

obtained in each case. In solution, the Norrish type II^a cleavage product **4** (Scheme I) predominated, accompanied by lesser amounts of the type II cyclobutanols **2** (cis) and **3** (trans).^{7b} In a typical low conversion run, the **2**:**3**:**4** ratio was 1.5:3.5:5. In contrast, the photoreaction of the platelike crystals was essentially completely stereoselective for *cis*-cyclobutanol **2** (>95% by gas chromatography), and the needlelike crystals, whether prepared by annealing or recrystallization, afforded the *trans*-cyclobutanol derivative **3** with greater than 90% stereoselectivity; in neither solid-state photoreaction was there any evidence for the formation of cleavage product.⁴ Control experiments showed that as little as 1% of this material could have been detected readily.

The photoproducts were isolated by silica gel column chromatography and identified on the basis of their spectroscopic properties.⁸ Particularly informative were the ¹³C NMR spectra, in which the ring junction C-H carbon of the *cis*-cyclobutanol **2** (easily identified by the attached proton test⁹) appears at 50.08 ppm, whereas the analogous signal for the *trans*-cyclobutanol **3** occurs at 43.71 ppm. This large chemical shift difference has been observed in nine other *cis*/*trans* pairs analogous to **2**/**3** and appears to be general;^{3,10} in four of the ten cases (but not in the case of compounds **2** and **3**), the stereochemical assignments were verified by X-ray crystallography.

Inspection of the conformational stereodiagrams reveals that, in the case of the plate dimorph (Figure 1a), there are two non-equivalent γ -hydrogen atoms, H5 and H20, whose abstraction must be considered in analyzing the solid-state photoreactivity; H5 lies 3.3 Å from O1 and H20 is situated 2.8 Å from O1'. Previous work from our laboratory has established an upper limit of ca. 3 Å for *d*, the C=O...H _{γ} distance,¹¹ and this makes it likely that H20 is the hydrogen atom that is abstracted in the solid state.¹² Also important in determining hydrogen abstractability is the angular relationship between the abstracting and abstracted atoms.^{11,13} Owing to the involvement of the oxygen atom n-orbital in the γ -hydrogen abstraction process,¹⁴ the angle τ , defined as the degree to which the γ -hydrogen atom deviates from the mean plane of the carbonyl group, should be as close to 0° as possible, and the C=O...H angle Δ should ideally lie in the range 90–120°. The values of τ for H5 and H20 are identical (52°), and the values of Δ are 53 and 82°, slightly favoring abstraction of H20. Regardless of which hydrogen atom is abstracted, however, formation of *cis*-cyclobutanol is predicted to be preferred. This follows from the fact that the abstracting oxygen atom and the nonabstracted γ -hydrogen (H19 or H6) bear a syn relationship to each other in the plate dimorph, and assuming a least-motion solid-state process involving retention of configuration at both centers, these atoms will end up *cis* to one another in the photoproduct. This

is precisely the experimentally observed result.

A similar analysis successfully rationalizes the formation of *trans*-cyclobutanol **3** from the needle dimorph of compound **1**. In this case, the γ -hydrogens to consider are H6 (*d* = 2.7 Å, τ = 49°, Δ = 85°) and H20 (*d* = 3.3 Å, τ = 57°, Δ = 58°). Abstraction of H6 is clearly preferred, and this leaves H5 and O1 in an anti relationship which becomes *trans* in the final photoproduct. Using similar reasoning it is apparent that abstraction of H20 should lead to *cis*-cyclobutanol, and 5–10% of this product is formed in the solid-state photolysis of the needle dimorph. It is difficult to say whether this is the result of abstraction of H20 or is due to loss of control of biradical closure following abstraction of H6. In this context, a brief discussion of the solution-phase photochemistry of **1** is in order. As was the case with the 16-, 18-, and 22-membered ring analogues,³ all selectivity is lost in this medium, a result that can be attributed to reaction from alternate conformers (of which there are many) and/or conformational isomerization of the intermediate 1,4-biradicals prior closure.

