Excited-state energetics and dynamics of magnesium tetraphenylporphyrin cooled in supersonic expansions

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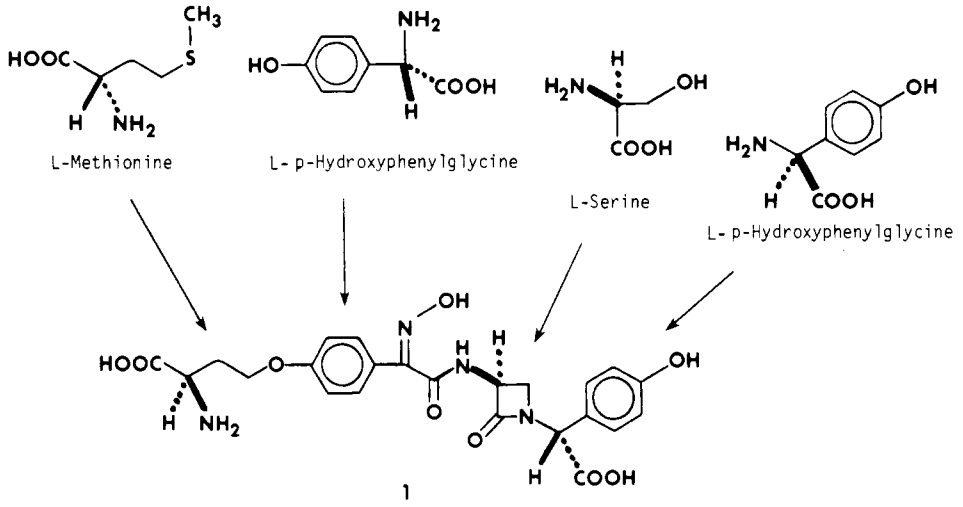
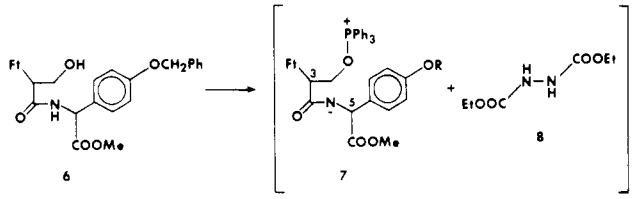
Chart I



the course of the cyclization indicated epimerization at one or more of the asymmetric centers. However, the absence of any detectable acrylamide product implied anion formation had not occurred at C-3.



Heartened by the success of the model reaction, we immediately sought to test this approach in an efficient, completely asymmetric synthesis of (−)-3-aminonocardicinic acid (**5**).[6,7,13,14] To that end *N*-phthaloyl-L-serine[15] was condensed with methyl D-(*p*-benzyloxyphenyl)glycinate[13] as above to afford **2** as a highly crystalline solid,[16] mp 189–191 °C, $[\alpha]_D = -118°$ (*c* 1.0, $CHCl_3$). The optically active peptide was treated under the dehydrating and workup conditions used previously. ^1H NMR analysis of the oily product again showed a 2:1 mixture of diastereomers **3a** and **4a**. Hydrogenation of this mixture gave **3b** and **4b** which upon crystallization from absolute ethanol gave pure **3b** [43%, mp 169–170 °C, $[\alpha]_D$ −239° (*c* 0.030, MeOH); lit.[13] mp 203–204°, $[\alpha]_D$ −236° (*c* 0.025, MeOH)],[17] establishing, as expected, that the stereochemical integrity of the serine α position remained intact throughout the reaction.[18] The optically pure β-lactam **3b** has been sequentially deprotected to (−)-3-aminonocardicinic acid (**5**) previously,[13] and hence its obtention constitutes formal completion of the synthesis.

