Table I. Band Positions (cm^{-1}) and Assignments for the 1:1 $(CH_3)_3Ga{\cdot}AsH_3$ Molecular Complex in Argon Matrices

product	parent[a]	assignment
520	526	ν_3, GaC_3 sym st
565	576	ν_{16}, GaC_3 antisym st
892, 895	912	ν_2, AsH_3 sym def
989	1003	ν_4, AsH_3 antisym def
2175, 2181	2140	ν_1, AsH_3 sym st
2191, 2201	2150	ν_3, AsH_3 antisym st

[a] From ref 13-15.

on a Mattson Cygnus FTIR spectrometer at 1-cm^{-1} resolution. A number of the matrices were irradiated by the 193-nm output of a Lambda Physik EMG 103 MSC laser. In some cases, samples were irradiated after deposition (in situ), while in other experiments, irradiation was concurrent with deposition. The laser repetition rate was 5 Hz, with a pulse duration of approximately 10 ns and a pulse energy of up to 200 mJ.

$(CH_3)_3Ga$ and AsH_3 were codeposited in a number of experiments, over a wide range of concentrations. When a sample of $Ar/(CH_3)_3Ga = 500$ was codeposited with a sample of $Ar/AsH_3 = 500$, several new absorptions were observed that were not present in the blank experiments of either reagent, as shown in Figure 1. These include sharp, intense bands at 520 and 565 cm^{-1}, a doublet at 892 and 895 cm^{-1}, a band of medium intensity at 989 cm^{-1}, and a multiplet of bands near 2190 cm^{-1}. When the concentration of either reagent was increased, the intensity of the product bands increased as well. When the reagents were premixed and codeposited in the single-jet mode, the same product absorptions were observed.

Each of the product absorptions falls near a fundamental of either[13] $(CH_3)_3Ga$ or[14] AsH_3, indicating that both reagents have maintained their structural integrity, yet are perturbed in the product species. Two fundamentals of $(CH_3)_3Ga$ were perturbed, the GaC_3 symmetric and antisymmetric stretching modes, which would be expected for an interaction at the gallium center. All four fundamentals of AsH_3 were perturbed, in the same direction as and of similar magnitude to their shifts in the $HF{\cdot}AsH_3$ complex.[15] These observations strongly support the formation of a complex between $(CH_3)_3Ga$ and AsH_3. Consideration of the dilutions employed here and the fact that only a single product species was observed argues that the stoichiometry of the complex is 1:1. *This, then, represents the first positive identification of the* $(CH_3)_3Ga{\cdot}AsH_3$ *adduct.*

Band assignments for the complex may be made by comparison to the spectra of the parent species[13,14] and are presented in Table I. It is interesting to note that the symmetric GaC_3 stretch is dramatically activated in the complex compared to the parent, where it is nominally forbidden. This indicates a significant distortion of the GaC_3 skeleton from planarity in the complex. Also, the antisymmetric GaC_3 stretch and the antisymmetric AsH_3 deformation, both of which are doubly degenerate in the parent species, did not split upon complex formation. This indicates that they remain degenerate and that the effective symmetry of the complex is C_{3v}.

In situ irradiation of matrices containing the adduct led to no changes in the spectrum. However, when samples were irradiated with the laser at 193 nm during deposition, several new features were observed, including bands at 493 and 1139 cm^{-1}. These bands were not present when either precursor was irradiated alone during deposition. While analysis and assignment of these product bands is in progress, these results suggest that the adduct undergoes photochemical rearrangements after excitation at 193 nm. Lack of photochemistry with in situ irradiation is likely due to recombination induced by the matrix cage.

The observation of a stable 1:1 adduct here suggests that this species should also be observable in the gas phase, and the spectral data reported here may guide researchers studying the gas-phase chemistry of this system. While the environment of a CVD reactor is quite different from the conditions in the present study, this adduct *may* also be present during the CVD process.