In summary, we draw attention to the analogy between our results with the macrocyclic diketones and the classic studies of Schmidt and co-workers on the solid-state [2 + 2] photodimerization of the cinnamic acids.¹⁵ In both cases, distance and geometric requirements for photoreaction have been established, and the structure and stereochemistry of the products are directly and simply related to the molecular and crystal structure of the reactants as shown by the study of polymorphic crystal modifications. Studies from our laboratory of other macrocyclic diketones support the general picture described above, and these results will be published in the near future.

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New Mode of Porphyrin Complexation with Nucleobase

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Molecular recognition of nucleobases by artificial receptors is of current interest in artificial receptor chemistry. By analogy with the interactions operating in DNA and/or RNA duplexes, the hydrogen-bond interaction is considered to be the most general and important driving force for molecular recognition of nucleobases.¹ Recently, we reported that nucleobases strongly interact with porphyrin metal complexes through coordination,² which suggests the possibility of another type of artificial receptor using a nonbiological recognition mode for nucleobases.³

Herein we report a new mode of adenine recognition by a porphyrin zinc complex involving both a hydrogen-bonding and

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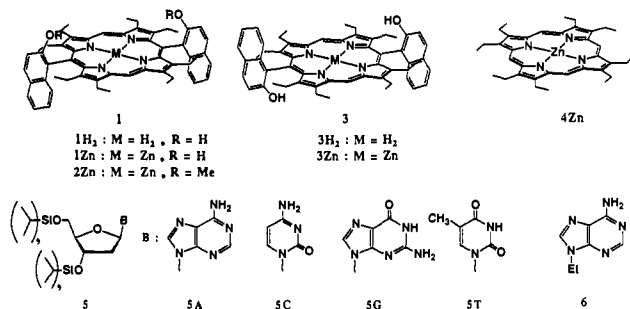
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Table I. Association Constants between Porphyrin and Nucleoside Derivatives^a

nucleoside	association constant, M ⁻¹ (SD) ^b					
	1Zn	2Zn	3Zn ^c	4Zn ^c	1H ₂	3H ₂
5A	5000 (400) ^e 410 (30) ^f	2400 (200)	1800 (100)	600 (100)	470 (100)	<i>d</i>
5G	1300 (200)	<i>d</i>	900 (200)	150 (50)	<i>d</i>	<i>d</i>
5C	300 (50)	650 (100)	170 (50)	80 (50)	<i>d</i>	<i>d</i>
5T	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>	—	—
6	41 000 (8000) ^e 2900 (500) ^f	5300 (600)	4300 (600)	1400 (100)	1900 (100)	<i>d</i>

^a In CH₂Cl₂, at 15 °C. ^b Standard deviations (SD) are given in parentheses. ^c A statistical correction, $K = K_{\text{obsd}}/2$, is applied because of the plane symmetry of porphyrin. ^d An appreciable absorption change is not observed. ^e The value for the first 1:1 complex formation. ^f The value for the second 1:2 complex formation (see text).

Chart I

a coordination interaction which operate independently to afford a new type of 1:2 complex between the porphyrin zinc complex and adenine derivatives.

The porphyrins investigated as artificial nucleoside receptors are octaethylporphyrin derivatives and their Zn complexes, 1–4⁴ (Chart I). Spectroscopic titrations using 3',5'-bis(*O*-triisopropylsilyl)deoxyribonucleosides 5⁵ in CH₂Cl₂ solution demonstrate that, by addition of nucleosides, except 5T, all Zn complexes show significant red shifts of their Soret bands, indicating complex formation.

The most interesting aspect of the present porphyrin–nucleoside complexation appears in the combination of 5A and 1, which has two hydroxyl groups on one side of porphyrin, i.e., 1 is unexpectedly found to form a complex with 5A even when the metal-free porphyrin, 1H₂, is employed. Since the trans isomer 3H₂ does not show such strong complexation with 5A, the observation indicates that 1H₂ may bind 5A through *simultaneous double hydrogen bondings without the assistance of coordination interaction*.⁶ These observations strongly suggest that 1Zn should be a potential “both-sides receptor” for adenine which utilizes a hydrogen-bonding side and a coordinate side as recognition sites. Thus, the titration experiment for 1Zn and 5A was very carefully analyzed. In this case, no tight isobestic point is found in the region of 380–460 nm, in contrast with other systems showing clear isobestic points, and a biphasic absorption change is observed at 420 nm as shown in Figure 1a, which indicates that the system contains not only 1:1 but also 1:2 complex formation. The nonlinear curve fitting analysis for the observed biphasic absorption change gives two association constants with excellent agreement of the theoretical curve with the experimental one. The association constants thus obtained are summarized in Table I together with those of other systems. It may be particularly noteworthy that, in contrast with 1Zn, both 2Zn and 3Zn form only simple 1:1 complexes with nucleoside derivatives. These results strongly indicate that the existence of two OH groups oriented toward the