Recognizing the similar acidities of the C-3, C-5, and amide hydrogens, the rapid and highly selective formation of β-lactam in the cyclization reaction is remarkable. Nonetheless, this observation linked with biosynthetic results[1] which show retention of both hydrogens in vivo at the serine β carbon through the course of four-membered-ring formation supports nucleophilic displacement of activated seryl hydroxyl[19] as the key step for β-lactam formation in nocardicin A.

Acknowledgment. We gratefully acknowledge financial support of the National Institutes of Health for the present work (5 R01 AI14937 and 5 S07 RR07041) and providing partial funding to acquire the Bruker WH-300 used (1P41 GM27512).

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(15) Hodges, R. S.; Merrifield, R. B. *J. Org. Chem.* **1974**, *39*, 1870–1872.

(16) Partial NMR (300 MHz, $CDCl_3$) δ 3.70 (s, 3 H, OMe), 4.05–4.13 (4 lines, 1 H, *A*BX H-4), 4.35–4.41 (4 lines, 1 H, A*B*X H-4), 4.98–5.02 (4 lines, 1 H, AB*X* H-3), 5.04 (s, 2 H, OCH_2Ph), 5.51 (d, J = 7 Hz 1 H, H-5), 6.96 (d, J = 8.5 Hz, 2 H, H-8), 7.30 (d, J = 8.5 Hz, 2 H, H-7); IR ($CHCl_3$) 1780, 1760 (sh), 1720, 1685, 1610, 1510, 1390, 1180 cm^{-1}.

(17) The overall yield of **3b**, after drying under high vacuum, is based on the *total* amount of peptide **2** used. The melting point observed in the present work for **3b** does not agree with that cited in the literature[13] and may represent an isomorph. However, with respect to all spectral data and specific rotation, agreement is exact.

(18) Facile base-catalyzed epimerization at C-5 has been observed in **3b**[13] and related esters.[6]

(19) Triethyl phosphite may be substituted for triphenylphosphine in the in vitro cyclization step with equal success.

Excited-State Energetics and Dynamics of Magnesium Tetraphenylporphyrin Cooled in Supersonic Expansions

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The merger between laser technology and supersonic beams[1] led to remarkable progress in spectroscopy of large molecules. Supersonic expansions[2] provide a source of ultracold "isolated" molecules, characterized by extreme rotational and vibrational cooling.[1,3,4] Laser spectroscopy of large molecules[3-14] seeded in

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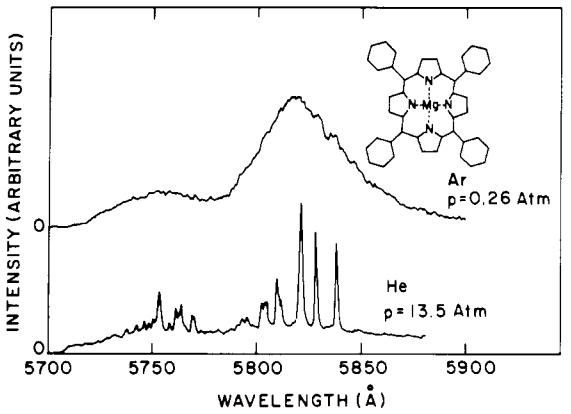

Figure 1. Fluorescence excitation spectrum in the region 5700–5900 Å of the isolated MgTPP molecule cooled in supersonic expansions. MgTPP heated in the sample chamber to 375 °C was seeded into Ar (p = 0.5 atm) or He (p = 13.5 atm) and expanded through a 100-μm nozzle. The exciting dye laser, with a spectral width of 0.3 cm^{-1}, crossed the beam at 1.5 mm down the nozzle.

