{T_c}^\ddagger$. Thus, the explanation for the temperature dependence observed is the freezing of the rotation of the quinone ring around the axis through the bridgeheads. In the frozen-in conformation the transannular anisotropic effect especially of the carbonyl groups results in making the 3-methyl as well as the 4-methyl groups two by two unequivalent.

As expected, the ring rotation is dependent on the sterical requirement of the substituents on the central ring. Although for **2** with $X = H$, Me, Cl and even Br the ¹H-NMR measurements down to 150 K (in 1,1-dichloroethylene, 500 MHz) did not result in a splitting of the methyl signals, the dicyanodimethoxybenzene-bridged system **4** ($X = CN$) shows already at room temperature two signals each for the 3- and 2-methyl groups ([D₂]1,1,2,2-tetrachloroethane, 360 MHz).



Coalescences occur at $T_c = 339$ K ($\Delta\nu = 39$ Hz at 253 K) for 3-Me and at $T_c = 317$ K ($\Delta\nu = 13$ Hz at 253 K) for 2-Me from which $\Delta G_{339\text{K}}^\ddagger = 16.9$ kcal/mol and $\Delta G_{317\text{K}}^\ddagger = 16.5$ kcal/mol, resp., were estimated.

For cyclophane-bridged porphyrins like **9**, which recently were synthesized as especially interesting systems for photoinduced electron transfer^[11,12], the methyl singlets remain split at higher temperatures. Here the sterical situation understandably does not at all allow the ring rotation process to occur. Of course, this complete hindrance of the rotation process has to be taken for granted also for systems like **10** and **11**^[11] where, however, due to the lack of substituents with anisotropic effects (quinone carbonyl, cyano groups) in the central ring of the triad no splitting of the porphyrin-methyl groups in ¹H-NMR measurements is observed.

The comparison of quinone-bridged octamethylporphyrin cyclophanes **2** with the corresponding tetraethyltetramethylporphyrin cyclophanes **3** shows that the ring-rotation in the bridges is only very slightly more hindered when replacing methyl groups on the porphyrin system by ethyl groups. For example, for **3(X = OMe)** a splitting of the methyl singlets is observed on cooling at 201 K; with $\Delta\nu = 40$ Hz (at 183 K) $\Delta G_{201\text{K}}^\ddagger = 9.8$ kcal/mol is obtained which is approximately 0.4 kcal/mol higher than the $\Delta G_{192\text{K}}^\ddagger$ -value of the corresponding **2(X = OMe)** mentioned above.

“Swinging Bridge” Process: When the temperature limit of ¹H-NMR measurements was lowered further to about 140 K (1,1-dichloroethylene or CS₂/CFCl₃, ≈ 1:1, 500 MHz) a third conformational process for porphyrin cyclophanes was observed. Since N–H/N tautomerisation was definitely excluded by N-deuteration (see above), and since this process is also observed in systems where ring rotation due to steric hindrance is not possible at all, there must be a further mode of internal motion which obviously in this group of porphyrin cyclophanes occurs quite generally and with rather small $\Delta G_{T_c}^\ddagger$ values. The conformational changes involved lead to a characteristic splitting of the methine protons on the porphyrin system (10,20-H) and of the N–H protons. In addition, the pattern of the signals of the methylene chains shows some temperature-dependent changes. The most reasonable explanation for this observation is a swinging back and forth of the cyclophane bridge between two equivalent unsymmetrical conformations. In contrast to the crystal structure analysis of **1(X = H)**, in these conformations the planes of the porphyrin and the six-membered rings in the bridges are no longer parallel but tilted against each other, and the ring centers are not vertically superimposed.

For this process it is typical that it also should be observed for the porphyrin cyclophane **4(X = OMe)** with the tetramethoxybenzene unit in the bridge for which neither the N–H/N tautomerism nor a ring-rotation would result in a temperature-dependent splitting of ¹H-NMR signals. For this compound a splitting of the singlets for the methine protons 10,20-H and of the NH protons was observed with coalescence temperatures $T_c = 153$ and 160 K (1,1-dichloroethylene, 500 MHz); with $\Delta\nu = 24$ and 147 Hz (at 139 K) respectively, free activation enthalpies $\Delta G_{153\text{K}}^\ddagger = 7.5$

kcal/mol and $\Delta G_{160\text{K}}^\ddagger = 7.3$ kcal/mol were estimated. From these data it is concluded that the splittings of the signals of the methine and NH protons are due to the same process and can be explained on the basis of the above-mentioned “swinging bridge” motion. Such a process is expected to show the strongest influence on the methine and NH protons. Most likely this process must be coupled with some torsional motions in the methylene chains, thus explaining the complex changes (broadenings and splittings) observed for these protons, too.

Table 1. Coalescence temperature T_c (± 5 K), splitting $\Delta\nu$ [Hz] and estimated free enthalpies of activation $\Delta G_{T_c}^\ddagger$ [kcal/mol] (a: 1,1-dichloroethylene; b: carbon disulfide/trichlorofluoromethane, ≈ 1:1)

Compound	Methine protons			NH protons			Solvent
	T_c	$\Delta\nu$	$\Delta G_{T_c}^\ddagger$	T_c	$\Delta\nu$	$G_{T_c}^\ddagger$	
2(X = OMe) ^[*]	143	≥16	≤7.1	148	≥32	≤7.2	a
2(X = Br)	153	13	7.7	163	90	7.6	b
4(X = OMe)	153	24	7.5	160	147	7.3	a
4(X = CN)	184	135	8.5	184	139	8.5	b
10	170	75	8.0	170	71	8.1	b
11	186	136	8.6	181	84	8.5	a

[*] Because of the low coalescence temperatures near the freezing point of the solvent, the obtained $\Delta G_{T_c}^\ddagger$ -values for this compound have to be regarded as an approximation.

