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Highly Crowded *trans*-Olefin. Molecular Structure of *trans*-1,2-Bis{*meso*-[nickel(II)octaethylporphyrinyl]}ethene

Ryouichi KITAGAWA, Yasushi KAI,* Gelii V. PONOMAREV,† Ken-ichi SUGIURA,††
Victor V. BOROVKOV,††, ††† Takahiro KANEDA,†† and Yoshiteru SAKATA*††
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565
†Institute of Biophysics of Russian Ministry of Health, Moscow 123182, Russia
††The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567

X-Ray analysis of *trans*-1,2-bis{*meso*-[nickel(II)octaethylporphyrinyl]}ethene has revealed that the compound has nonplanar structure and the nickel-coordination planes of porphyrin rings are close to perpendicular (72.5°) to the plane of the central double bond. Both porphyrin rings have saddle-shaped structure due to the steric repulsion between ethyl substituents.

Highly crowded olefins have been attracted attention from several points of view and various crowded stilbenes have been prepared.[1-3] When bulky groups are introduced in 1,2-diarylethene, aryl groups rotate around the single bond between the aryl and ethylene groups to avoid steric congestion. The dihedral angle between the planes of aryl groups and the central double bond reaches to 90° in highly crowded *cis*-compound.[3] On the other hand, *trans*-diarylethene is affected by less steric strain and the relief of the steric congestion is achieved by the rotation of aryl groups with smaller angle.[4] Here we report the molecular structure of the title compound **1a** having bulky nickel(II)-octaethylporphyrin groups; large steric strain is anticipated for a planar conformation.

Free base *trans*-isomer **1b** was prepared, as previously reported,[5] by heating of 1,2-bis(*meso*-octaethylporphyrinyl)ethane in acetic acid at 70 °C. Metallation of **1b** was carried out by treatment with nickel

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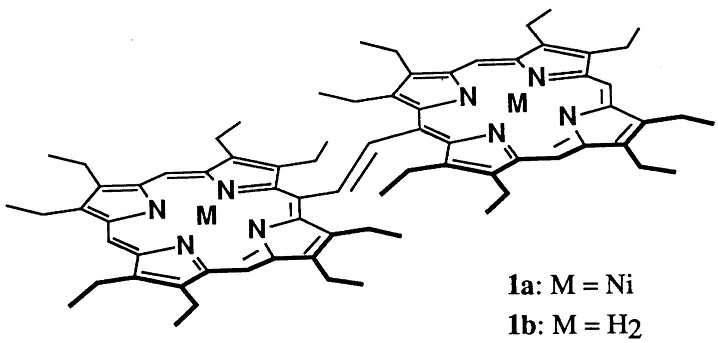
acetate in DMF at 105-110 °C. A single crystal of **1a**6) suitable for X-ray analysis7) was obtained by recrystallization from $CHCl_3$ - MeOH.



1a: M = Ni
1b: M = H_2

The ORTEP drawing (Fig. 1) clearly illustrates that the two porphyrin rings, correlated by a center of symmetry, are not coplanar but are arranged parallel with each other. The two carbon and two hydrogen atoms which constitute the central double bond are in a plane with the maximum deviation of 0.07 Å and the dihedral angle between the plane and the least-squares plane of four nitrogen atoms in nickel-coordination plane is 72.5° (Fig. 2). As far as our knowledge is concerned, this value is the largest compared with those of *trans*-1,2-diarylethenes reported so far.8) The deviation of the dihedral angle from the complete orthogonality may be due to avoidance of the short contact between the ethyl groups which are located around the double bond. The large steric repulsion in the planar conformation is relieved by rotation in a conrotatory fashion around the *meso*-porphyrinyl-ethylene single bonds. Similar steric relief is observed for *trans*-1,2-di(10-bromo-9-anthryl)ethene,9) but the dihedral angle between the anthracene rings and the central double bond remains smaller (60.7°).

