Table II. Absolute Energies of $SiLi_4$ Isomers (-au)

species	point group	3-21G// 3-21G	ZPE^a	3-21G(*)// 3-21G(*)	ZPE^a	6-31G*//3-21G*	
						HF/	MP2/
$SiLi_4$ **1**	C_{2v}	316.99166 (0)	3.49	317.04146 (0)	3.56	318.67089	318.82634
2	C_{4v}	316.98563 (1)	3.39	317.03554		318.66598	318.82102
3	C_{3v} inv	316.98919 (0)	3.14	317.03815 (2)	3.11	318.66796	318.82108
4	T_d	316.98818 (3)	2.88	317.03555^b (3)	2.86	318.66523	318.81587
5	D_{4h}	316.98018^b (2)	3.35	317.02816^b		318.65759	318.80920
triplets	C_{2v}	316.96421					
(UHF)	D_{4h}			317.01504			
$SiLi_3$, 1π	D_{3h} UHF	309.57633^b (0)	2.04	309.62483^b		311.20688	311.31576
Li		7.38151		7.38151		7.43137	7.43137

^{a}Zero-point energies in kcal/mol (unscaled). ^{b}*The Carnegie-Mellon Quantum Chemistry Archive*; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds., 3rd ed.; Carnegie-Mellon University: 1983. ^{c}Frequencies in cm^{-1} 107.5 (b_1), 110.5 (a_1), 160.3 (a_1), 200.0 (b_1), 204.7 (a_2), 390.1 (a_1), 400.8 (b_2), 421.0 (a_1), and 492.0 (b_1).

Geometry optimizations and frequency calculations on a number of $SiLi_4$ structures (**1**-**5**; Scheme I) were carried by using the GAUSSIAN 82 program[7] with the 3-21G and 3-21G(*) basis sets. Geometries at the latter level are given in Scheme I, where the number of imaginary frequencies for each stationary point is given in parentheses. The single point MP2/6-31G*//3-21G(*) energies were corrected for zero-point energy differences to yield the "final" relative energies in Table I.[9] As seen from this table, the relative energies are rather insensitive to the level of theory, except that the T_d and D_{4h} structures are even less favored at the correlated MP2 level. Nevertheless, the entire $SiLi_4$ potential energy surface (PES) lies within an energy bound of only 12 kcal/mol. The triplet PES was not examined as extensively, as this is indicated to be of higher energy (even at the SCF level) than the singlet. At UMP2/6-31G*//3-21G(*) + ZPE, **1** is bound by 48.2 kcal/mol relative to Li and $SiLi_3$ (D_{3h}) and by 64 kcal/mol relative to Li_2 and $SiLi_2$ (linear triplet).

Remarkably, $SiLi_4$ is not tetrahedral; the T_d structure **4** has *three* degenerate imaginary frequencies (46i cm^{-1} at 3-21G(*)). At 3-21G(*), **1** (C_{2v}) is the only minimum located on the PES. The axial and equatorial lithiums in **1** can interchange through a C_{4v} transition structure, **2**, which is only 3.2 kcal/mol higher in energy. The potential energy surface around **3**, lying 2.9 kcal/mol above **1**, is quite flat. Hence by involving **2** and structures closely related to **3**, all the lithiums in $SiLi_4$ can change places in all possible configurations with activation energies of only a few kcal/mol. This is the first eight valence electron AX_4 molecule predicted to be fluxional.

Unusual chemical bonding in $SiLi_4$ is responsible for this behavior. The natural charges (by natural population analysis[10]) on Si, more negative than -2 in all forms of $SiLi_4$, reveal that the bonds are partially ionic. In addition, natural bond orbital (NBO) analysis[11] indicates the presence of a high occupancy (1.90-1.93e) Si lone pair of 90% s-character in structures **1**-**3**. These essentially doubly occupied Si 3s orbitals are inactive[12] with respect to Si-Li covalent bonding, which involves only the Si 3p orbitals. This is consistent with the greater radial extension of 3p than 3s orbitals.[13] By contrast, 2s and 2p orbitals have similar radial extensions,[13] and a tetrahedral geometry is favored for CLi_4.[14] NBO analysis of the C_{2v} form indicates two two-center-two-electron $Si-Li_{eq}$ bonds and a three-center-two-electron $Li_{ax}-Si-Li_{ax}$ bond. These three bonds delocalize strongly into the low-lying, low-occupancy 2s (and 2p) orbitals of other lithium atoms, leading to attractive Li-Li interactions[15] and the inward bending of the Li-Si-Li bond angles with respect to an ideal trigonal bipyramid (see Scheme I); this inward bending is greater than in the superficially analogous ten valence electron C_{2v} species SF_4 and SeF_4.[2b,c]

The electronic structure of $SiLi_4$ will be discussed in more detail subsequently.

