Photoelectron Spectroscopy of the Trimethylenemethane Negative Ion. The Singlet−Triplet Splitting of Trimethylenemethane†

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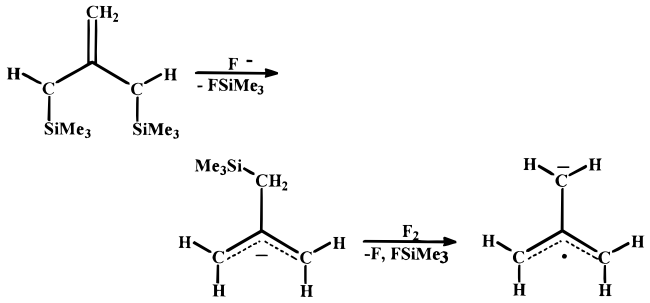
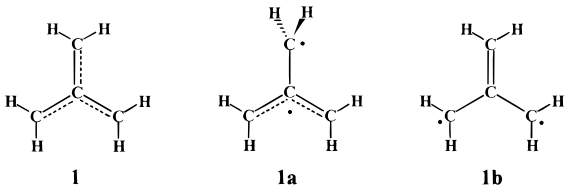
Few reactive organic intermediates have elicited as much attention by experimentalists and theorists as trimethylenemethane (TMM, **1**).[1,2] The theoretical significance of this archetypal non-Kekule molecule was recognized by Moffitt and Coulson nearly 50 years ago,[3] and it has since inspired numerous computational studies spanning the entire gamut of theoretical methods. TMM serves as a paradigm for basic theoretical concepts such as free valence, disjoint orbital analysis, and negative spin density in π systems, and it has been a consistently challenging subject for electronic structure calculations.[4] Although trimethylenemethanes were commonly invoked as intermediates in the formation and rearrangement of methylenecyclopropanes,[5] little was known experimentally about these molecules until 1966, when Dowd[6] reported the EPR spectrum for **1** isolated in a glassy matrix at 88 K. Subsequent work by Dowd and co-workers verified the triplet ground state with 3-fold (D_{3h}) symmetry that had been predicted for TMM.[7,8] Many elegant spectroscopic and chemical experiments with TMM by the Pittsburgh group[1a] and with monocyclic derivatives by Berson and co-workers at Yale University[1b] have elevated our understanding of trimethylenemethanes to a high level. Practical applications of TMM derivatives now include organic ferromagnets,[9] synthetic reagents,[10] and even DNA-cleaving agents.[11] Recently, Maier and co-workers reported low-temperature matrix IR spectra for triplet **1** and its d_2, d_4, and d_6 isotopomers.[12,13]

In contrast to the wealth of information available for the ground state of **1**, very little is known experimentally about the excited singlet states. Of fundamental importance is the energy difference between the lowest energy singlet and triplet states, i.e., the "singlet−triplet splitting". *Ab initio* molecular orbital and valence-bond calculations predict values of 14−20 kcal/mol for the energy splitting between the $\tilde{X}^3A'_2$ state and the $\tilde{a}^1B_1$ state, **1a**, which has one methylene group twisted out of the plane of the molecule.[14,15] The lowest energy singlet state of planar **1** is predicted to be the Jahn−Teller distorted $\tilde{b}^1A_1$ state, **1b**, which is a minimum at the MCSCF(4,4)/6-31+G* level of theory,[16] and is calculated to lie 0−6 kcal/mol higher in energy than the $^1B_1$ state.[14] Dowd and Chow[17] report an experimental estimate of 7 kcal/mol for the singlet−triplet splitting in **1**, which is based on the activation energy for the disappearance of the EPR signal for the matrix-isolated triplet and on the assumption that the decay process in the temperature range 120−135 K corresponds to ring closure to methylenecyclopropane via the singlet state. This estimate is 7−13 kcal/mol lower than the most reliable calculated values for the $\tilde{X}^3A'_2 \rightarrow \tilde{a}^1B_1$ energy difference[14] and, moreover, is lower by *ca.* 8 kcal/mol than the lowest energy singlet−triplet surface crossing on the calculated potential energy surface for ring closure.[15,18] We now report the photoelectron spectrum of the trimethylenemethane negative ion $\mathbf{1}^{\bullet-}$. From this spectrum we have obtained the electron affinity and singlet−triplet splitting of planar TMM. The results are in good agreement with the theoretical predictions and further support the contention that the estimated splitting based on the EPR data of Dowd and Chow is too low.

The measurement of the photoelectron spectrum of the trimethylenemethane negative ion was made possible by the

Scheme 1





1 **1a** **1b**

† Dedicated to Paul Dowd, in recognition of his landmark contributions to the study of trimethylenemethane.