supersonic expansions of inert gases allows for an increase of spectral resolution by about 3 orders of magnitude over conventional room-temperature gas-phase spectroscopy. It will be extremely interesting to apply these novel techniques to explore the excited-state energetics and intramolecular dynamics of electronically–vibrationally excited states of very large isolated molecules, which constitute models for the molecular systems involved in the basic processes of energy acquisition and storage in photobiology. We report the results of an experimental study of the fluorescence excitation spectrum of magnesium tetraphenylporphyrin (MgTPP) seeded in supersonic expansions of He. We have interrogated the two lowest $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ spin-allowed electronic transitions of the isolated, ultracold MgTPP molecule. These electronic vibrational excitations of MgTPP are of interest in relation to large-amplitude nuclear motion of nonrigid molecules and for the characterization of low-lying frequencies of photosynthetic pigments.[16] Novel spectroscopic information was obtained concerning the interstate coupling of the S_2 state in isolated MgTPP. In almost every porphyrin the $S_0 \rightarrow S_2$ excitation, giving rise to the celebrated Soret band, is extremely diffuse.[15] A notable exception involves the Soret band of zinc tetrabenzoporphine.[17] It is an open question whether the huge width ($\sim$1000 cm^{-1}) of the Soret band originates from ultrafast ($\sim 10^{-14}$s) intramolecular electronic radiationless transitions or is due to the "trivial" effects of thermal inhomogeneous broadening. Our experimental data demonstrate the occurrence of an electronic radiationless transition in the S_2 state of MgTPP on the ps (10^{-12} s) rather than on the fs (10^{-15} s) time scale.

The supersonic expansion of MgTPP (heated in the sample chamber to 350–380 °C) in He at pressures p = 3–13 atm and in Ar at p = 0.1–0.5 atm was conducted through a nozzle with a diameter D = 100 μm. The supersonic beam apparatus has been described elsewhere.[18] We have monitored the laser-induced fluorescence excitation spectrum from the seeded beams.

The fluorescence excitation spectra of MgTPP in the range 5700–5900 Å are shown in Figure 1. The supersonic expansion

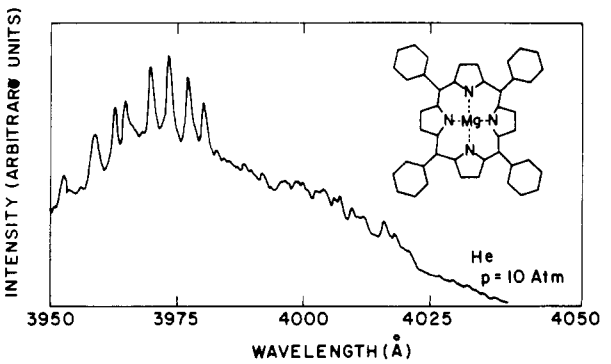

Figure 2. Fluorescence excitation spectrum in the region 3950–4050 Å of MgTPP heated in the sample chamber to 350 °C and cooled in a supersonic expansion of He. Other experimental conditions as in Figure 1.

of the nonrigid MgTPP in Ar at moderate pressures (p = 0.2–0.5 atm) results in a vibrationally hot molecule characterized by an unresolved "chemical-type", vibrationally congested spectrum. It is striking to note (Figure 1) the metamorphosis in the spectrum induced by effective cooling of MgTPP in high-pressure He. We have demonstrated that the fluorescence excitation spectrum of MgTPP in He corresponds to the bare molecule rather than to van der Waals complexes, as increasing the downstream temperature by varying the stagnation pressure from 15.5 to 6.7 atm did not affect the position and the relative intensities of the narrow spectral features, resulting only in the enhancement of the background quasi-continuous absorption which originates from low-frequency vibrational sequences. The spectrum of Figure 1 is due to the $S_0 \rightarrow S_1$ transition, i.e., the Q band.[15] Individual spectral features of this transition have a width (fwhm) of $\delta \sim$ 3 cm^{-1}, presumbably due to unresolved rotational structure. The four, intense, narrow, lowest-energy spectral features of MgTPP expanded in the He (Figure 1), whose relative intensities are independent of the downstream temperature, were attributed to excitations from the origin, $S_0(0)$, of the ground electronic state. The lowest-energy intense feature located at 5838 Å is assigned to the electronic origin of the $S_0 \rightarrow S_1$ transition. Two intense low-lying vibrational features in the S_1 manifold are observed peaking at 29 and 49 cm^{-1} above the electronic origin $S_1(0)$, which are attributed to 0–2 transitions of two distinct vibrational modes. The two low-frequency vibrational modes of $\sim$15 and $\sim$25 cm^{-1} involve large-amplitude torsional motion and/or out-of-plane and inplane bending of the phenyl groups relative to the prophyrin ring. Eight moderately weak vibrational features in the energy range 110–390 cm^{-1} above $S_1(0)$ are in good agreement with the positions of the fundamental frequencies of chlorophyll-a[16] interrogated by absorption spectroscopy and resonance Raman spectroscopy in n-octane at 4.2 K, providing interesting information regarding the characterization of model systems of biophysical interest.