For the dimethoxy-*p*-benzoquinone-bridged porphyrin **2(X = OMe)** and the corresponding dibromo-*p*-benzoquinone compound **2(X = Br)** very similar temperature dependences were observed. Coalescence data and $\Delta G_{T_c}^\ddagger$ values derived therefrom are listed in Table 1 together with those of some other examples. Of special interest with regard to the conformational process involved are the data for those porphyrin cyclophanes for which due to strong sterical hindrance the ring rotation occurs either only at rather high temperature like for **4(X = CN)** or not at all like for **10** and **11**. The experimental finding is that in spite of the very different sterical structures of these compounds the $\Delta G_{T_c}^\ddagger$ values are all in the narrow range of 7.1–8.9 kcal/mol. This result strongly supports the “swinging bridge” process since for this motion the barriers are expected to be rather insensitive to the different sterical situations present in these porphyrin cyclophanes.

For the porphyrin cyclophanes **6** and **7**, due to the replacement of 10,20-H by space-filling phenyl groups, the “swinging bridge” motion might be expected to be sterically hindered. In fact, for the methylene-chain protons in low-temperature ¹H-NMR spectra new signals and broadenings appear indicating conformational processes which so far could not be as clearly assigned as the conformational interconversions dealt with above. For the doubly-bridged porphyrin cyclophanes of type **1**, too, the internal mobility with the exception of the N–H/N tautomerisation (see above) is not yet fully understood. Here the situation is complicated by the possibility of independent ring rotations in each of the bridges the freezing-in of which may result in two different diastereoisomers. In order to better understand the rather complex systems of different, but partially inter-

related conformational processes in these porphyrin cyclophanes further work including line-shape analyses of $^1\text{H-NMR}$ as well as molecular-dynamics calculations has been started.

Conclusions: From the results of temperature-dependent $^1\text{H-NMR}$ measurements completed so far, it became evident that the internal mobility of the porphyrin cyclophanes in spite of their rather tightly bridged vertical structures is more pronounced than originally expected. For the single-bridged porphyrin cyclophanes of type **2–5** it was possible to distinguish clearly between a) N-H/N tautomerisation, b) ring rotation in the cyclophane bridges and c) the “swinging bridge” process. For the structure dependence of photoinduced electron-transfer reactions the last-mentioned conformational interconversion is of special interest: this process implies that the conformations stable within the time scale of electron-transfer rates should not be those with par-

allel and mutually centered quinone and porphyrin rings but those with a tilted orientation of the ring planes and consequently with a smaller overlap between the π -systems involved. On the basis of quantum-chemical calculations it has recently been suggested that for the single-bridged porphyrin-cyclophanes of our series conformations with a tilted orientation of quinone and porphyrin planes are expected to be slightly more stable than the conformation with parallel planes^[13]. The experimental findings reported now on the basis of $^1\text{H-NMR}$ data confirm in principle these theoretical predictions. As a consequence of these results, the question arose how electron-transfer rates depend on tilted versus parallel orientations of porphyrin and quinone units. In an attempt to approach this question, porphyrin-quinone cyclophanes had to be synthesized in which due to *fourfold* bridging the porphyrin and quinone units should be forced more tightly into a parallel and centered orientation. Syn-

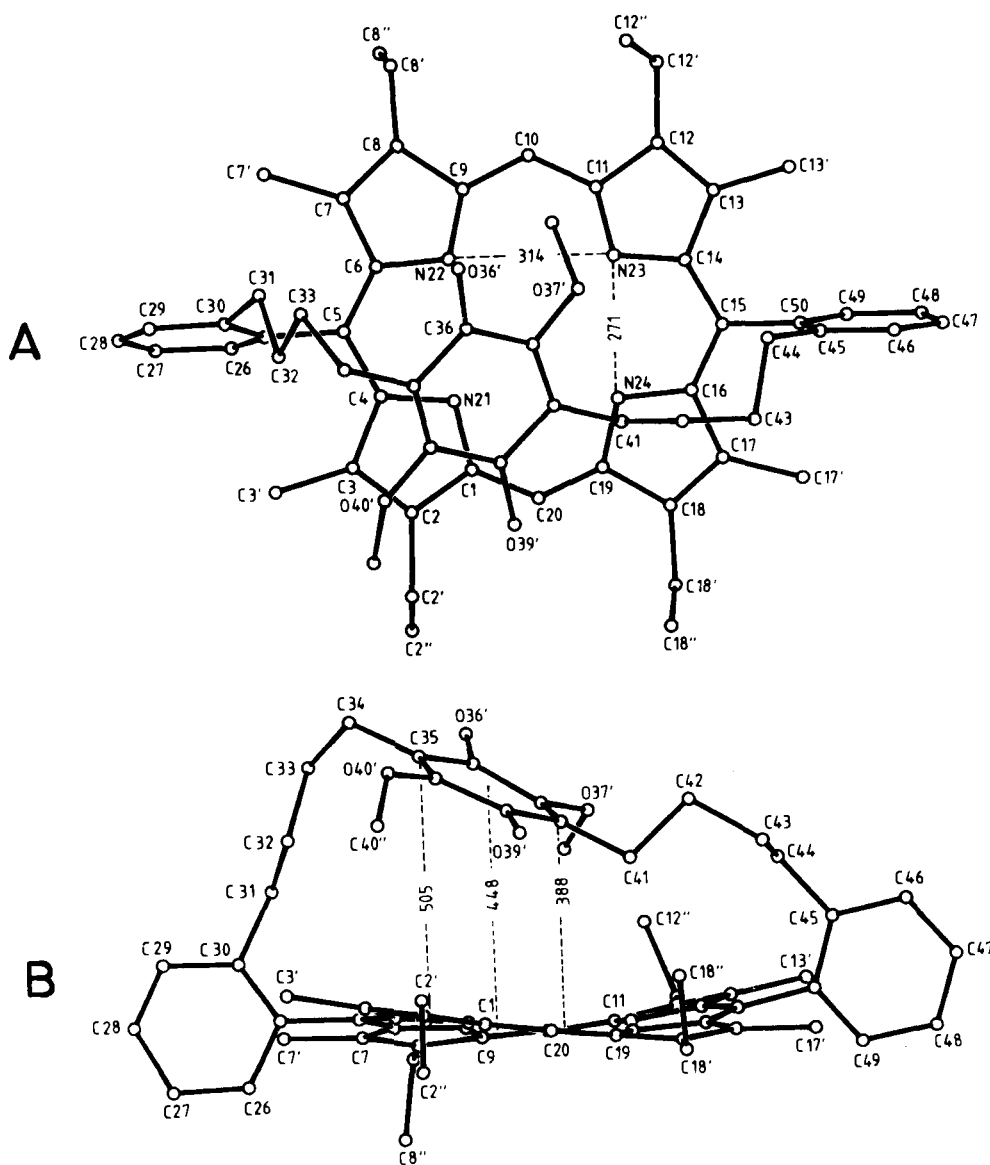


Figure 1. Molecular structure of **3**(X = OMe) in a top view onto the mean plane of the porphyrin (A) and in a side view along the C10...C20 axis (B)

theses and properties of such porphyrin cyclophanes with "bird-cage" structure will be reported separately^[14].