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Synthesis of Completely Fixed Porphyrin–Quinone Compounds and the Mutual Orientation Effect on Electron Transfer

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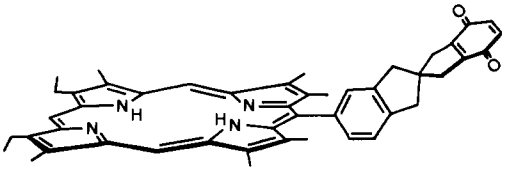
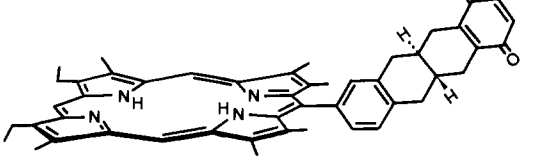
The requirements of structural factors (the separation distance and the mutual orientation of a redox pair) for electron transfer have been the subject of lively investigations in recent years in connection with the primary process of photosynthesis, and a number of model compounds have so far been prepared.[1] The distance dependence[2] on electron-transfer rates is well-recognized by the synthesis of systematic donor–acceptor linked molecules with rigid organic spacers at fixed distances,[3-5] while little is known about the orientation effect[6] because of the lacking of suitable compounds with fixed orientation of different kinds. We report here the synthesis of compounds **1**[7] and **2**, where a porphyrin and



1



2

a quinone ring are connected with a rigid spacer of spiro[4.4]-

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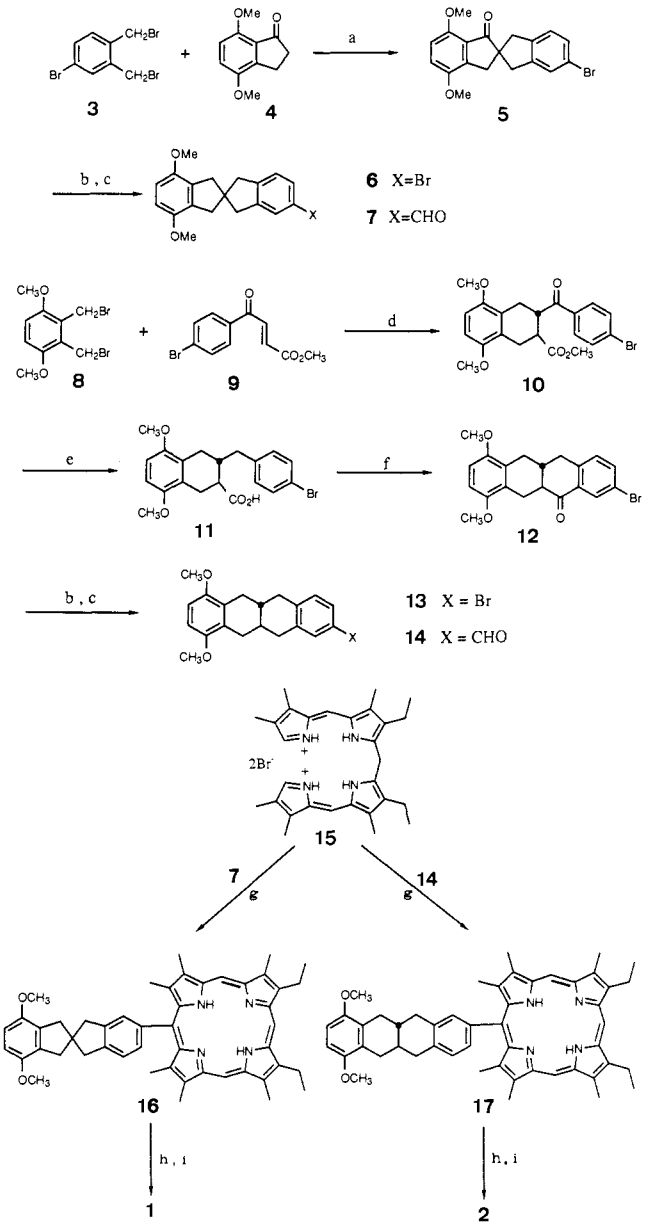
Scheme I[a]