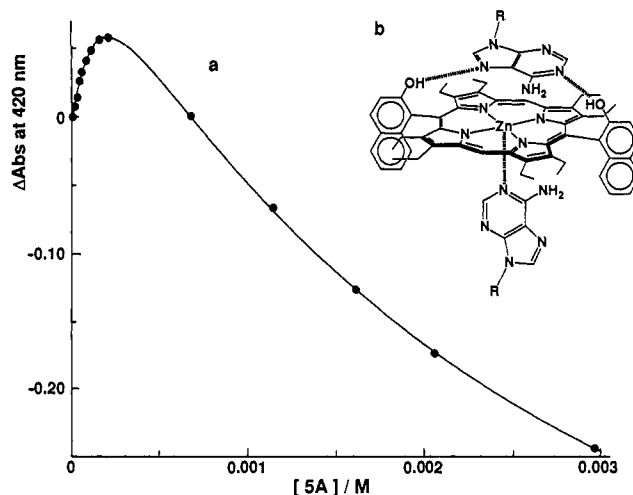


Figure 1. (a) Absorption change at 420 nm observed for titration with 5A. [1Zn]_{total} = 5.0 × 10⁻⁶ M, at 15 °C in CH₂Cl₂ (●, observed points; —, theoretical curve). The theoretical curve for independent binary equilibrium is generated from the equation $\Delta\text{Abs} = (\epsilon_1 - \epsilon_0)[1\text{Zn}\cdot 5\text{A}] + (\epsilon_2 - \epsilon_0)[1\text{Zn}\cdot 5\text{A}_2]$, where ϵ_0 , ϵ_1 , and ϵ_2 are molar extinction coefficients of 1Zn, 1Zn·5A, and 1Zn·5A₂, which concentrations are calculated by using K_1 and K_2 . In calculation, the values of 33 000 (SD 1000) and -120 000 (SD 3000) cm⁻¹ M⁻¹ are used as $\epsilon_1 - \epsilon_0$ and $\epsilon_2 - \epsilon_0$, which are also optimized by the least-squares method. (b) One possible structure of the 1:2 complex of 1Zn and 5A or 6.

same side of the porphyrin plane is essential for 1:2 complex formation.

When more sterically unhindered 9-ethyladenine (6) is used as a guest molecule, the behavior of complex formation is very similar to that of 5A, i.e., titration patterns for 1Zn and other porphyrins are again biphasic and monophasic, respectively, though the observed association constants are 2–8 times larger than those for 5A, and 6 is also bound by the metal-free porphyrin, 1H₂, but not by 3H₂ (Table I). These observations suggest that two adenine molecules are bound by 1Zn at two independent recognition sites, for example, as shown in Figure 1b.⁷ The existence of the hydrogen bonds between 1Zn and 6 is confirmed by ¹H NMR experiments, which show a significant downfield shift of the signal of OH protons of 1Zn together with upfield shifts of those of adenine protons.⁸ Since these hydrogen bondings are observed even at the low concentration of 6 where the 1:1 complex is dominant, the first binding step is tentatively assigned to that for the hydrogen-bonding site.⁹ Finally, it should be noted that the association constant (K_1) for this first binding step of 6 is one of

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(6) The association constant of 2-naphthol with 5A in CH₂Cl₂ at 15 °C is evaluated to be less than 80 M⁻¹.

(7) The preliminary X-ray analysis of the complex of octaethylporphyrin-Rh(III) with 9-ethyladenine shows that adenine coordinates on Rh(III) at the N1 position.

(8) For example, the following values of $\Delta\delta$ (ppm), $\delta(1\text{Zn} + 6) - \delta(1\text{Zn}$ or 6), are observed under the conditions [1Zn] = 1.5 mM, [6] = 3.0 mM in CDCl₃ at 24 °C: +2.45 (OH of 1Zn), -3.09 (2 H of 6), -0.86 (8 H of 6), -1.35 (CH₂ of 6), -0.66 (CH₃ of 6).

