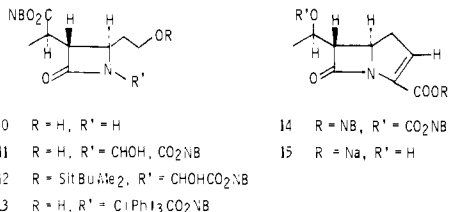


from thienamycin as shown in an accompanying publication.⁵



8-Oxo-2,2-dimethyl-7- α -(1'-hydroxyethyl)-3-oxa-1-aza-bicyclo[4.2.0]octane (**8**)⁶ was converted to its *o*-nitrobenzyl-carbonate **9** (C₆H₄NO₂CH₂O₂CCl, 2 equiv of Me₂NC₅H₄N, 2 equiv of CH₂Cl₂, 0 °C \rightarrow room temperature, 3 h) and the two isomers at C-9 were separated by HPLC (silica gel, 30% EtOAc-C₆H₁₂). The acetonide function of the 9*R* isomer of **9** was hydrolyzed (TFA, H₂O, room temperature, 12 min) to give the alcohol **10** (85%; IR 3430 (OH and NH), 1750 (β -lactam and carbonate), 1530 (NO₂); NMR 7.3–8.3 (m, O-C₆H₄NO₂), 6.53 (s, NH), 5.6 (s, CH₂Ar), 5.2 (2 q, CH₃CH), 3.8 (t and m, CH₂OH and C-4 H), 3.1 (q, *J* = 2, *J* = 9 Hz, C-3 H), 2.3 (s, OH), 1.93 (q, CH₂CH₂OH), 1.48 (d, *J* = 6 Hz, CH₃-) which was condensed with *o*-nitrobenzyl glyoxylate to give the diol **11** (70%). The primary alcohol of **11** was protected as the *tert*-butyl dimethylsilyl ether (*t*-BuMe₂SiCl, DMF, Et₃N) and the product **12** (90% yield) was converted to the ylide as described for **2**. The *tert*-butyldimethylsilyl ether was then hydrolyzed (0.5% concentrated HCl, DMF) to give the ylide-alcohol **13** (62% from **12**). Oxidative cyclization (Me₂SO, Ac₂O) gave the protected *dl*-descysteaminyllthienamycin **14**: IR 1780 (β -lactam), 1742 (carbonate), 1722 (ester); NMR 7.3–8.3 (m, O-C₆H₄NO₂), 6.6 (t, C-2 H), 5.7 (AB q, ArCH₂ of ester), 5.6 (s, ArCH₂ of carbonate), 5.3 (m, CH₃CH), 4.36 (sextet, *J* = 8, *J* = 2 Hz, C-5 H), 3.46 (q, *J* = 2, *J* = 8 Hz, C-6 H), 2.96 (sextet, C-1 H), 1.6 (d, *J* = 6 Hz, CH₃-); 28% (accompanied by 50% methyl thiomethyl ether of **13**). Photolysis of **14** (dioxane, 50% H₂O, pH 7 phosphate buffer 0.5 M, 5%) gave *dl*-descysteaminyllthienamycin (**15**) which after purification on a XAD-2 column⁵ was identical by NMR and UV with the product obtained from thienamycin.⁵

The use of this synthesis to prepare other analogues of thienamycin will be the subject of future communications.

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References and Notes

- Papers presented at the Sixteenth Interscience Conference on Antimicrobial Agents and Chemotherapy, Chicago, Ill., Oct 1976: (a) "Thienamycin, A New β -Lactam Antibiotic. I. Discovery and Isolation" by J. S. Kahan, F. M. Kahan, R. Goegelman, S. A. Currie, M. Jackson, E. O. Stapley, T. W. Miller, A. K. Miller, D. Hendlin, S. Mochales, S. Hernandez, and H. B. Woodruff; (b) "Thienamycin, A New β -Lactam Antibiotic. II. *In Vitro* and *In Vivo* Evaluation" by H. Kropp, J. S. Kahan, F. M. Kahan, J. Sundelof, G. Darland, and J. Birnbaum.
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- D. H. Shih and B. G. Christensen describe the antibiotic activity of **15**: *J. Am. Chem. Soc.*, preceding paper in this issue.
- D. B. R. Johnston, S. M. Schmitt, F. A. Bouffard, and B. G. Christensen, *J. Am. Chem. Soc.*, **100**, 313 (1978).
- IR Spectra were run on thin film and are reported in cm⁻¹; NMR spectra were run in CDCl₃ on a Varian T-60 instrument and are reported in δ units.
- Compound **7** could not be lyophilized without considerable decomposition. IR and NMR spectra of **7** are therefore not available; its presence in aqueous solution is inferred from its UV maxima at 262 nm (NH₂OH extinguishable) similar to descysteaminyllthienamycin. Reductive cleavage of benzyl or

