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 feasability 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 known[7-9]), 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 Guth[10] 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 experimental[2-10] and theoretical[11-20] studies. The most critical energetic quantity in the theoretical studies has been the barrier for rotation of singlet TMM from its "orthogonal" con-
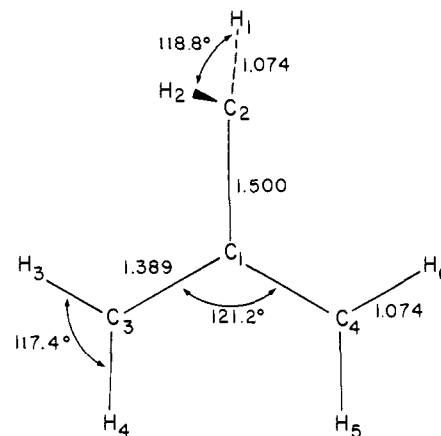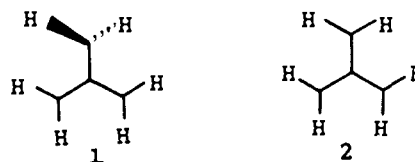

Figure 1. Predicted equilibrium geometry for the $^1B_1$ state of trimethylenemethane.

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 agreement[21] 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 Berson[8] and Dowd and Chow[9] 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
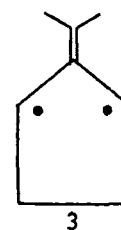
that for the unsubstituted TMM, Platz and Berson[8] conclude that there may be a serious disagreement between theory and experiment. The latter possibility is given further support by the work of Dowd and Chow,[9] who report an activation energy of 7.3 ± 0.3 kcal for the ring closure of triplet TMM to 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 theory[23] using a standard double ζ (DZ) basis set.[24] This singlet structure and that previously optimized[20] 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

Table I. Predicted Singlet–Triplet Separations for Trimethylenemethane

level of theory	$E(^3A_2')$, hartrees	$\Delta E(^3A_2' - {}^1B_1)$, kcal/mol
DZ SCF	−154.8295	15.1
DZ + central d SCF	−154.8482	14.9
DZ + d SCF	−154.8844	14.9
DZ 4e⁻ CI[a]	−154.8787	17.6
DZ 8e⁻ CI[a]	−154.9167	17.3
DZ 10e⁻ CI[a]	−154.9396	14.6
DZ 14e⁻ CI[b]	−154.9871	14.3
DZ 14e⁻ CI[a]	−155.0063	

[a] Four highest virtual orbitals excluded from CI. [b] Eight highest virtual orbitals excluded from CI.

slightly, to 14.9 kcal.

The effects of electron correlation frequently change predicted electronic excitation energies by 10 kcal/mol or more.[25] In the present research, the configuration interaction (CI) method was used to describe correlation effects, and the DZ basis set was adopted since d functions had little effect on ΔE at the SCF level of theory. All Hartree–Fock interacting[26] single and double excitations were included in the CI, and a series of ΔE values was predicted by respectively correlating the 4, 8, 10, and 14 outermost valence electrons. The largest calculation included 8723 triplet configurations, spatially adapted for the C_{2v} subgroup. The predicted singlet–triplet separation of 14.3 kcal suggests that electron correlation lowers $\Delta E(^3A_2' - {}^1B_1)$ by only 0.8 kcal. Combining this with our DZ + d SCF result of 14.9 kcal suggests a "final" prediction of 14.1 kcal for the singlet–triplet separation.

One should be cautious about concluding that the theoretical prediction of $\Delta E(^3A_2' - {}^1B_1) = 14$ kcal is in conflict with the 7.3-kcal experimental activation energy[9] for TMM ring closure. Davidson and Borden have pointed out[27] that the 7-kcal experimental energy may not refer to the orthogonal singlet equilibrium geometry at all. They suggested that the 7 kcal might be the height (above the lowest vibrational state for the triplet surface) at which the triplet is crossed by one of the two singlet surfaces arising from the planar $^1E'$ state. However, preliminary calculations[28] have not yet provided substantive support for this possibility.

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**Optical Rotatory Dispersion Studies. 125.[1]
Independent Evidence for Preference of Axial
Deuterium vs. Axial Hydrogen through
Variable-Temperature Circular Dichroism Spectra of
(4S)-2,2-Dimethyl-4-deuteriocyclohexanone and
(3S)-3-Deuterio-4,4-dimethylcyclohexanone**

Sir:

In a recent communication[2] we reported on the temperature-dependent circular dichroism spectra of $(3R)$-2,2-dimethyl-3-deuteriocyclohexanone (I) and $(5S)$-2,2-dimethyl-5-deuteriocyclohexanone (II) and concluded that the observed intensity changes reflect a shift of the equilibrium toward that conformer in which the deuterium is in the axial orientation.
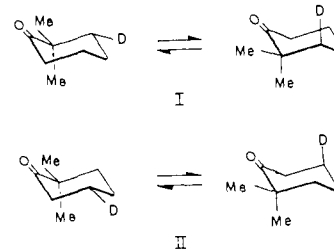
The enthalpy differences between both conformations were calculated to be −7.2 and −2.1 cal/mol, respectively,[3] and represent the first quantitative estimates for the slight preference of axial deuterium vs. axial hydrogen. We now present independent and additional evidence supporting our earlier conclusions[2] through the synthesis and variable-temperature CD measurements of $(4S)$-2,2-dimethyl-4-deuteriocyclohexanone (III)—a substance with axial or equatorial deuterium in a symmetry plane but possessing a *gem*-dimethyl "chiral probe"[2]—and $(3S)$-3-deuterio-4,4-dimethylcyclohexanone (IV)—a compound in which the *gem*-dimethyl group cannot act as a "chiral probe"[2] since it lies in a symmetry plane.

$(4S)$-2,2-Dimethyl-4-deuteriocyclohexanone (III) was synthesized by methylation (Ireland's method[4]) of (+)-$(2R,4R)$-2-methyl-4-isopropenylcyclohexanone[5] (optical purity >95%) to $(4R)$-2,2-dimethyl-4-isopropenylcyclohexanone, ethylene ketal formation and successive ozonolysis,