Figure 2 portrays the fluorescence excitation spectrum of MgTPP in the range 3950–4050 Å, which corresponds to the $S_0 \rightarrow S_2$ excitation. The spectrum reveals a low-energy background, presumably due to traces of vibrational sequence congestion. The most striking feature of the Soret band is the well-resolved vibrational structure originating at 3980 Å. The mean spacing between adjacent lowest-lying vibrational features is 22 $\pm$ 2 cm^{-1}, which is tentatively attributed to even-parity vibrational excitations of the torsional motion of the phenyl groups. This large amplitude motion is characterized by a vibrational frequency of $\sim$11 cm^{-1} in the S_2 state. The line widths of these low-energy vibrational features (fwhm) in the S_2 state are $\bar{\delta} \simeq$ 8 cm^{-1}, being higher than typical widths $\delta \simeq$ 3 cm^{-1} in the S_1 configuration. Assuming that the excess line width in the S_2 state $\Delta = \bar{\delta} - \delta \simeq$ 5 cm^{-1} originates from intramolecular interstate radiationless transitions, probably involving the $S_1 \rightarrow S_2$ internal conversion, the lifetimes of the lowest vibrational excitations in the S_2 state of MgTPP are characterized by the decay lifetime $\tau = \hbar/\Delta \simeq 10^{-12}$ s. This approximate estimate of the lifetime of vibrational excitations in

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the Soret band of the isolated MgTPP molecule, together with the previous data[17] on the Soret band of zinc tetrabenzoporphine in solid Ar, strongly indicates that the almost universal extensive broadening reported for the Soret band of porphyrins[15] originates from thermal inhomogeneous broadening effects rather than from lifetime broadening. This conclusion is pertinent for the understanding of the quantitative aspects of intramolecular interstate radiationless processes in the photosynthetic pigments.

Chiral Catalysis of Additions of Alkyllithiums to Aldehydes[1]

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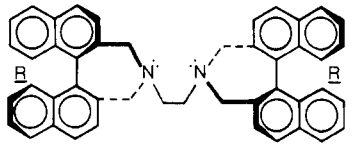
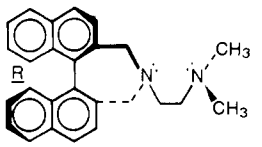
The well-known activation of organolithium reagents by complexation with tetramethylethylenediamine[2] suggested that derivatives **1** and **2** might serve as chiral catalysts for asymmetric induction in reactions of organometallic reagents. Hosts 1 and 2 were chosen for the following reasons. (1) Molecular models (CPK) of organometallic complexes of **1** and **2** indicate that the rigid naphthalene rings, coupled with the spirane structures, provide a high degree of "sidedness" to carbonyl groups ligated to complexed organometallics and that high asymmetric induction should result. (2) Both hosts contain C_2 axes, which reduces the number of possible conformations for diastereomeric transition states. Less averaging of host–guest interactions that favor opposite enantiomeric products should result. (3) The key intermediate in the synthesis of **1** and **2** is 2,2′-bis(bromomethyl)-1,1′-binaphthyl (**3**). The maximum rotations[3] and absolute configurations[4] of the enantiomers of **3** have been established and provide a convenient means of determining these properties for the enantiomers of **1** and **2**. We report here studies of chiral catalysis using (*R*,*R*)-**1**[5,6] and (*R*)-**2**[5,6] in the additions of alkyllithiums to aldehydes to give alcohols.