p-nitrobenzyl used as protecting groups gave **7** in very low yield. The yield and antibiotic activity of **7** is calculated using an assumed ϵ 7800 similar to descysteaminyllthienamycin.

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Nitrogen Fixation via Photoenhanced Reduction on p-GaP Electrodes

Sir:

The fixation of N₂ under mild ambient conditions has been an extremely important and long-standing objective of much international research. A system is reported here which produces N₂ fixation at room temperature and atmospheric pressure by a photoenhanced reduction process. The system is a photoelectrochemical cell which contains a p-GaP cathode and an aluminum metal anode immersed in a nonaqueous electrolyte of titanium tetraisopropoxide and AlCl₃ dissolved in glyme (1,2-dimethoxyethane). When N₂ is passed through the electrolyte and the p-GaP electrode is illuminated with band-gap light, the N₂ is reduced and is recovered as NH₃; aluminum is consumed in the process and acts as the reducing agent. Although the reduction of N₂ to NH₃ with aluminum is thermodynamically favored ($\Delta G < 0$), the reaction does not proceed in the cell in the dark. The activation energy for the process is provided by light absorbed in the p-GaP electrode; hence, this system is an example of photocatalysis in a photoelectrochemical cell. The cell has been successfully operated in both flow and static modes; in the former, N₂ is continuously bubbled through the electrolyte. Experiments using ¹⁵N₂ have also been carried out and ¹⁵NH₃ has been identified from Fourier transform IR spectra.

The cell and electrolyte used in this work are closely related to those used by Van Tamelen and co-workers¹⁻³ to demonstrate normal electrolytic fixation of N₂. In those previous experiments, an external voltage source was used with either two Pt electrodes¹ or with an aluminum anode and a Nichrome cathode² to fix molecular nitrogen. In the present system, no external voltage source is required to achieve N₂ fixation; the activation energy for the reaction is provided by light alone.

The flow experiments were conducted in a closed quartz cell by bubbling high purity (99.999%) nitrogen gas through 80 mL of glyme containing 40 mmol of titanium isopropoxide and 60 mmol of AlCl₃; the effluent N₂ gas was then passed through a 0.2 N H₂SO₄ trap before exiting to the atmosphere. The p-GaP cathode was fabricated from a 1-mm-thick Zn-doped single-crystal wafer ((111) orientation) with an area of 1 cm², a carrier density of 5 \times 10¹⁷ cm⁻³, and a conductivity of 5.4 Ω^{-1} cm⁻¹. The crystal was polished with alumina powder and etched in a 3:1:1 H₂SO₄-H₂O₂-H₂O solution at 60 °C for 10 min; a 3000-Å film of a 1% Zn in gold alloy was then evaporated on the Ga face (111), and this was followed by heat treatment in 90% Ar-10% H₂ at 600 °C for 10 min to produce an ohmic contact to the crystal.

The anode consisted of ultra-high-purity aluminum wire. A low-impedance Keithley K616 ammeter or a PAR 179 coulometer was connected between the electrodes to measure current or total charge flow. The N₂ flow rate was \sim 14 cm³/min, and the light intensity was \sim 100 mW/cm² of simulated sunlight from a 150-W xenon lamp. A typical run lasted 24 h.