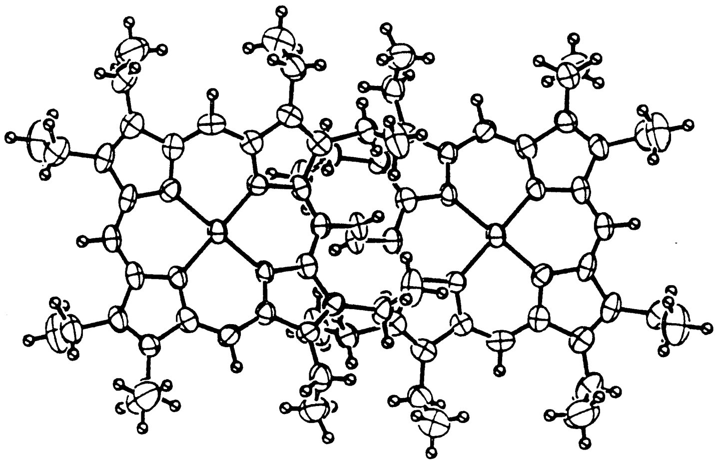


Fig. 1. ORTEP drawing of **1a**.

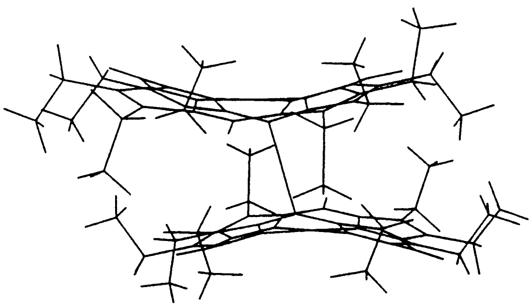


Fig. 2 Line bond drawing of **1a** perpendicular to the central double bond.

The perpendicular distance between the two nickel-coordination planes is 4.27 Å, which is shorter by 0.3 Å than that of the related compound,10) where the ethylene spacer in **1a** is replaced by an ethane linkage. The corresponding bond distances and angles of the two porphyrin rings in **1a** are similar to those of nickel(II)octaethylporphyrin (NiOEP).11-13) The macrorings of **1a** are not planar, but are saddle-shaped with pseudo S4 axis at the center of the rings (Fig. 3, Table 1). The ruffled structure is quite similar to the tetragonal crystal form of NiOEP, but the averaged dihedral angle of the adjacent pyrrole rings are smaller (26.8°) compared with that of NiOEP (32.8°).11) The distance of the central double bond is unusually short (1.29 Å) compared with the usual olefins. Probably dynamical disorder is responsible for the shortening, since the same behavior is often seen in stilbene derivatives.4)

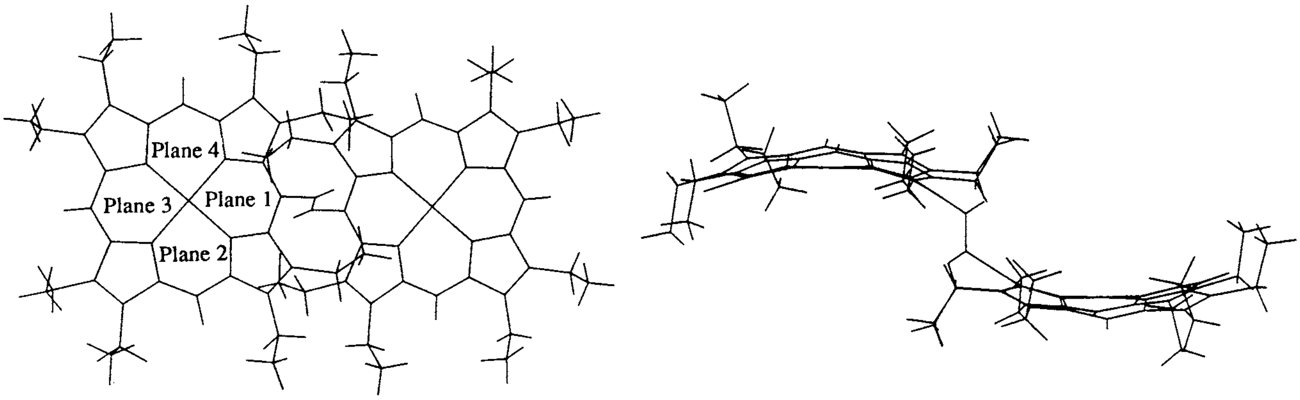


Fig. 3. Saddle-shaped structure of porphyrin rings.