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(9) The RHF/3-21G(*) wave functions for all structures of $SiLi_4$ except **4** (T_d) were found to be unstable with respect to UHF (suggestion of a referee). Relaxation of the RHF/3-21G(*) wave function for **1** resulted in an energy decrease of 6.1 kcal/mol and strong spin contamination (S^2 = 0.93). However, when electron correlation is included (MP4SDTQ), the RHF reference state leads to an energy 10.0 kcal/mol *lower* than the UHF "state" (9.7 kcal/mol lower at MP2), due to the very strong spin polarization of the UHF function. Furthermore, UHF/3-21G(*) optimization does not lead to qualitative changes in the relative energies [in kcal/mol: 0.0 (**1**), 1.9 (**2**), 1.2 (**3**), 10.4 (**4**); **5** (D_{4h}) optimizes to **2**(C_{4v})] or in the geometries (the bond lengths are about 0.1 Å longer, but the Li-Si-Li angles are reduced; this gives a smaller **1**-**3** energy difference). MCSCF calculations (Prof. R. Janoschek, personal communication) show only two configurations to be important and **2** to be 3.5 kcal/mol higher in energy than **1**.

(10) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(11) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 1736. Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.

(12) This is reminiscent of the "inert s-pair effect" see, e.g.: Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper & Row: New York, 1978; p 723. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 327.

(13) Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272; *Angew. Chem.* **1984**, *96*, 262.

(14) Würthwein, E.-U.; Sen, K. D.; Pople, J. A.; Schleyer, P. v. R. *Inorg. Chem.* **1983**, *22*, 496. Reed, A. E.; Schleyer, P. v. R., to be published.

(15) The attractive/repulsive nature of the interactions was judged by bond orders based on NPA/NLMO analysis (ref 10 and 11). The Mulliken overlap populations led in all cases to the same conclusions.

Synthesis of Naphthalene-Bridged Porphyrin Dimers and Their Orientation-Dependent Exciton Coupling

Atsuhiro Osuka and Kazuhiro Maruyama*

Department of Chemistry, Faculty of Science
Kyoto University, Kyoto 606, Japan

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The recent X-ray analysis of a bacterial photosynthetic reaction center from Rhodopseudomonas viridis dramatically shows the critical arrangement of six interacting tetrapyrroles at the active site.[1] Since these results strongly suggest the importance of the interchromophore distance and orientation in the efficient charge separation, development of porphyrin aggregates having systematically changing geometries is highly desirable.

We now report the synthesis of naphthalene-bridged dimeric porphyrins (NDP) and the remarkable splitting of the Soret band, which depends on the spatial arrangement of the two porphyrin rings. Two porphyrin rings in NDP are rigidly held in a certain geometry by the combined steric restrictions of the naphthalene spacer and the flanking ethyl groups. Consequently, the naphthalene bridge remains perpendicular to the mean porphyrin plane,

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(1) Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385-398.