X-Ray Structure Analyses of Single-Bridged Porphyrin-Cyclophanes

The X-ray analysis of **1** ($X = H$) proved a highly symmetrical structure with parallel and centered quinone and porphyrin rings not unexpected on the basis of molecular models^[2,7]. Thus, and due to the lack of other X-ray structure analyses, we were prejudiced in favor of applying the structural elements of **1** ($X = H$) to other porphyrin cyclophanes with the same type and size of cyclophane bridges, including the single-bridged porphyrin cyclophanes of type **2–5**. The crystal structures now to be reported for three examples of these single-bridged porphyrin cyclophanes, however, demonstrate clearly that the porphyrin-quinone orientation in these systems is significantly different from that present in **1**. Although conformational features derived from crystal structures only very limitedly can be transferred to the molecules in solution, it seems quite clear that the structures of these single-bridged porphyrin cyclophanes re-

fect very well the conformational mobility determined by temperature-dependent ¹H-NMR for these compounds.

X-Ray Structure Analysis of 5,15-[3,6-Dimethoxy-p-benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzo)]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin [3(X = OMe)]: The molecular conformation obtained for **3** ($X = OMe$) differs strikingly from the C_2 -symmetry originally expected in view of the structure of **1**. The side and top views (Figure 1) show the quinone plane to be neither parallel nor centered to the porphyrin plane. The quinone unit instead is shifted away from the porphyrin center and is tilted by an angle of 26° with regard to the mean plane of the porphyrin. The vertical distance from the quinone center to the porphyrin plane with 448 pm is considerably longer than the interplanar quinone–porphyrin distance in **1**. In the perpendicular projection onto the porphyrin plane the center of the quinone unit is shifted against the center of the porphyrin system by 155 pm resulting in a center-to-center distance of 474 pm. The porphyrin nitrogens do not form a square like in **1** but a rectangle with N··N distances of 271 and 314 pm which is the result of a widening of the angles C9–C10–

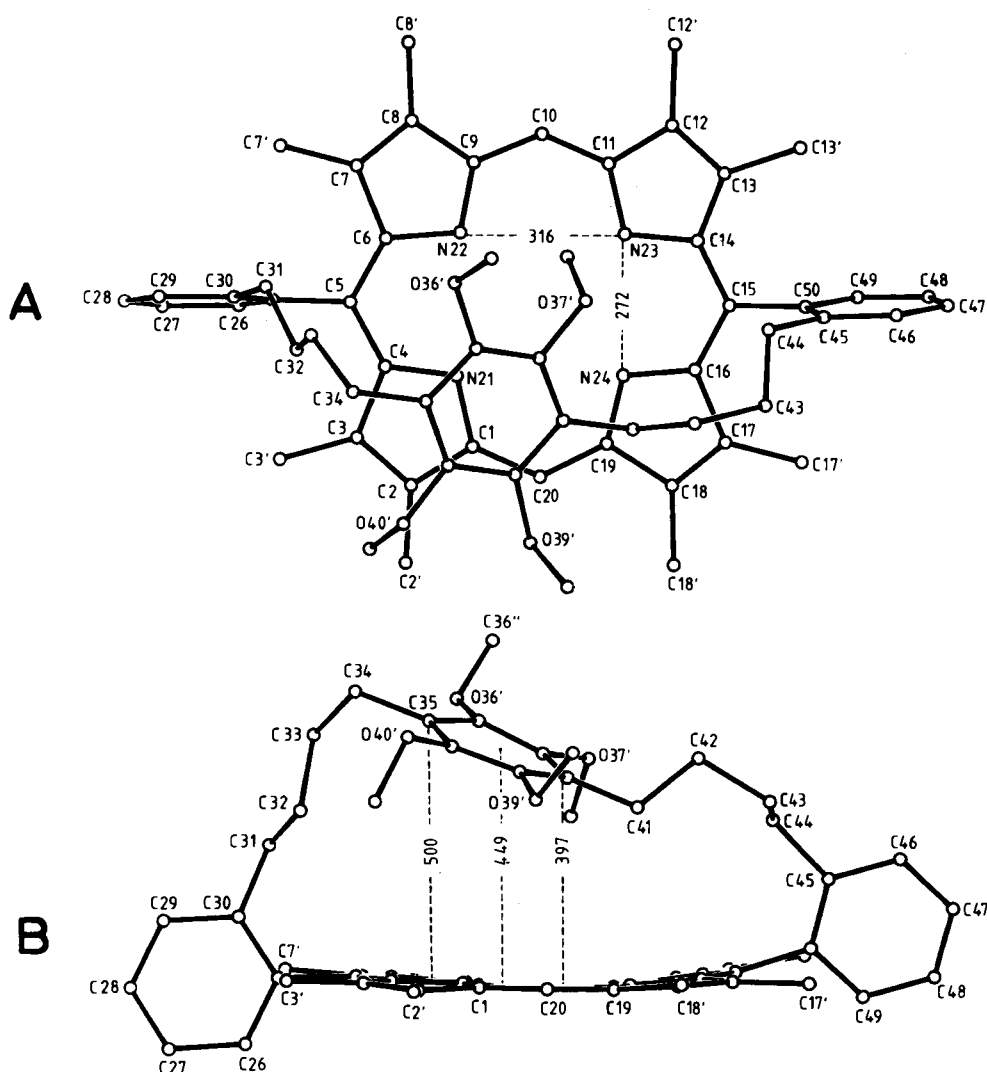


Figure 2. Molecular structure of **4** ($X = OMe$) in a top view onto the porphyrin plane (A) and in a side view along the C10··C20 axis (B)