Table 1. Dihedral Angles between Least-squares Planes

	Plane 1 b)	Plane 2	Plane 3	Plane 4
[1] a)	+18.6°	-16.5°	+14.5°	-16.5°

a) least-squares plane formed by nickel and four nitrogens.
b) least-squares plane formed by N-C-C-C-N moieties.

Reflecting unique structure, **1a** shows different behavior in electronic spectra from that of usual *trans*-diarylethenes. Thus, the Soret band of **1a** appears as doublet at 405 and 417 nm in $\mathrm{CHCl_3}$ in consequence of the exciton coupling between the two transition dipoles of the porphyrin chromophores in the molecule. Since this kind of splitting is observed14) in non-conjugated diporphyrin chromophores rigidly linked in a molecule, the spectra indicate that **1a** has the same rigid structure in a solution as seen in Figs. 1 - 3.

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References

1) J. Saltiel and J. L. Charton, “Rearrangements in the Ground and Excited States,” ed by P. DeMayo, Academic Press, New York (1980), vol. 3, p.25.

2) T. Arai and K. Tokumaru, *Chem. Rev.*, **93**, 23 (1993).

3) J. E. Gano, B.-S. Park, G. Subramaniam, D. Lenoir, and R. Gleiter, *J. Org. Chem.*, **56**, 4806 (1991).

4) K. Ogawa, T. Sano, S. Yoshimura, Y. Takeuchi, and K. Toriumi, *J. Am. Chem. Soc.*, **114**, 1041 (1992) and references cited therein.

5) A. M. Shul'ga and G. V. Ponomarev, *Khim. Geterotsikl. Soedin.*, **1988**, 339; *Chem. Abstr.*, **110**, 192493x (1989).

6) Spectroscopic data for compound **1a**: see, G. V. Ponomarev, V. V. Borovkov, K. Sugiura, Y. Sakata, and A. M. Shul'ga, *Tetrahedron Lett.*, 1993 in press.

7) Crystal data for **1a**: $C_{74}H_{88}N_8Ni_2 \cdot 2CHCl_3$, M=1445.72, triclinic, space group $P\bar{1}$, a=12.992(2), b =14.938(2), c=10.399(2) Å, α=109.32(1)°, β=96.42(2)°, γ=103.45(1)°, Z=1, U=1812.6(6) Å^3, D_c=1.324 gcm^{-3}, F(000)=760, Ni-filtered Cu-$K\alpha$ radiation (λ=1.54178 Å), μ=30.82 cm^{-1}, 5382 unique reflections measured ($2\theta_{max}$=120.1°) by the use of four-circle diffractometer. The structure was solved by the direct method and refined by the full-matrix least-squares technique to R=0.071. Some of H atoms were locate on a difference electron density maps and the others were generated by geometrical calculations. Atomic coordinates and bond lengths have been deposited at the Cambridge Crystallographic Data Centre.

8) For example, the dihedral angle of (E)-2,3-diphenyl-2-butene is reported to be 74.2°: J. E. Gano, B. S. Park, A. A. Pinkerton, and D. Lenoir, *Acta Crystallogr., Sect. C,* **47**, 162 (1991); G. Valle, V. Busetti, and G. Galiazzo, *Cryst. Struct. Commun.*, **10**, 867 (1981).

9) H.-D. Becker, L. M. Engelhardt, L. Hansen, V. A. Patrick, and A. H. White, *Aust. J. Chem.*, **37**, 1329 (1984).

10) P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, **1983**, 2127.

11) E. F. Meyer, Jr., *Acta Crystallogr., Sect. B,* **28**, 2162 (1972).

12) D. L. Cullen and E. F. Meyer, Jr., *J. Am. Chem. Soc.*, **96**, 2095 (1974).

13) T. D. Brennan, W. R. Sheidt, and J. A. Shelnutt, *J. Am. Chem. Soc.*, **110**, 3919 (1988).

14) A. Osuka and K. Maruyama, *J. Am. Chem. Soc.*, **110**, 4454 (1988).

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