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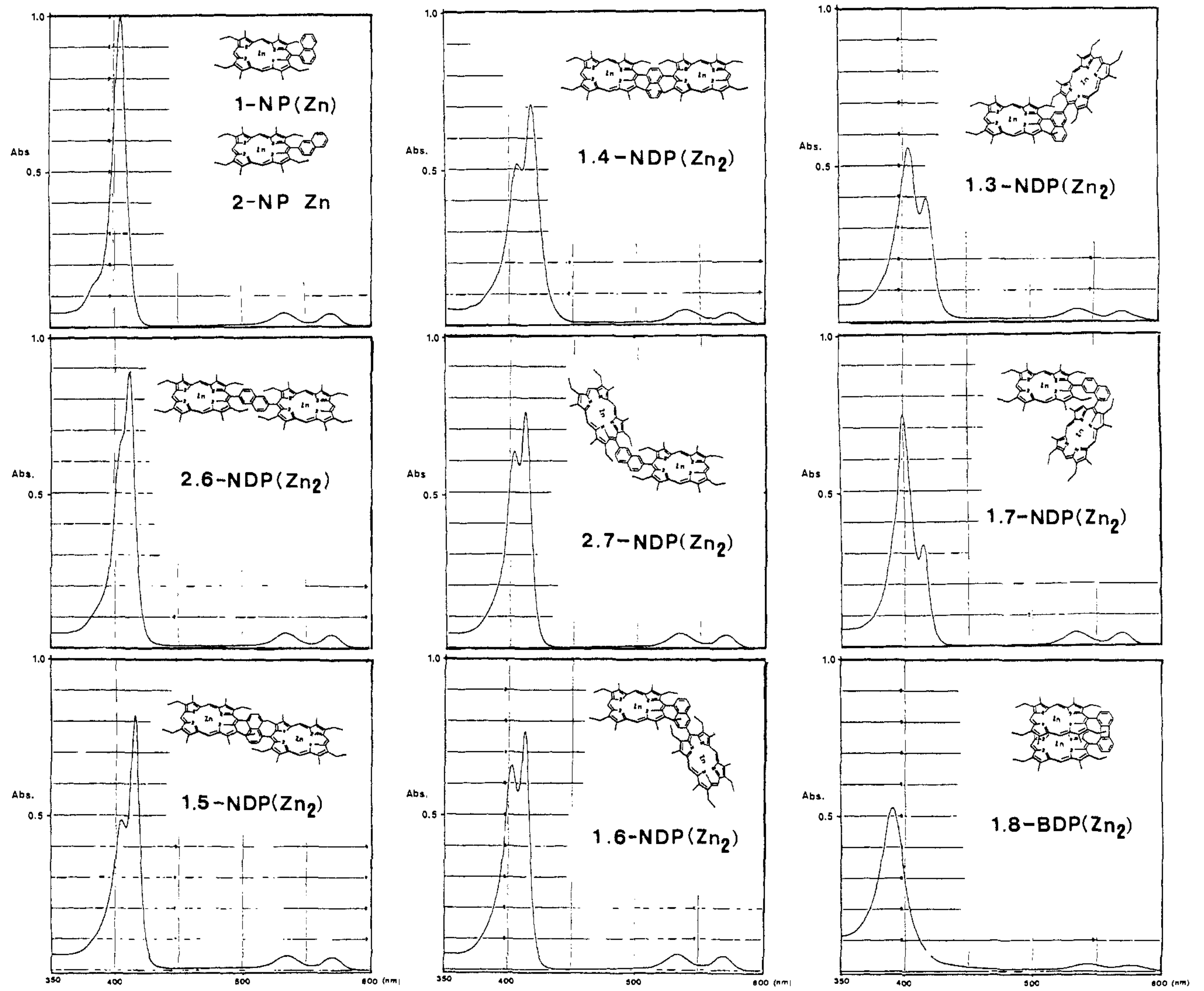
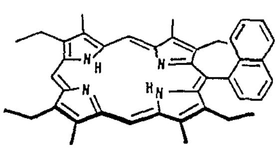
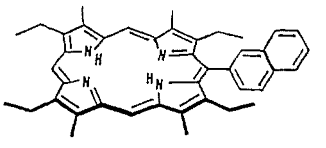


Figure 1. Absorption spectra of NP(Zn) and NDP(Zn$_2$) in CH$_2$Cl$_2$. Concentrations were 2.0 × 10^{-6} M for NP(Zn) and 1.0 × 10^{-6} M for NDP(Zn$_2$).

thereby minimizing direct π–π interaction between the porphyrin and the bridge.