C11 and C19–C20–C1 at the unsubstituted methine positions C10 and C20 to $134(1)^\circ$ and $131(1)^\circ$, resp. In the porphyrin ring the nearly planar pyrrole units show an inclination of about 9° against the least-squares plane of the porphyrin. The two phenyl rings in the methine positions are almost perpendicular to the mean porphyrin plane (angle 80°). As expected the methoxy groups on the quinone for steric reasons are not coplanar with the quinone ring. The direction of this torsion as well as that of the ethyl groups on the porphyrin unit is demonstrated in Fig. 1 (B). In the two tetramethylene chains linking the quinone to the

phenyl rings on porphyrin the methylene groups occupy energetically favorable positions: the torsional angles within these methylene chains on either side correspond approximately to the energy minima at 180 and 60° , the maximum deviation from these preferred torsional angles amounting to 20° . Probably this is one of the factors stabilizing the specific bridge conformation observed. There are no short intermolecular interactions which might explain the unsymmetrical arrangement of these C_4 -chains. In the elementary cell the orientation of the molecules is such that the porphyrin planes point towards each other in a distance of 360

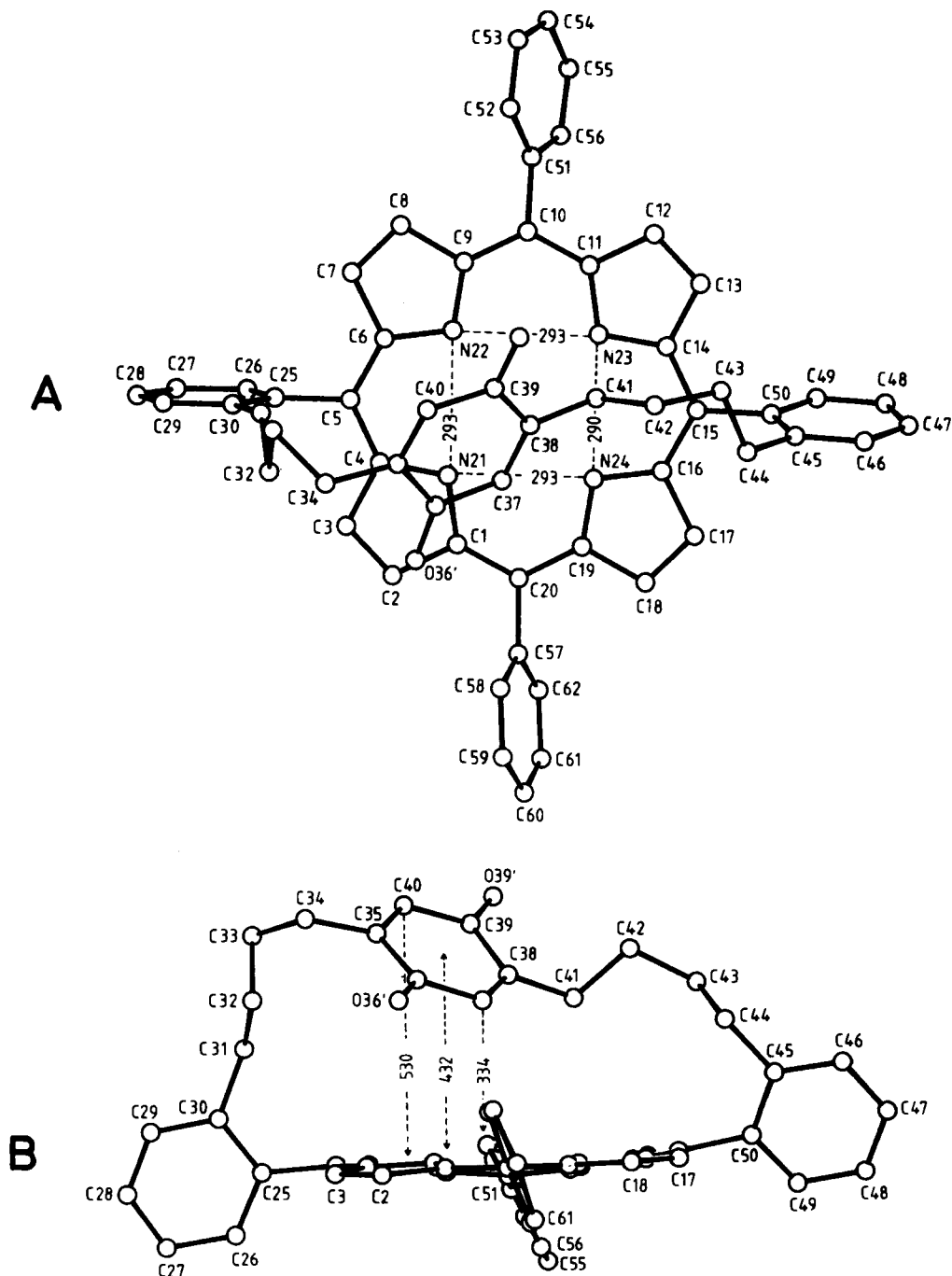


Figure 3. Molecular structure of 6 in a top view onto the porphyrin plane (A) and in a side view (B)

pm. The shortest lateral intermolecular distances are those between the quinone carbonyl oxygens and the ethyl groups on porphyrin with 327 and 334 pm, resp. (for crystallographic details see Experimental).