[a] (a) NaH, THF. (b) CF_3CO_2H, Et_3SiH. (c) *n*-BuLi, THF, DMF. (d) Zn, dioxane. (e) NH_2NH_2, KOH, $(HOCH_2CH_2)_2O$. (f) CH_3SO_3H. (g) HBr, CH_3OH. (h) BBr_3, CH_2Cl_2. (i) PbO_2, CH_2Cl_2.

nonane or *trans*-decalin unit, so that the mutual orientation of the two chromophores is fixed at a similar separation distance without rotational freedom.[8] On the basis of molecular model consideration, edge-to-edge (or center-to-center) distances are quite similar in **1** and **2**; i.e., 8.2 Å (12.5 Å) for **1**[9] and 8.6 Å (12.9 Å) for **2**. Moreover, the angle between a line passing through the meso position attaching to the phenyl group and the transannularly situated meso position and a line connecting the two centers of the benzene ring and the quinone ring is the same (150°) in **1** and in **2**. The only major structural difference is the mutual orientation of the two π-systems. Thus, the dihedral angle of the two ring planes is 150° in **1**, while the corresponding planes of **2** are perpendicular with each other.

Table I. Fluorescence Lifetimes (τ) and Electron-Transfer Rates (k_{et}) of **1**, **2**, and Related Compounds

compd	solvent	τ (ns)	k_{et} (s^{-1})
1	THF	2.6	3.3×10^8
16	THF	16.8	
2	THF	8.2	6.5×10^7
17	THF	17.4	
1	DMF	2.0	4.4×10^8
16	DMF	16.8	
2	DMF	6.9	8.7×10^7
17	DMF	17.3	

The synthesis of **1** and **2** was carried out as shown in Scheme I. The coupling reaction of **3** and **4** afforded spiroketone **5** in 17% yield, which was reduced with Et_3SiH–CF_3CO_2H to give **6** in 69% yield. Treatment of **6** with BuLi and then with DMF gave **7** in 62% yield. Diels–Alder adduct **10**, derived from **8** and **9**, was reduced with Wolff–Kishner reagents to yield **11** in 86% yield. Ring closure of **11** with methanesulfonic acid gave a 1:1 mixture of the cis and trans fused isomer of **12** in 30% yield. Treatment of the mixture with a solution of 5% NaOH in H_2O–EtOH (1:1) under reflux for 4 h gave quantitatively the trans isomer **12**. The stereochemistry of the junction was determined to be trans on the basis of the value of the vicinal coupling constant (J = 14 Hz) in J resolved 2D NMR. Aldehyde **14** was prepared in two steps from **12** in a total yield of 64% in a manner similar to the synthesis of **7** from **5**. Condensation reaction of **7** or **14** with linear tetrapyrrole **15**[11] was carried out in the usual manner[12] to give **16** in 42% yield and **17** in 17% yield. The dimethyl ethers **16** and **17** were demethylated by treatment with BBr_3, oxidized with PbO_2, and purified by preparative layer chromatography (silica gel, chloroform–ether 19:1) to afford **1**[13] (82% yield) and **2**[14] (88% yield).

Electronic spectra show that there is no appreciable interaction in the ground state between the two composite chromophores in **1** and **2**. Fluorescence intensities of the quinone-linked porphyrins are decreased as compared with those of the corresponding reference compounds **16** and **17**. Thus, the relative fluorescence yields (I/I_0) in THF are 0.16 for **1** and 0.55 for **2**. Fluorescence lifetimes of **1**, **2**, **16**, and **17** were measured in two solvents by the single photon counting technique by using a picosecond dye laser (second harmonic of pyridine-1) exciting at 355 nm with a pulse width of 0.8 ps (fwhm), and the values are summarized in Table I. Reflecting their rigid structure, the observed fluorescence decays fit to single exponential curves. On the basis of the fluorescence lifetimes, electron-transfer rates, summarized in Table I, are estimated by using the following relation: $k_{ET} = \tau^{-1} - \tau_{ref}^{-1}$ with k_{ET} = electron-transfer rate, τ = lifetime of the quinone-linked porphyrins, and τ_{ref} = lifetime of the reference substances. We also examined picosecond time-resolved absorption spectra of **1** and observed the $S_n \leftarrow S_1$ absorption spectra, the decay time of which agreed with that of fluorescence. However, it was difficult to clearly detect the porphyrin–quinone ion pair state because of its charge recombination decay being faster than the charge separation[15] in the polar solvents examined here, which is largely

(8) The rotation of the mesophenyl groups in **1** and **2** is restricted by neighboring methyl groups. See: ref 8 in Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562–5563.