Reduced nitrogen yields were based on analyses of both the 0.2N H₂SO₄ trap and the residual electrolyte. The acid trap was analyzed directly for NH₄⁺, while the residual electrolyte was first digested in sulfuric acid and then treated with 8 N

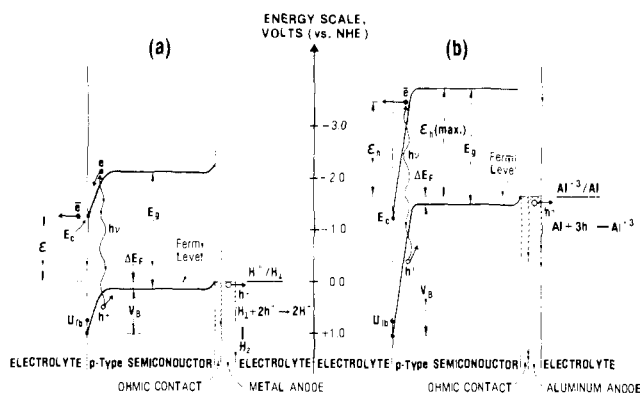


Figure 1. Energy level diagrams for photoenhanced reduction process; (a) redox potential of the reducing agent (H_2) is more positive than the conduction band edge (E_c), and photogenerated electrons are injected into the electrolyte after full intraband relaxation in the depletion layer; (b) redox potential of the reducing agent (Al) is more negative than E_c , and photogenerated electrons are injected before they undergo full intraband relaxation ("hot" electron injection). The values for the flat-band potential (U_{fb}) and the redox potentials of H_2/H^+ and Al^{3+}/Al are for aqueous electrolyte at pH 0; it is assumed that the relative differences between U_{fb} and the respective redox couples are not drastically different in nonaqueous electrolyte.

NaOH to generate NH_3 , which was separately trapped in acid and analyzed as NH_4^+ . The NH_4^+ analyses were done using either ion specific electrodes, Kjeldahl's method, pulse polarography, or Nessler's reagent. In a typical run the reduced nitrogen yields, expressed as moles of NH_4^+ per mole of titanium, varied between ~ 2 and 5%. This corresponds to a reaction rate of $\sim 10^{-4}$ mol of $NH_3/(h\text{ cm}^2)$ (electrode surface). Blank runs (no N_2 or no light or p-GaP replaced by Pt) produced insignificant yields of NH_4^+ . Runs in which the aluminum electrode was replaced by a Pt electrode in contact with H_2 also produced insignificant yields of NH_4^+ .

The static experiments were performed in a closed cell containing ~ 20 mL of the glyme-based electrolyte described above and ~ 20 cm³ of N_2 gas at atmospheric pressure. The electrolyte was agitated with a small Teflon-coated magnetic stirrer during irradiation. The electrolyte was analyzed for reduced nitrogen after the run, as described above; reduced nitrogen yields were typically several percent.

An experiment was also performed in which $^{15}N_2$ was used in the closed static cell. The electrolyte was treated in the usual manner, except that the acid trap was further treated with NaOH to generate $^{15}NH_3$, which was then collected in a gas sampling bulb. The gas collected from the $^{15}N_2$ experiment was examined via Fourier transform IR spectroscopy. The IR data showed unequivocally that $^{15}NH_3$ was produced; the most intense $^{15}NH_3$ umbrella bands at 962 and 927 cm^{-1} were clearly indicated, while the corresponding $^{14}NH_3$ bands at 968 and 932 cm^{-1} were absent. The spectral resolution of the data was better than 2 cm^{-1} . This experiment proves that the NH_3 produced in the system comes from the reduction of molecular nitrogen and not from adventitious nitrogen species.

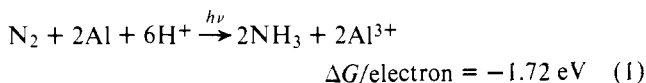
The chemical processes occurring in solution are equivalent to those for the pure electrolytic case as described by Van Tamelen et al.¹⁻³ Titanium(IV) isopropoxide is first reduced to a state wherein molecular N_2 can be bound; this is evidenced by the development of an intense blue-black color which is attributed to a Ti(II) complex. The reduced titanium-molecular nitrogen complex is then reduced further to produce a reduced nitrogen-reduced titanium complex. Finally, ammonia is produced through protonation of the reduced nitrogen-reduced titanium complex. Alternatively, Van Tamelen has suggested that reduced nitrogen in the reduced complex is transferred to an aluminum(III) complex, and then ammonia is produced via protonation of the reduced nitrogen-alum-