X-Ray Structure Analysis of 5,15-[2,3,5,6-Tetramethoxybenzene-1,4-diylbis(4,1-butanediyl-2,1-benzo)]-2,3,7,8,12,13,17,18-octamethylporphyrin [4(X = OMe)]: Considering the fact that 4(X = OMe) differs from 3(X = OMe) by being a non-quinoid porphyrin cyclophane which, in addition, contains an octamethylporphyrin instead of the tetraethyltetramethylporphyrin unit in 3(X = OMe), the agreement between the two structures is striking. The plane of the tetramethoxybenzene ring is tilted against the porphyrin mean plane by 24°; the vertical projection of the center of the aromatic ring onto the porphyrin plane amounts to 449 pm, the center-to-center distance being 502 pm. Again the torsional angles in the tetramethylene chains differ from the energetically favored angles only by 20° at the most. The overall planarity of the porphyrin is more distinct than in 3(X = OMe); the N...N distances are different in pairs (272 and 316 pm) for the reasons mentioned above [angles C9–C10–C11: 130(1)°, C19–C20–C1: 132(1)°]. The two phenyl rings are nearly perpendicular to the porphyrin plane

Table 2. Crystal and data collection parameters for 3(X = OMe), 4(X = OMe), and 6

	3(X = OMe)	4(X = OMe)	6
Formula	C ₆₀ H ₆₆ N ₄ O ₄	C ₅₈ H ₆₄ N ₄ O ₄ · C ₄ H ₈ O ₂	C ₅₈ H ₄₆ N ₄ O ₂
Molecular mass	907.2	969.3	831.0
<i>a</i> [pm]	1745.0(2)	1867.9(4)	1150.5(2)
<i>b</i> [pm]	1576.1(4)	1601.9(4)	1277.1(2)
<i>c</i> [pm]	1882.6(5)	2065.4(4)	1522.6(2)
α [°]	—	—	95.12(2)
β [°]	103.25(4)	116.55(3)	91.43(2)
γ [°]	—	—	99.12(2)
Space group	P2 ₁ /n ^[a]	P2 ₁ /n ^[a]	P1 ^[b]
<i>Z</i>	4	4	2
<i>D</i> _x [gcm ⁻³]	1.196	1.164	1.255
Max. sin Θ/λ [nm ⁻¹]	6.2	6.2	6.2
No. of reflection measured	9832	9067	7723
No. of reflection with <i>I</i> ≥ 3.0σ(<i>I</i>)	3867	3710	3828
<i>R</i>	0.082	0.10	0.059
Crystal size [mm]	0.15 × 0.15 × 0.05	0.35 × 0.20 × 0.1	0.4 × 0.3 × 0.1
Crystallized from	methylcyclohexane	methylcyclohexane (ethyl acetate)	dichloromethane/methanol (water)

^[a] No. 14. Intern. Tables. — ^[b] No. 2, Intern. Tables.

Table 3. Atomic coordinates and equivalent isotropic thermal parameters *U*_{eq} of non-hydrogen atoms of 3(X = OMe) (*U*_{eq} = $\frac{1}{3} \sum U_{ij} a_i \cdot a_j a_i^* a_j^*$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} · $\frac{10^{-3}}{\text{pm}^2}$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq} · $\frac{10^{-3}}{\text{pm}^2}$
C(1)	0.3476(6)	0.1560(8)	0.6364(6)	48(3)	C(35)	0.2653(6)	0.4671(8)	0.5241(6)	59(4)
C(2)	0.3021(7)	0.1798(9)	0.6861(6)	67(4)	C(36)	0.2933(6)	0.4470(7)	0.4583(6)	57(4)
C(3)	0.2255(6)	0.1884(8)	0.6498(6)	61(4)	C(37)	0.3675(6)	0.3942(7)	0.4718(5)	47(3)
C(4)	0.2244(6)	0.1677(7)	0.5760(6)	47(3)	C(38)	0.4108(6)	0.3768(7)	0.5335(6)	47(3)
C(5)	0.1596(6)	0.1597(7)	0.5143(6)	45(3)	C(39)	0.3830(7)	0.4031(8)	0.5983(7)	70(4)
C(6)	0.1659(6)	0.1359(7)	0.4451(5)	38(3)	C(40)	0.3061(7)	0.4490(8)	0.5887(6)	63(4)
C(7)	0.1047(5)	0.1186(7)	0.3840(6)	46(3)	C(41)	0.4876(7)	0.3301(7)	0.5436(7)	66(4)
C(8)	0.1378(6)	0.0947(7)	0.3254(6)	49(3)	C(42)	0.5556(6)	0.3844(7)	0.5289(7)	60(4)
C(9)	0.2228(5)	0.1021(7)	0.3584(6)	43(3)	C(43)	0.6232(6)	0.3281(7)	0.5186(6)	55(4)
C(10)	0.2777(6)	0.0943(7)	0.3144(5)	42(3)	C(44)	0.6072(6)	0.2943(7)	0.4405(6)	52(4)
C(11)	0.3608(5)	0.1022(7)	0.3341(5)	37(3)	C(45)	0.6558(6)	0.2168(7)	0.4322(6)	44(3)
C(12)	0.4061(6)	0.1083(7)	0.2780(5)	45(3)	C(46)	0.7305(6)	0.2245(8)	0.4182(7)	62(4)
C(13)	0.4825(5)	0.1175(7)	0.3159(6)	47(3)	C(47)	0.7733(6)	0.1526(9)	0.4096(7)	79(4)
C(14)	0.4808(5)	0.1167(7)	0.3909(5)	36(3)	C(48)	0.7452(6)	0.0731(8)	0.4143(7)	68(4)
C(15)	0.5463(5)	0.1193(6)	0.4515(6)	43(3)	C(49)	0.6718(6)	0.0634(8)	0.4266(7)	60(4)
C(16)	0.5401(5)	0.1157(7)	0.5245(5)	33(3)	C(50)	0.6272(6)	0.1333(7)	0.4361(5)	43(3)
C(17)	0.6017(6)	0.1137(7)	0.5880(6)	44(3)	C(2')	0.3372(8)	0.204(1)	0.7654(7)	112(5)
C(18)	0.5664(6)	0.1151(7)	0.6461(5)	39(3)	C(2'')	0.3493(9)	0.128(1)	0.8115(9)	145(7)
C(19)	0.4822(5)	0.1227(7)	0.6155(5)	42(3)	C(3')	0.1598(7)	0.213(1)	0.6837(7)	106(5)
C(20)	0.4275(6)	0.1404(7)	0.6561(5)	51(4)	C(7')	0.0156(6)	0.1265(8)	0.3719(7)	69(4)
N(21)	0.3008(4)	0.1508(5)	0.5706(4)	39(2)	C(8')	0.0990(6)	0.0659(8)	0.2501(5)	57(4)
N(22)	0.2362(4)	0.1257(5)	0.4276(4)	34(2)	C(8'')	0.0790(9)	-0.0235(9)	0.2438(7)	100(5)
N(23)	0.4060(4)	0.1092(6)	0.3987(4)	34(2)	C(12')	0.3720(6)	0.1079(8)	0.1974(5)	56(4)
N(24)	0.4696(4)	0.1180(5)	0.5438(4)	31(2)	C(12'')	0.3347(8)	0.1912(9)	0.1683(6)	82(5)
C(25)	0.0799(6)	0.1692(7)	0.5307(6)	51(4)	C(13')	0.5494(7)	0.126(1)	0.2795(6)	89(5)
C(26)	0.0458(6)	0.1003(8)	0.5561(7)	66(4)	C(17)	0.6894(6)	0.1067(8)	0.5973(6)	58(4)
C(27)	-0.0291(7)	0.1024(8)	0.5686(7)	76(4)	C(18')	0.6037(6)	0.1169(8)	0.7258(6)	53(4)
C(28)	-0.0686(7)	0.1769(9)	0.5578(7)	78(4)	C(18'')	0.6211(7)	0.2034(9)	0.7599(7)	84(5)
C(29)	-0.0392(7)	0.2462(8)	0.5332(7)	81(4)	O(36')	0.2620(5)	0.4739(6)	0.3962(4)	82(3)
C(30)	0.0350(7)	0.2417(8)	0.5165(7)	72(4)	O(37')	0.3915(4)	0.3710(5)	0.4099(4)	68(3)
C(31)	0.0614(8)	0.318(1)	0.4779(9)	107(6)	O(39')	0.4215(5)	0.3837(7)	0.6604(5)	108(3)
C(32)	0.1069(8)	0.380(1)	0.5212(7)	100(5)	O(40')	0.2804(5)	0.4705(7)	0.6489(5)	110(3)
C(33)	0.1188(7)	0.4597(9)	0.4730(7)	80(4)	C(37'')	0.3386(8)	0.3221(9)	0.3537(8)	94(5)
C(34)	0.1886(7)	0.5133(8)	0.5116(7)	77(4)	C(40'')	0.295(1)	0.432(1)	0.7133(9)	154(8)