(9) The distances were estimated by assuming planar conformation for indan framework. In view of the fact[10] that cyclopentane has several conformations due to the puckering motion with low-energy barrier (few kcal/mol), similar conformational change might be possible for the spiro[4.4]nonane units of **1**. However, even in the envelope conformation with shortest edge-to-edge distance between the two chromophores, the distance remains roughly unchanged (8.0 Å).

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(13) **1**: UV-vis (THF) 248, 401, 500, 531, 572, 625 nm; ^{1}H NMR (360 MHz, $CDCl_3$) δ 10.13 (s, 2 H), 9.92 (s, 1 H), 7.73 (d, 1 H, J = 7 Hz), 7.57 (s, 1 H), 7.38 (d, 1 H, J = 7 Hz), 6.64 (s, 2 H), 4.04 (q, 4 H, J = 7 Hz), 3.61 (s, 6 H), 3.52 (s, 6 H), 3.08 (s, 2 H), 2.79 (d, 2 H, J = 17 Hz), 2.64 (s, 2 H), 2.54 (d, 2 H, J = 17 Hz), 2.38 (s, 6 H), 1.87 (t, 6 H, J = 7 Hz), −3.20 (br s, 2 H); MS 698 (M^+).

(14) **2**: UV-vis (THF) 248, 403, 502, 533, 573, 627 nm; ^{1}H NMR (360 MHz, $CDCl_3$) δ 10.13 (s, 2 H), 9.93 (s, 1 H), 7.79 (d, 1 H, J = 7 Hz), 7.73 (s, 1 H), 7.42 (d, 1 H, J = 7 Hz), 6.52 (d, 1 H, J = 10 Hz), 6.40 (d, 1 H, J = 10 Hz), 4.06 (q, 4 H, J = 8 Hz), 3.63 (s, 6 H), 3.52 (s, 6 H), 2.50 (s, 3 H), 2.49 (s, 3 H), 1.88 (t, 6 H, J = 8 Hz), 1.8–3.4 (m, 10 H), −3.1 (br s, 2 H); MS 712 (M^+).

determined by its energy gap dependence.[16] Table I shows that the electron transfer in **1** is faster than **2** by about a factor of 5 both in THF and in DMF. The difference is probably attributable to the favorable orientation of **1** for the electron transfer, since the donor and acceptor are separated by almost the same distance and the same number of bonds (seven bonds) in **1** and **2**. However, there is some possibility[17] that the σ-orbitals of the spacer in **1** are much more involved in electron transfer by super exchange mechanism than is **2**. Quantitative evaluation of electron-transfer rates by such a mechanism is difficult at this stage, and further interpretation must await theoretical calculations of the interaction matrix element[18] for electron transfer. Compounds **1** and **2** clearly demonstrate that the relative orientation between the porphyrin and quinone is a factor in the photodriven charge separation reaction.

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Biosynthesis of Sinefungin: On the Mode of Incorporation of L-Ornithine