(*R*,*R*)-1



(*R*)-2

Exploratory additions of $CH_3(CH_2)_3Li$ to C_6H_5CHO with (*R*)-**2** as catalyst established the following facts. (1) Without the catalyst, the reaction takes place with 81% yield at −120 °C in Et_2O. (2) Under the same conditions with molar ratios of catalyst to RLi that varied between 1.1 and 1.4, (*R*)-$C_6H_5CH(OH)(CH_2)_3CH_3$ was produced with 57% enantiomeric excess (ee). With a ratio of 0.0077, only 7% ee of (*R*)-alcohol was produced. Thus the catalyzed addition rate exceeds the noncatalyzed rate by orders of magnitude but by a factor too small to provide useful catalyst turnover. Ratios of 1.2 ± 0.2 were used in subsequent *stoichiometric catalysis* experiments. (3) Optical yields increased sequentially from 4 to 58% (ee) as the solvent was changed from THF (−100 °C) to $C_6H_5CH_3$ (−80 °C) to $CH_3(CH_2)_3CH_3$–Et_2O (30:1, v/v, −120 °C) to $(CH_3O)_2CH_2$–$(CH_3)_2O$ (1:1, v/v, −120 °C) to $(CH_3O)_2CH_2$–Et_2O (1:1, v/v, −120 °C) to Et_2O at −120 °C. Variation in the volume of Et_2O by a factor of 10 provided the same results. Those reported here were obtained at the dilute end of the scale for convenience only. The reactions in Et_2O of methyl-, ethyl-, propyl-, and butyllithium with benzaldehyde complexed with (*R*,*R*)-**1** or (*R*)-**2** (molar ratios of 1.2 ± 0.2) and that of phenyllithium with pentanal were studied at −120 °C. The absolute configurations of the four product alcohols have been determined,[8] and maximum rotations have been reported.[9] We determined the dominant configurations and optical purities of our products from their optical rotations. The optical purities were also determined from the 200-MHz ^1H NMR spectra of their (+)-α-methoxy-α-[(trifluoromethyl)phenyl]acetic esters by Dale's method.[10] Table I records the results.

Chiral catalysis occurred in runs 1–9 to give optical yields of 92–22% ee.[11] The differences in free energies of the diastereomeric transition states leading ultimately to the two enantiomeric alcohols varied from 1 to 0.1 kcal mol^{-1}. The higher values are associated with three structural features: (1) the reactants with the higher steric requirements, (2) the more highly shaped and sterically confining catalyst, and (3) the use of benzaldehyde rather

† C.N.R.S. Postdoctoral Fellow, 1978.

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(5) All new compounds prepared here gave C and H analyses within 0.30% of theory and the expected ^1H NMR (200 MHz) and mass spectra.