(85°). Bond distances and bond angles, as in **3**(X = OMe), do not exhibit significant deviations from normal values. Again there are no especially short intermolecular distances to which the specific unsymmetrical structure found could be attributed. Top and side views of **4**(X = OMe) are shown in Figure 2 (A and B) (for crystallographic details see Experimental).

X-Ray Structure Analysis of 5,15-[p-Benzoquinone-1,4-diylbis(4,1-butanediyl-2,1-benzo)]-10,20-diphenylporphyrin (6): The quinone-bridged tetraphenylporphyrin **6** was primarily of interest as a system containing the partial structure of a quinone-porphyrin-porphyrin triad which was recently synthesized for studies on photoinduced electrontransfer reactions^[16]. In the context of the conformational problems discussed in the present paper, **6** forms the link between the doubly quinone-bridged compounds of type **1** and the single-bridged quinone-porphyrin cyclophanes of types **2** and **3** which contain diphenylporphyrin units. Because of this intermediate position, **6** also was an interesting compound with regard to the measurements of electron-transfer rates in quinone-porphyrin cyclophanes. Synthesis and properties of **6** are described in a separate paper^[8].

Similar to the structures of **3**(X = OMe) and **4**(X = OMe), the quinone ring in **6** is oriented neither parallel nor centered to the porphyrin plane (Figure 3, A and B). In contrast to the other single-bridged porphyrin cyclophanes and obviously as a result of the sterical requirements of the two phenyl substituents in the 10- and 20-positions of the porphyrin the quinone plane is tilted stronger against the porphyrin plane (44°). In the projection onto the porphyrin plane (Figure 3, A) the center of the quinone ring is shifted against the porphyrin center by about 160 pm; the direct center-to-center distance (432 pm) is slightly shorter than in **3**(X = OMe) and **4**(X = OMe). The two phenyl rings at C5 and C15 into which the cyclophane bridges insert deviate from the orthogonal position to the porphyrin plane by 9° and 21°, resp.; for the phenyl rings at C10 and C20 the corresponding deviations are 28° and 21°, respectively. The porphyrin nitrogens in this case form a square with equal distances of 293 pm for N21...N22 and N22...N23. In contrast to **3** and **4**, in **6** all four methine positions are aryl-substituted, and the intracyclic angles at C5, C10, C15 and C20 are very similar [124.8(3) to 125.8(3)°] (for crystallographic details see Experimental).

Table 4. Atomic coordinates and equivalent isotropic thermal parameters U_{eq} of non-hydrogen atoms of **4**(X = OMe) ($U_{eq} = \frac{1}{3} \sum \sum U_{ij} a_i \cdot a_j a_i^* a_j^*$); isotropic refinement