1-NP



2-NP

Naphthalene-bridged diporphyrins (NDP) as well as 1,8-anthracene-bridged diporphyrin (1,8-ADP) and 1,8-biphenylene-bridged diporphyrin (1,8-BDP) were synthesized from the corresponding aryl dialdehydes by the method of Chang.[2,3] The absorption spectra of 1-NP(Zn) and 2-NP(Zn) showed a Soret band (S$_2$) at 405.5 nm and Q bands (S$_1$) at 532.5 and 570 nm in dichloromethane. All bis(zinc) complexes of NDP showed split Soret bands (Figure 1), but the shape and peak position of Q bands of these dimers were unchanged relative to 1-NP(Zn) and 2-NP(Zn), except for 1,3-NDP(Zn$_2$) and 1,4-NDP(Zn$_2$), which showed Q bands at 538 and 573 nm. While the head-to-tail dimer 2,6-NDP(Zn$_2$) displayed a mainly red-shifted Soret band at 412 nm, the face-to-face dimers 1,8-ADP(Zn$_2$) and 1,8-BDP(Zn$_2$) displayed a blue-shifted Soret band at 392 and 388 nm, respectively. The relative intensities of the split Soret bands changed depending upon the dihedral angle of the two porphyrin rings.[4] These split Soret bands did not exhibit a solvent and temperature dependence, reflecting the restricted orientations of

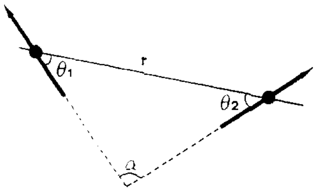
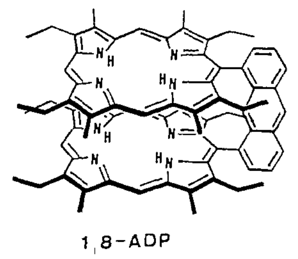
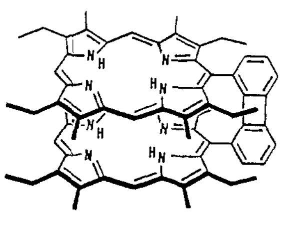


Figure 2. Oblique arrangement of two transition dipole moments.



1,8-ADP



1,8-BDP

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(2) (a) Chang, C. K.; Abdalmuhdi, I. *J. Org. Chem.* **1983**, *48*, 5388–5390. (b) Chang, C. K.; Abdalmuhdi, I. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 164–165.

(3) The synthetic details and characterization by mass, UV–vis, and ^{1}H NMR spectroscopy of the molecules discussed in this paper will be reported elsewhere.

(4) The naphthalene-linked free-base porphyrins showed broadened Soret bands, the peak positions of which were also orientation-dependent as follows: 1-NP (403 nm), 2,6-NDP (409 nm), 1,3-NDP (409 nm), 1,7-NDP (398 nm), 1,8-ADP (386 nm), and 1,8-BDP (372 nm).

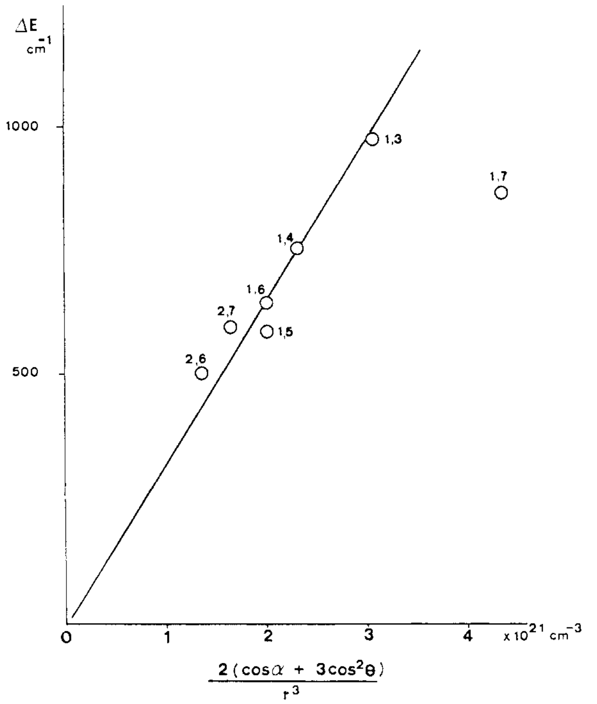

Figure 3. Plot of exciton coupling energy ΔE vs geometrical parameters, $2(\cos\alpha + 3\cos\theta_1\cos\theta_2)/r^3$.