(9) Although it is difficult to measure association constants for other simple alkylated nucleobases because of their low solubilities, the association constant for 1Zn–9-ethylguanine (1:1) is tentatively determined to be 3000 (SD 1000) M⁻¹.

the largest values ever reported for artificial adenine receptors.¹

Taking account of the wide variety of functions of porphyrin complexes, the present new 1:2 complex of **1**Zn with adenine derivatives is expected to offer unique applications both for nucleoside recognition and for its reactions. The detailed characteristics of the present nucleobase recognition are now being investigated in our laboratory.

Tertiary Amine Stabilized Dialane

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Tertiary amine adducts of alane are of interest as hydride sources for hydroalumination of unsaturated substrates,² for formation of derivatives of other metal complexes,³ and as precursors for chemical vapor deposition of aluminum metal.^{4,5} Despite this there are only a few structural studies, notably on monomeric H_3AlNMe_3 (**1**) (gas phase),⁶ $\text{H}_3\text{AlN}^n\text{Bu}_3$ (**2**),⁷ and $\text{H}_3\text{Al}(\text{NMe}_2)_2$ (**3**),⁸ polymeric $\text{H}_3\text{Al}(\text{TMEDA})$ (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) (**4**),⁹ and ionic species $[\text{H}_2\text{Al}(\text{N,N,N',N',N''-pentamethyldiethylenetriamine})]^+[\text{AlH}_4]^-$ and *trans*- $[\text{H}_2\text{Al}(\text{N,N,N',N''-tetramethylcyclam})]^+[\text{AlH}_4]^-$.

Using X-ray diffraction data we have shown that dimeric species possessing two bridging hydrides are a common solid-state structural unit for a variety of alane adducts with unidentate tertiary amines, including the well-known compound **1**, and we report a high-level theoretical study on the model compound H_3AlNH_3 . A dimeric structure for **1** alone has implications regarding (i) conflicting molecular weight determinations for this compound in solution, monomer versus some association; (ii) the higher vapor pressure of compound **3** compared to compound **1**;¹¹ and (iii) the generally accepted view that **1** is monomeric,⁴ as in the solid-state structure of the corresponding gallium compound, H_3GaNMe_3 .¹² In addition, the dimeric structures can be con-

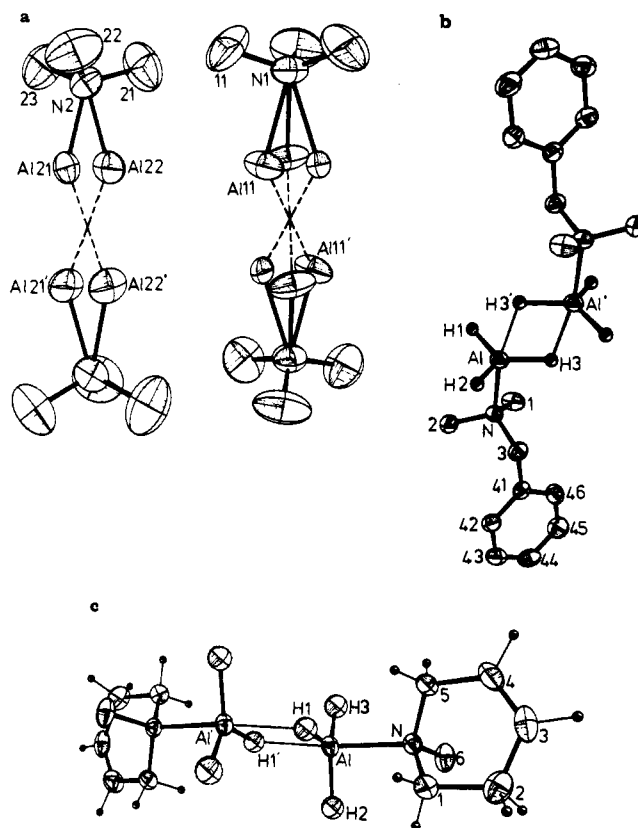
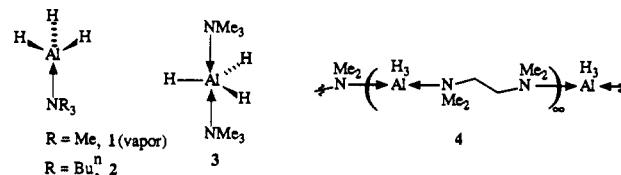