Atom	x	y	z	$U_{eq} \cdot 10^{-1} \text{ pm}^2$	Atom	x	y	z	$U_{eq} \cdot 10^{-1} \text{ pm}^2$
C(1)	0.3598(6)	0.6296(7)	0.6584(6)	45(4)	C(34)	0.4191(7)	0.3848(9)	0.9094(6)	61(5)
C(2)	0.3697(6)	0.6854(8)	0.7138(6)	49(4)	C(35)	0.3660(6)	0.3846(8)	0.8284(6)	47(4)
C(3)	0.4485(6)	0.6732(8)	0.7673(6)	50(4)	C(36)	0.3768(6)	0.3290(8)	0.7833(6)	50(4)
C(4)	0.4869(6)	0.6137(8)	0.7417(5)	41(4)	C(37)	0.3322(6)	0.3335(8)	0.7097(6)	48(4)
C(5)	0.5655(6)	0.5844(8)	0.7747(6)	43(4)	C(38)	0.2668(6)	0.3844(8)	0.6761(6)	51(4)
C(6)	0.5956(6)	0.5286(8)	0.7408(6)	46(4)	C(39)	0.2522(6)	0.4369(7)	0.7227(6)	50(4)
C(7)	0.6782(6)	0.4942(7)	0.7682(6)	45(4)	C(40)	0.3030(6)	0.4362(8)	0.7969(6)	50(4)
C(8)	0.6788(6)	0.4462(8)	0.7136(6)	42(4)	C(41)	0.2175(7)	0.3857(9)	0.5972(6)	61(4)
C(9)	0.6008(6)	0.4482(7)	0.6573(5)	35(4)	C(42)	0.1677(7)	0.3100(9)	0.5640(6)	61(4)
C(10)	0.5784(6)	0.4019(8)	0.5936(6)	52(4)	C(43)	0.1432(7)	0.3037(9)	0.4819(6)	65(5)
C(11)	0.5062(6)	0.3882(8)	0.5324(6)	44(4)	C(44)	0.2106(7)	0.2717(8)	0.4662(6)	61(4)
C(12)	0.4924(6)	0.3284(8)	0.4784(6)	49(4)	C(45)	0.1973(7)	0.2914(8)	0.3886(6)	57(4)
C(13)	0.4119(7)	0.3261(9)	0.4355(6)	65(5)	C(46)	0.1447(7)	0.2394(9)	0.3319(7)	68(5)
C(14)	0.3742(6)	0.3868(7)	0.4585(6)	45(4)	C(47)	0.1275(7)	0.2559(9)	0.2602(6)	71(5)
C(15)	0.2956(6)	0.4094(8)	0.4298(6)	44(4)	C(48)	0.1665(7)	0.320(1)	0.2455(6)	80(5)
C(16)	0.2671(6)	0.4730(8)	0.4579(6)	48(4)	C(49)	0.2186(7)	0.3682(9)	0.3006(6)	64(5)
C(17)	0.1832(6)	0.5050(8)	0.4275(6)	53(4)	C(50)	0.2348(6)	0.3563(8)	0.3712(6)	48(4)
C(18)	0.1842(6)	0.5621(8)	0.4762(6)	48(4)	C(2')	0.3079(7)	0.7388(9)	0.7175(8)	85(5)
C(19)	0.2667(6)	0.5690(8)	0.5336(6)	44(4)	C(3')	0.4813(8)	0.7185(9)	0.8378(6)	77(5)
C(20)	0.2870(6)	0.6191(8)	0.5954(6)	53(4)	C(7')	0.7467(7)	0.5108(9)	0.8404(7)	74(5)
N(21)	0.4302(5)	0.5886(6)	0.6745(5)	46(3)	C(8')	0.7478(7)	0.3983(9)	0.7159(6)	63(5)
N(22)	0.5505(5)	0.4954(6)	0.6717(5)	44(3)	C(12')	0.5582(8)	0.279(1)	0.4733(7)	95(6)
N(23)	0.4342(5)	0.4227(6)	0.5181(4)	42(3)	C(13')	0.3762(8)	0.267(1)	0.3696(7)	103(6)
N(24)	0.3136(5)	0.5151(6)	0.5207(5)	40(3)	C(17')	0.1144(7)	0.4873(9)	0.3579(7)	72(5)
C(25)	0.6216(6)	0.6192(7)	0.8455(6)	46(4)	C(18')	0.1158(7)	0.6092(9)	0.4762(8)	78(5)
C(26)	0.6603(7)	0.6932(9)	0.8474(6)	63(4)	O(36')	0.4418(4)	0.2765(5)	0.8124(4)	66(3)
C(27)	0.7107(7)	0.7329(8)	0.9120(7)	71(5)	O(37')	0.3504(4)	0.2825(6)	0.6643(4)	65(3)
C(28)	0.7266(7)	0.693(1)	0.9761(6)	74(5)	O(39')	0.1905(4)	0.4958(5)	0.6953(4)	67(3)
C(29)	0.6901(6)	0.6167(8)	0.9732(6)	57(4)	O(40')	0.2816(5)	0.4861(6)	0.8418(5)	75(3)
C(30)	0.6383(6)	0.5781(8)	0.9106(6)	50(4)	C(36'')	0.4237(8)	0.194(1)	0.8065(8)	98(6)
C(31)	0.6059(6)	0.4950(8)	0.9143(6)	52(4)	C(37'')	0.4135(8)	0.313(1)	0.6529(9)	131(7)
C(32)	0.5215(6)	0.4906(7)	0.9041(6)	49(4)	C(39'')	0.1167(8)	0.464(1)	0.6857(9)	119(7)
C(33)	0.5058(7)	0.4074(8)	0.9267(6)	61(5)	C(40'')	0.3001(8)	0.575(1)	0.8422(9)	108(7)

Conclusion: The molecular structures of single-bridged porphyrin cyclophanes of which X-ray analyses have been solved so far agree in their essential features with the unsymmetrical conformations derived for the individual molecules in solution from temperature-dependent $^1\text{H-NMR}$ measurements. Especially, the planes of the quinoid or aromatic rings in the cyclophane bridges are found to be neither parallel nor centered with regard to the porphyrin planes. This applies also to the quinone-tetraphenylporphyrin cyclophane **6** which from the series of single-bridged quinone-porphyrin cyclophanes is the compound most closely related to **1**. The parallel and perfectly centered orientation of the ring planes as determined by X-ray analysis for **1(X = H)**, thus, does not apply to the single-bridged systems for which unsymmetrical structures with tilted planes seem to be generally favored. On the basis of these results it appears likely that the high S_4 symmetry found for **1(X = H)** is not an inherent molecular property but the result of crystal packing^[2,7].

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Experimental

Syntheses: The preparations of the porphyrin cyclophanes dealt with in this paper have been described in ref.^[2,3] or are reported in a forthcoming paper^[8].

$^1\text{H-NMR}$ Measurements: Bruker HX-360 and AM-500. The temperature determination was made by using a calibration curve based on ohmmetric measurements: A sample tube containing a Pt₁₀₀-resistor immersed in methanol was placed into the same position of the probe as the samples to be examined; the reading of the resistance thermometer was set at 273.1 K for an ice-water mixture and proved with liquid nitrogen to agree with the calibration curve of the thermometer itself. Within the range of 303–143 K the Bruker PVT 1000 variable temperature unit was set in 10-K steps, and for each setting the temperature indicated by Pt-thermometer was read after a waiting time of 5 min. – For the solvents used and the coalescence data obtained see above.