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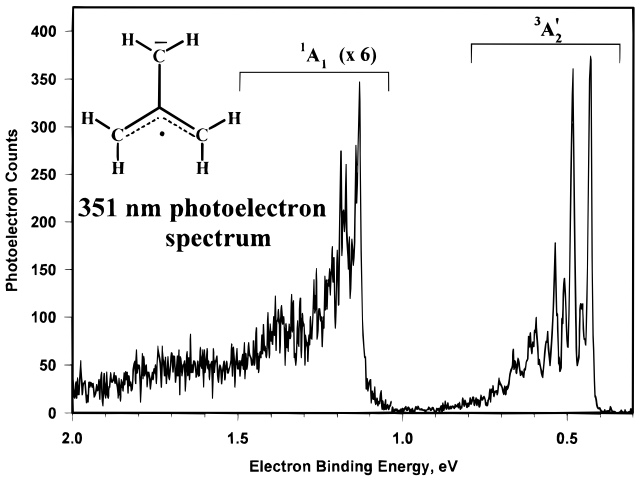

Figure 1. Photoelectron spectrum of the trimethylenemethane negative ion.

recent discovery that this ion can be prepared in high yield in the gas phase by the reaction of 2-[(trimethylsilyl)methyl]allyl anion with molecular fluorine, F_2 (Scheme 1).[19] The identity of $\mathbf{1}^{\bullet-}$ as the trimethylenemethane negative ion was verified by its gas-phase reactivity and by deuterium-labeling experiments, which indicate a structure possessing three chemically equivalent methylene groups.[19] We have now used the reaction sequence shown in Scheme 1 in the flowing afterglow source of a negative ion photoelectron spectrometer[20] to prepare intense beams (10−40 pA) of $\mathbf{1}^{\bullet-}$. For these experiments, the flowing afterglow ion source was cooled with liquid nitrogen in order to minimize spectral features due to ions in excited vibrational and rotational states.[21] The photoelectron spectrum obtained for $\mathbf{1}^{\bullet-}$ using 351.1 nm laser light is shown in Figure 1. Two prominent features are observed in the spectrum, corresponding to detachment to at least two electronic states of **1**. The lower energy feature is assigned to detachment to form the ground state, triplet trimethylenemethane. The electron affinity of **1** is found to be 0.431 ± 0.006 eV, slightly lower than those obtained for allyl radical (0.481 ± 0.008 eV) or the 2-methylallyl radical (0.505 ± 0.006 eV).[22] The extensive, resolved vibrational structure in both states is readily interpreted, and a complete analysis of the spectrum will be presented in a forthcoming publication.[23]

The onset of the higher energy feature is a sharp peak at an electron binding energy of 1.130 ± 0.006 eV. The fact that the onset is relatively intense and narrow indicates that the geometry of the neutral detachment product is similar to that of the anion, a species that is calculated to have an essentially planar, near C_{2v} ground state.[24] On this basis, we assign this feature to formation of the $\tilde{b}^1A_1$ state of TMM, **1b**. Detachment from the planar ion to form the twisted, $^1B_1$ state, **1a**, is expected to suffer from extremely poor Franck−Condon factors and is unlikely to be observed.

The heat of formation of trimethylenemethane can be calculated with eq 1, where EA(**1**) and EA(2-MeAllyl) are the electron affinities of **1** and 2-methylallyl radical, respectively,[22] $\Delta H_{acid}(Me_2C{=}CH_2)$ and ΔH_{acid}(2-MeAllyl) refer to the 298 K gas-phase acidities of 2-methylpropene (390.3 ± 2.3 kcal/mol)[25] and 2-methylallyl radical (394 ± 2 kcal/mol),[26] respectively, and the remaining data are taken from the literature.[27] The small

$$\Delta H_{f,298}(\mathbf{1}) = EA(\mathbf{1}) + \Delta H_{acid}(\text{2-MeAllyl}) + EA(\text{2-MeAllyl}) + \Delta H_{acid}(Me_2C{=}CH_2) + \Delta H_{f,298}(Me_2C{=}CH_2) - DH_{298}(H_2) - 2IP(H) \quad (1)$$

(<0.3 kcal/mol) temperature correction required for eq 1 has been neglected. The heat of formation of **1** is determined to be 70 ± 3 kcal/mol. This value closely matches the bond additivity estimate for TMM, 68.4 ± 3.3 kcal/mol, which can be derived from the known heat of formation[27a] and C−H bond energy[28] of 2-methylpropene. According to simple Hückel theory, the heat of formation of **1** should be greater than bond additivity by 0.2β. Calculations at the MCSCF(4,4)/6-31G* and CASPT2N/6-31G* levels of theory predict heats of formation that are 2.2 kcal/mol less than[29] and 0.6 kcal/mol greater than[14d] bond additivity, respectively.

The energy difference between the origins of the triplet and singlet features in the spectrum provides a direct measure of the singlet−triplet splitting in planar **1**. The value obtained for the $\tilde{X}^3A'_2$−$\tilde{b}^1A_1$ energy splitting, 0.699 ± 0.006 eV (16.1 ± 0.1 kcal/mol), is within the range predicted by the *ab initio* calculations.[14,15] Although the $\tilde{X}^3A'_2$−$\tilde{a}^1B_1$ energy splitting cannot be determined from the present experiments, the most reliable calculations predict that this quantity should be 0−3 kcal/mol smaller than the splitting between the $^3A'_2$ and the $^1A_1$ states.[14] This suggests that the $^1B_1$ state lies 13−16 kcal/mol above the triplet state.

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