the porphyrin rings relative to each other.[5] These systematic spectral changes are qualitatively in accord with the simple selection rule[6] predicted from the theory of exciton coupling,[7] which has often been used to explain the unusual electronic spectral properties of noncovalent porphyrin aggregates[8] and covalently linked porphyrin dimers.[2,9] However, to the best of our knowledge, there exists no reliable and systematic synthetic model for certification of the theory in fluid solution containing porphyrins, particularly on the dependence of coupling energy upon the geometrical parameters. According to the theory,[7] the dipole-dipole exciton splitting energy, ΔE, in the oblique geometry as shown in Figure 2, is given by the equation:

$$\Delta E = \frac{2|M|^2(\cos\alpha + 3\cos\theta_1\cos\theta_2)}{r^3} \qquad (1)$$

where M is the transition dipole moment of the monomer.[10] As shown in Figure 3, a plot of (ΔE) vs the geometrical parameter,[11] $2(\cos\alpha + 3\cos\theta_1\cos\theta_2)/r^3$, showed a good linear correlation between these two quantities.[12] From the slope, the magnitude of the transition dipole moment of the monomer effective for the exciton coupling was determined to be 7.9 D. This is in good agreement with the value (9.7 D) of the transition dipole moment of the monomer, which is calculated from the absorption spectra of 1-NP(Zn). These results indicate the appropriateness of the treatment of the simple exciton theory for this covalently linked system in solution.

The fluorescence properties of NDP(Zn_2) were virtually identical with those of 1-NP(Zn) and 2-NP(Zn) except for 1,3-NDP(Zn_2) and 1,4-NDP(Zn_2), indicating the absence of significant perturbation in their S_1 states in contrast to the strong exciton coupling of their S_2 states. The slightly perturbed fluorescence spectra and reduced fluorescence lifetimes[13] of 1,3-NDP(Zn_2) and 1,4-NDP(Zn_2), which is in line with their red-shifted Q bands, may be due to through-bond interaction. The fluorescence quantum yield of 1,8-ADP(Zn_2) was about one-third those of NP(Zn), and 1,8-BDP(Zn_2) was nearly nonfluorescent. These observations indicated the maximal exciton interaction in the face-to-face geometry, which resulted in the significant perturbation even in their S_1 states.

Geometry-restricted dimeric porphyrins described in this paper will be useful for studies on intramolecular excitation energy transfer and electron-transfer processes. We are currently using fast optical techniques to prove the orientation dependence of these processes in these dimeric porphyrins.

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(5) Restricted geometry of NDP is also deduced from the fact that all their monozinc complexes exhibit a single rapidly decaying component (10–30 ps) in the fluorescence of the zinc porphyrin, which is due to an efficient excitation energy transfer from the zinc porphyrin to the free-base porphyrin. A. Osuka and K. Maruyama, unpublished results.

(6) A simple selection rule for dimers of dye molecules was given by Kasha in ref 7a as follows: a spectral blue-shift for the face-to-face dimer, a spectral red-shift for the head-to-tail dimer, and band splitting for the oblique dimer.

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(10) On the basis of the C_{2v} symmetry of π-system of the zinc 5-aryl-2,3,7,8,12,13,17,18-octaalkylporphyrin, it may be appropriate to place the Soret transition (π–π*) dipole moment of the monomer to the 5–15 direction.

(11) The split Soret bands of NDP were fitted to two gaussian bands, from which the exciton splitting energy ΔE was estimated. The geometrical parameters were estimated from space-filling models.

(12) The deviation of 1,7-NDP(Zn_2) from the plot may indicate the limitation of the theory based on the dipole–dipole approximation, which may fail at very small separation r.

(13) From picosecond time-correlated single photon counting measurement, the fluorescence lifetimes of 1,3-NDP(Zn_2) and 1,4-NDP(Zn_2) were determined to be 1.25 and 1.28 ns, respectively, while those of 1-NP(Zn), 2-NP(Zn), and the other NDP(Zn_2) were found to be 1.5 ns.

A Novel Photorearrangement of 1-Silyl 1,2-Diones: Generation of Siloxyketenes

Bradford B. Wright†

Science Research Laboratory
Corporate Research Laboratories
3M Company, 201-3N-05, St. Paul, Minnesota 55144

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The photochemistry of acylsilanes has been extensively studied.[1] Upon excitation a 1,2-shift of silicon from the carbonyl carbon to oxygen occurs which results in a siloxycarbene.[2] The siloxycarbene then undergoes a chemical reaction with an added trapping agent, or thermally reverts back to the initial acylsilane.[3]

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