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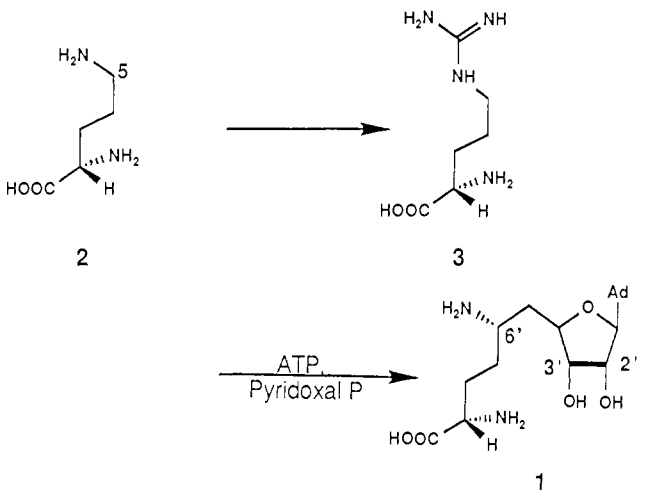
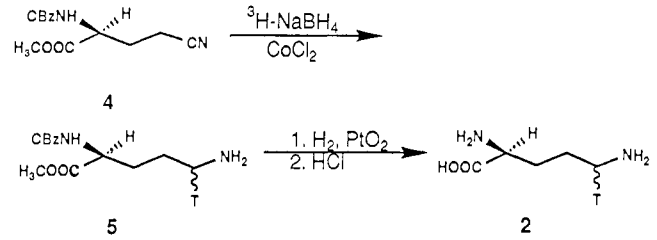
Sinefungin (**1**) is a nucleoside antibiotic isolated from the fermentation broth of *Streptomyces griseolus* and *Streptomyces incarnatus*.[1,2] Sinefungin exhibits antifungal[1] and antiviral[3] activity as well as potent activity against a number of protozoal parasites.[4] It is also a powerful inhibitor of *S*-adenosylmethionine dependent methyltransferases.[5] The biosynthesis of sinefungin was first scrutinized by Berry and Abbott.[6] These authors administered a number of ^{14}C-labeled compounds to *S. griseolus*, and on the basis of the observed incorporation levels, they suggested that sinefungin is formed by the condensation of L-ornithine (**2**) with adenosine. More recently, the biosynthesis of sinefungin has been examined in cell-free extracts of *S. incarnatus* by Robert-Gero and co-workers.[7] The results of these investigations suggested that sinefungin is biosynthesized from L-arginine (**3**)

Scheme I



Scheme II



and ATP, with a requirement for pyridoxal phosphate (Scheme I). We now present the results of our own studies on the mode of incorporation of L-ornithine into sinefungin. These studies shed additional light on the mechanism of sinefungin biosynthesis.

Preliminary incorporation experiments were carried out by administration of [U-^{14}C]-L-ornithine and [U-^{14}C]-L-arginine to *S. griseolus*. Since the incorporation levels were similar (data not shown), additional experiments were conducted with L-ornithine, which is known to be the precursor of L-arginine in vivo.[8] (5-^{13}C)-L-Ornithine was synthesized from (^{13}C)KCN by using a procedure developed to prepare the corresponding ^{14}C-labeled compound.[9] Administration of this precursor to *S. griseolus* yielded sinefungin that exhibited clear enrichment at the expected position of the antibiotic (Table I, experiment 1). Ornithine is thereby shown to be a specific precursor of sinefungin. We next examined the origin of the amino group present at C-6′ of the antibiotic. (5-^{15}N,5-^{13}C)-L-Ornithine synthesized from (^{15}N, ^{13}C)KCN was supplied to the sinefungin fermentation and the isolated antibiotic examined by ^{13}C NMR spectrometry. Since the enriched signal for C-6′ appeared as a doublet, one can conclude that the amino group present at C-6′ is derived from the δ-amino group of ornithine (Table I, experiment 2).

The most novel feature of sinefungin biosynthesis is the formation of a carbon–carbon single bond between C-5 of ornithine and C-5′ of an adenylyl moiety. The stereochemistry of C–C bond formation is therefore a matter of some interest. This problem was first approached by utilizing (5*RS*)-[5-^{3}H]-L-ornithine as a sinefungin precursor. The labeled ornithine was synthesized by reduction of the nitrile ester **4**[9] with sodium borotritide in the presence of cobalt chloride[10] to yield the tritiated amine **5**. The labeled amine was then converted into tritiated L-ornithine by hydrogenolysis of the CBz group and hydrolytic removal of the methyl ester (Scheme II). Administration of the tritiated L-ornithine to *S. griseolus* in conjunction with [U-^{14}C]-L-ornithine

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