Figure 1. Projections of (a) $[\text{H}_3\text{AlNMe}_3]_2$ (**1**), (b) $[\text{H}_3\text{Al}(\text{NMe}_2\text{CH}_2\text{Ph})]_2$ (**5**), and (c) $[\text{H}_3\text{Al}(\text{NMe}_2\text{CH}_2\text{CH}=\text{CHCH}_2)]_2$ (**6**) with 20% thermal ellipsoids for non-hydrogen atoms and arbitrary radii for hydrogen atoms where shown. Molecules of **1** are disordered across 2 and 3 symmetry sites, Al(21,22) and Al(11).

sidered as tertiary amine adducts of the elusive dialane, $[\text{H}_2\text{Al}(\mu\text{-H})_2]$, for which theory predicts a binding energy comparable to that of the ubiquitous diborane, $[\text{H}_2\text{B}(\mu\text{-H})_2]$.¹³



The new adducts of alane, $[\text{H}_3\text{Al}(\text{NMe}_2\text{CH}_2\text{Ph})]_2$ (**5**) and $[\text{H}_3\text{Al}(\text{NMe}_2\text{CH}_2\text{CH}=\text{CHCH}_2)]_2$ (**6**), were prepared by treating LiAlH_4 with the hydrochloride salt of the amine, eq 1, and purified by sublimation in vacuo at 100 °C (0.1 mmHg) (for **5**) or recrystallization (for **6**).¹⁴ They decompose, yielding alu-

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(14) Compound **5**: To a slurry of LiAlH_4 (1.0 g, 26.2 mmol) in diethyl ether (50 mL) at -78 °C was added the anhydrous hydrochloride salt of *N*-benzylidimethylamine (4.5 g, 26.2 mmol) over 30 min. After 1 h at ca. 20 °C, volatiles were removed in vacuo and the product sublimed as colorless prisms (1.43 g, 33% yield): mp 75-76 °C dec >150 °C; ¹H NMR (250 MHz, C_6D_6 , 25 °C, TMS) δ 2.09 (s, 6 H, Me), 3.82 (s, 4 H, CH_2), 4.19 (br s, AlH), (m, 5 H, Ph); ¹³C NMR δ 42.6 (NMe), 61.0 (NCH₂), 128.4, 131.1, 132.1 (Ph); IR ν (cm⁻¹) 1770 (br, AlH); UV λ_{max} (nm) 219, 253. Found: C, 64.32; H, 9.41; N, 8.5. Calcd: C, 66.20; H, 8.58; N, 8.58. Compound **6**: To a slurry of LiAlH_4 (1.0 g, 26.2 mmol) in diethyl ether (20 mL) at 0 °C was added the anhydrous hydrochloride salt of 1-methyltetrahydropyridine (3.6 g, 26.9 mmol) over 10 min. After 1 h at ca. 20 °C, volatiles the mixture was filtered, concentrated in vacuo to ca. 10 mL, and cooled to -30 °C, yielding massive prisms (2.43 g, 70% yield): mp 68-71 °C dec >120 °C; ¹H NMR (250 MHz, C_6D_6 , 25 °C, TMS) δ 1.53 (m, 2 H, H_2C_5), 2.01 (s, 3 H, CH_3), 2.46 (t, 2 H, H_2C_6 , $J = 4.4$ Hz), 2.88 (m, 2 H, H_2C_2), 4.09 (br s, AlH), 4.97, 5.27 (2 m, 2 H, $\text{HC}_3,4$); ¹³C NMR δ 20.5 (C₅), 41.8 (CH₃), 49.9 (C₆), 52.5 (C₂), 121.5, 124.4 (C_{3,4}); IR ν (cm⁻¹) 1720 (br, AlH); UV λ_{max} (nm) 218. Found: C, 55.85; H, 10.95; N, 10.79. Calcd: C 56.67; H, 11.10; N, 11.02.