inum(III) complex.¹⁻³

In the photoelectrochemical experiments, the initial photocurrent is typically ~ 0.6 mA/cm² and it decreases somewhat as the blue-black color develops. During the run, the aluminum anode is oxidized and loses weight. This weight loss is always much greater (factor of 5 to 10) than that calculated on the basis of the measured charge passed through the external circuit. This means that the aluminum anode also undergoes a direct redox reaction with the electrolyte in addition to the redox reaction which is coupled to the p-GaP cathode. It is believed that the direct redox reaction of the aluminum anode is with titanium(IV) isopropoxide to produce aluminum(III) isopropoxide and titanium(III) and/or titanium(II) isopropoxide. This assumption is consistent with the observation that the blue-black color and concomitant N_2 reduction, indicative of Ti(II), could be developed without first having passed at least 1 faraday of charge per initial mole of Ti(IV) through the external circuit (Van Tamelen et al.¹⁻³ had reported that all of the Ti(IV) must first be reduced to Ti(III) by electrolysis before Ti(II) could form and N_2 fixation could proceed).

It is believed that the aluminum anode does not react directly with the molecular nitrogen complexes, but rather that the nitrogen reduction step occurs at the p-GaP electrode, with the aluminum providing the counteroxidation reaction required to complete the cell circuit (see Figure 1b). This hypothesis is supported by the observation that the reduced nitrogen yield is consistent with the total charge passed through the external circuit.

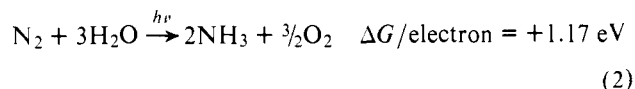
In the present system, the overall reaction can be represented as



Although reaction 1 is favored in the dark, it does not proceed because of the high activation energy of intermediate steps. The occurrence of reaction 1 in the present system under illumination is an example of a photocatalyzed reduction process; as discussed below, this is one of two possible classes of photoenhanced reduction processes.

The energetics of general photoenhanced reduction on p-type semiconductors is represented in Figure 1, and is based on the usual principles of photoelectrochemistry with semiconductor electrodes.⁴ In Figure 1a, the energy level scheme is shown for the case where the reducing agent (e.g., H_2) has a redox potential which lies within the band gap of the semiconductor (e.g., p-GaP). Illumination of the semiconductor with band-gap light creates electrons in the semiconductor which are available for reduction at a redox potential more negative than the standard redox potential of the reducing agent oxidized at the anode. Thus, the system produces a photoenhanced reduction effect.

If the standard redox potential of the cathodic reaction is more positive than that of the anodic reaction, then the overall reaction is thermodynamically favored in the dark and the light-driven reaction is photocatalytic (this is the situation with the present cell driving reaction 1). On the other hand, if the standard redox potential of the cathodic reaction is more negative than that of the anodic reaction, then the overall photoenhanced reduction reaction would be endoergic and light would be converted into stored chemical free energy. This would be the case, for example, with the following reaction:



An important aspect of the present experiments is that they provide evidence for a "hot-carrier injection" process.⁵ For thermalized injection, the energy of the injected electrons (and,

hence, the nature of the allowed cathodic reaction) would be independent of the nature of the anodic reaction (and, hence, independent of V_B) since the energy level of E_c is pinned at the semiconductor-electrolyte interface (Figure 1). Furthermore, anodic reactions with redox potentials above that of E_c would not be effective in producing photoenhanced reduction. Therefore, the observation that N_2 reduction in the present system only occurs with aluminum anodes, and not with H_2/Pt anodes, means that the cathodic reaction is dependent on V_B , and strongly suggests that hot electron injection is occurring. This is consistent with theoretical calculations on the feasibility of hot carrier injection processes.⁶

It is to be noted that the important point of this work is not that N_2 can be fixed by reducing metals and metal complexes (this is well known⁷⁻⁹), but that interesting photocatalytic effects can be achieved on semiconducting electrodes, including the photoenhanced reduction of N_2 by aluminum, and that these effects appear to involve hot carrier injection processes.