X-Ray Analyses: Enraf-Nonius CAD 4 (Mo- K_α radiation, graphite monochromator, $2\Theta/\Theta$ -scan technique). The structure solutions were possible by direct methods (MULTAN or SIR). For the re-

Table 5. Atomic coordinates and equivalent isotropic thermal parameters U_{eq} of non-hydrogen atoms of **6** ($U_{\text{eq}} = \frac{1}{3} \sum \sum U_{ij} a_i \cdot a_j a_i^* a_j^*$); * disordered

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}} \cdot 10^{-1} \text{pm}^2$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}} \cdot 10^{-1} \text{pm}^2$
C(1)	0.5251(4)	0.1766(3)	0.2913(3)	53(1)	C(33)	0.5914(5)	0.1929(5)	-0.1262(4)	122(2)
C(2)	0.5762(4)	0.0869(3)	0.2592(3)	67(1)	C(34)	0.4693(6)	0.1564(4)	-0.0931(4)	110(2)
C(3)	0.6695(4)	0.1221(4)	0.2126(3)	69(1)	C(35)	0.4216(4)	0.2369(4)	-0.0297(3)	73(1)
C(4)	0.6813(4)	0.2347(3)	0.2137(3)	54(1)	C(36)	0.3901(4)	0.2082(4)	0.0594(3)	78(2)
C(5)	0.7683(4)	0.3021(3)	0.1758(3)	57(1)	C(37)	0.3606(4)	0.2933(4)	0.1238(3)	70(1)
C(6)	0.7844(4)	0.4122(3)	0.1854(3)	56(1)	C(38)	0.3530(4)	0.3908(4)	0.1032(3)	63(1)
C(7)	0.8800(4)	0.4804(4)	0.1487(3)	68(1)	C(39)	0.3726(4)	0.4145(4)	0.0121(3)	69(1)
C(8)	0.8724(4)	0.5819(4)	0.1777(3)	65(1)	C(40)	0.4086(5)	0.3340(4)	-0.0513(3)	74(2)
C(9)	0.7709(4)	0.5777(3)	0.2323(3)	53(1)	O(36 [*])	0.3858(4)	0.1182(3)	0.0803(3)	122(1)
C(10)	0.7325(4)	0.6669(3)	0.2758(3)	51(1)	O(39 [*])	0.3625(3)	0.5031(3)	-0.0114(2)	90(1)
C(11)	0.6278(4)	0.6655(3)	0.3215(3)	51(1)	C(41)	0.3278(4)	0.4778(4)	0.1698(3)	72(1)
C(12)	0.5752(4)	0.7557(3)	0.3508(3)	57(1)	C(42)	0.2073(4)	0.5090(4)	0.1598(3)	66(1)
C(13)	0.4726(4)	0.7208(3)	0.3862(3)	54(1)	C(43)	0.1809(4)	0.5790(4)	0.2412(3)	62(1)
C(14)	0.4586(4)	0.6085(3)	0.3828(3)	47(1)	C(44)	0.1361(4)	0.5142(3)	0.3160(3)	59(1)
C(15)	0.3644(3)	0.5409(3)	0.4145(3)	45(1)	C(45)	0.1526(3)	0.5738(3)	0.4060(3)	46(1)
C(16)	0.3557(3)	0.4296(3)	0.4124(3)	45(1)	C(46)	0.0610(4)	0.6163(3)	0.4459(3)	56(1)
C(17)	0.2626(4)	0.3624(3)	0.4505(3)	57(1)	C(47)	0.0768(4)	0.6731(4)	0.5277(3)	66(1)
C(18)	0.2790(4)	0.2619(3)	0.4305(3)	60(1)	C(48)	0.1832(4)	0.6889(4)	0.5711(3)	67(1)
C(19)	0.3832(4)	0.2653(3)	0.3797(3)	49(1)	C(49)	0.2765(4)	0.6468(3)	0.5333(3)	55(1)
C(20)	0.4274(4)	0.1751(3)	0.3442(3)	53(1)	C(50)	0.2626(3)	0.5893(3)	0.4519(3)	42(1)
N(21)	0.5912(3)	0.2642(3)	0.2620(2)	55(1)	C(51)	0.8071(4)	0.7749(3)	0.2751(3)	54(1)
N(22)	0.7193(3)	0.4749(3)	0.2345(2)	54(1)	C(52)	0.8295(4)	0.8255(4)	0.1995(3)	65(1)
N(23)	0.5541(3)	0.5771(2)	0.3421(2)	48(1)	C(53)	0.8961(4)	0.9278(4)	0.2041(3)	75(1)
N(24)	0.4281(3)	0.3685(2)	0.3700(2)	47(1)	C(54)	0.9385(5)	0.9790(4)	0.2836(4)	90(2)
C(25)	0.8598(4)	0.2497(4)	0.1283(3)	66(1)	C(55)	0.9192(5)	0.9292(4)	0.3597(4)	96(2)
C(26)	0.9604(4)	0.2436(4)	0.1743(3)	74(2)	C(56)	0.8541(4)	0.8287(4)	0.3545(3)	78(2)
C(27)	1.0505(4)	0.1938(4)	0.1361(4)	93(2)	C(57)	0.3618(4)	0.0692(3)	0.3623(3)	57(1)
C(28)	1.0327(5)	0.1540(4)	0.0515(4)	116(2)	C(58)	0.2944(4)	0.0057(4)	0.2964(3)	74(2)
C(29)	0.9343(6)	0.1595(6)	0.0030(4)	154(2)	C(59)	0.2287(5)	-0.0897(4)	0.3136(4)	91(2)
C(30)	0.8446(5)	0.2074(5)	0.0403(4)	139(2)	C(60)	0.2282(5)	-0.1213(4)	0.3962(4)	96(2)
C(31) [*]	0.7346(9)	0.2133(6)	-0.0144(6)	282(8)	C(61)	0.2966(5)	-0.0587(4)	0.4613(4)	98(2)
C(32) [*]	0.6241(7)	0.1362(6)	-0.0474(5)	169(6)	C(62)	0.3630(5)	0.0356(4)	0.4452(3)	78(2)

finement all non-hydrogen atoms were included with anisotropic temperature factors; the hydrogen positions were included into the refinement without a refinement of coordinates and temperature factors. Crystal and data collection parameters are given in Table 2; atomic coordinates and equivalent isotropic thermal parameters are given in Tables 3 to 5. For further details see ref.^[15].

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