(6) Treatment of **3**[3] with 0.5 mol equiv. of $H_2NCH_2CH_2NH_2$ in C_6H_6–Et_3N (reflux 65 h) gave **1** (79%). Racemic **3** gave a 1.2 ratio of meso[5] to racemic, **1**,[5] the latter of which was easily resolved with (−)-dibenzoyltartaric acid in 95% EtOH to give 41% of (*S*,*S*)-**1**,[5] $[\alpha]^{25}_{546}$ +256° (*c* 1.1, $CHCl_3$), and 31% of (*R*,*R*)-**1**,[5] $[\alpha]^{25}_{546}$ −251° (*c* 1.1, $CHCl_3$). From (*R*)-**3**[3] of $[\alpha]^{25}_{546}$ +197° (*c* 1, C_6H_6) was similarly produced 85% of (*R*,*R*)-**1** of $[\alpha]^{25}_{546}$ −255° (*c* 1, $CHCl_3$). Racemic **3**[3] with 2 mol equiv of $(CH_3)_2NCH_2CH_2NH_2$ gave 88% of racemic **2**,[5] which was resolved with (−)-dibenzoyltartaric acid in 95% EtOH to give 34% of (*R*)-**2**,[5] $[\alpha]^{25}_{546}$ −413° (*c* 0.9, EtOH), and 39% of (*S*)-**2**,[5] $[\alpha]^{25}_{546}$ +413° (*c* 1.1, EtOH). From (*R*)-**3**[3] was obtained 93% of (*R*)-**1**, $[\alpha]^{25}_{546}$ −410° (*c* 1.1, EtOH). The mass spectral cracking patterns of **1** and **2** confirmed their structures.

(7) We warmly thank Dr. S. Bruce Brown for developing the practical synthesis of the 2,2′-dicarboxy-1,1′-dinaphthyl used in the preparation of racemic (*R*)- and (*S*)-**3**.

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(11) Ether and toluene were distilled from lithium aluminum hydride and THF from sodium benzophenone ketyl. Reactions were conducted under dry N_2. Reagent solutions were added by syringe. Commercial CH_3Li, LiBr, $CH_3(CH_2)_3Li$, and C_6H_5Li were used directly, and CH_3CH_2Li and $CH_3(CH_2)_2Li$ were prepared [Meyers, A. I; Smith, R. K.; Whitten, C. E. *J. Org. Chem.* **1979**, *44*, 2250–2256]. The procedure for run 1 is illustrated. A solution of 3.12 g of (*R*,*R*)-**1** of maximum rotation in 150 mL of Et_2O was cooled to −50 °C, and 2 mL of a 2.2 M solution of $CH_3(CH_2)_3Li$ in hexane was added. The solution was stirred for 1.3 h at −50 °C, and cooled to −120 °C. A solution of 0.133 g of freshly distilled C_6H_5CHO in 1 mL of Et_2O was added dropwise with stirring. The mixture was stirred for 1 h at −120 °C and rapidly quenched with 100 mL of 1 N aqueous HCl and allowed to come to 25 °C. The white precipitate of (*R*,*R*)-**1**·2HCl was filtered, thoroughly washed with water and ether, dried, and converted with KOH back to unaltered (*R*,*R*)-**1**, 3.09 g (99%), $[\alpha]^{25}_{546}$ −256° (*c* 1, $CHCl_3$). The ether layer of the original filtrate was washed with three 200 mL portions of H_2O, dried, filtered and evaporated. The residue was chromatographed on a preparative TLC plate (SiO_2, CH_2Cl_2), and the desired $C_6H_5CH(OH)(CH_2)_3CH_3$ was collected in ether. The ether was evaporated, and the residue dried under vacuum for 30 min at 25 °C to give 0.150 g (73%) pure by TLC and ^1H NMR, $[\alpha]^{25}_D$ 36.1° (*c* 3, C_6H_6). After submission to a second preparative TLC and a preparative gas chromatogram (5% SE 30 on firebrick at 150 °C), the sample gave $[\alpha]^{25}_D$ 35.7° (*c* 3, C_6H_6), 95% ee of (*R*)-$C_6H_5CH(OH)(CH_2)_3CH_3$, mp ca. 30 °C. At 22 °C, $[\alpha]_D$ was 35.8°, and at 18 °C was 36.0°. The original sample was esterified with excess (+)-α-methoxy-α-[(trifluoromethyl)phenyl]acetyl chloride,[9] and the ester was chromatographed on a preparative TLC plate (SiO_2, CH_2Cl_2). The ^1H NMR (200 MHz) spectrum gave the major CH_3O singlet at 3.447 ppm and the minor at 3.538 ppm, whose integration indicated an 89% ee of one enantiomer of the original alcohol.

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