Finally, it is also to be noted that the endoergic photoreduction of N_2 using H_2O (reaction 2) would be a very important achievement and that such a process has been claimed by Schrauzer and Guth¹⁰ using n-type oxide semiconductor powders. It would appear, however, that homogeneous n-type semiconductors would be extremely poor photocatalysts for reduction since electrons can only be injected into the liquid via tunneling through large and thick potential barriers. In such semiconductors, only holes are efficiently injected into the electrolyte. A second region with a larger work function in contact with the n-type semiconductor, such as that existing in a photochemical diode,¹¹ is required for both efficient electron and hole injection.

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Planar $^3A_2'$ - Orthogonal 1B_1 Energy Separation for Trimethylenemethane

Sir:

During the past few years, the previously mystical trimethylenemethane (TMM)¹ radical $C(CH_2)_3$ and its precursors have been the subject of an increasing number of experimental²⁻¹⁰ and theoretical¹¹⁻²⁰ studies. The most critical energetic quantity in the theoretical studies has been the barrier for rotation of singlet TMM from its "orthogonal" con-

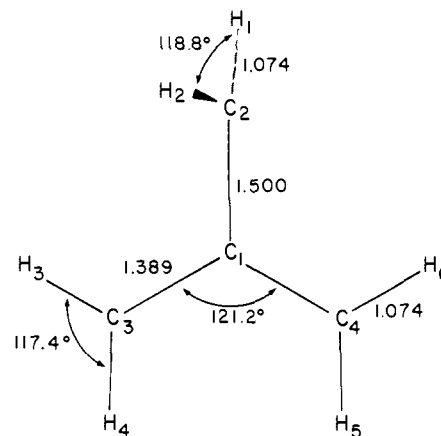
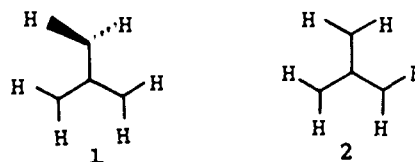
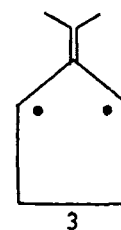


Figure 1. Predicted equilibrium geometry for the 1B_1 state of trimethylenemethane.

figuration (1B_1 electronic state) (1) to the energetically higher planar arrangement ($^1E'$ electronic state) (2). In this regard there now appears to be general agreement²¹ that the $^1E' - ^1B_1$ barrier to rotation is small, of the order of 1-3 kcal/mol.



As noted by Davidson,²² however, the singlet-triplet separation $\Delta E(^3A_2' - ^1B_1)$ has been predicted^{14,17-19} to be 17-21 kcal in a relatively "casual" manner, since no experimental ΔE value was available. In this light the recent experimental findings of Platz and Berson⁸ and Dowd and Chow⁹ are particularly thought provoking. For the TMM derivative 3 Platz and Berson deduce a value $\Delta E < 1.4-3.5$ kcal from their kinetic studies. After noting that zero-differential overlap considerations suggest that 3 should have a ΔE value similar to



that for the unsubstituted TMM, Platz and Berson⁸ conclude that there may be a serious disagreement between theory and experiment. The latter possibility is given further support by the work of Dowd and Chow,⁹ who report an activation energy of 7.3 ± 0.3 kcal for the ring closure of triplet TMM to methylenecyclopropane (MCP).

In the present communication we report a state-of-the-art ab initio study of the TMM singlet-triplet separation $\Delta E(^3A_2' - ^1B_1)$. Our first step was the prediction of the optimum geometrical structure of the orthogonal singlet, or 1B_1 state. Given the constraint of C_{2v} symmetry, the equilibrium geometry seen in Figure 1 was obtained at the self-consistent-field (SCF) level of theory²³ using a standard double ζ (DZ) basis set.²⁴ This singlet structure and that previously optimized²⁰ for the triplet ground state were used in all ensuing predictions of $\Delta E(^3A_2' - ^1B_1)$. The DZ SCF value of ΔE , seen in Table I, is 15.1 kcal, somewhat lower than any previous theoretical prediction, but still significantly higher than the $\Delta E < 7$ kcal value inferred from experiment. In this light, d functions were appended, first to the central carbon atom and then to all four carbon atoms. The predicted singlet-triplet separation is decreased only