# Trimethylenemethane Radical Cation Chemistry from a Diazene Precursor

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Oxidation of most neutral closed-shell molecules generates radical cations which possess nearly coincident spin and positive charge distributions, as approximated by the spatial density of the singly occupied molecular orbital (SOMO). However, radical cations derived from certain neutral organic biradicals can possess a more novel electronic structure, one in which spin and charge distributions are noncoincident. This is possible because a biradical contains its two frontier electrons in a set of two degenerate or nearly degenerate molecular orbitals.[1] Electron loss from a biradical can thus give a radical cation whose spin distribution is a function of one orbital space and whose charge distribution is a function of *another* orbital space. If these two orbitals differ spatially, then the resultant radical cation will be distonic,[2] that is, possess different spin and charge sites, even within a fully conjugated π system. The simplest organic π-delocalized biradical expected to yield a distonic radical cation is trimethylenemethane (TMM).[3] Here, we report the generation of an alkyl-substituted TMM radical cation,[4] provide a preliminary description of its reactivity, and address the question of its preferred electronic ground state.
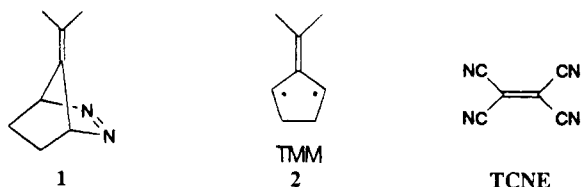
Diazene **1** has a rich chemical history as a precursor to TMM **2**,[5] and we postulated that it would also serve as a precursor to TMM radical cation **2**[.+] upon oxidative deazetation. We find that **1** forms a charge-transfer (CT) complex with tetracyanoethylene (TCNE) in solution[6] (λ_m 406 nm in CH_3CN) from which **2**[.+] may be generated photochemically.

Selective photolysis of the **1**−TCNE complex ($\lambda > 400$ nm) results in gas evolution and the formation of three main products: **3**, **4**, and **5** (eq 1). These products are formal cycloadducts of the diazene-derived TMM fragment and TCNE. Adducts **3** and **4** derive from TMM addition across the TCNE CC π bond, and adduct **5** derives from TMM addition across the TCNE cyano group. We refer to **3** and **4** as fused and bridged CC adducts, respectively (f-CC and b-CC), and to **5** as

the fused CN adduct (f-CN). The photoreaction product distribution strongly depends upon solvent medium. In CD_3CN, adduct **3** predominates, but in CD_2Cl_2, adduct **5** is the major product. In $CDCl_3/CD_3CN$ mixtures, the **3:5** product ratio changes from 0.14 to 3.3 as the fraction of CD_3CN is increased. The addition of salt ($LiClO_4$) to the CD_3CN reaction medium further increases the **3:5** photoproduct ratio. In contrast, the f-CC:b-CC product ratio **3:4** is rather solvent insensitive. The data are summarized in Table 1. Product yields are reported after 10 min of irradiation, and product ratios do not vary significantly with the extent of reaction up to 90% azo decay.
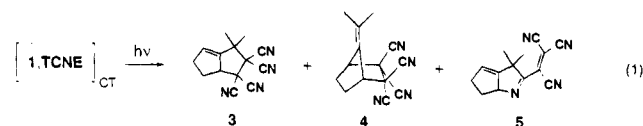
While examples of photosensitized azoalkane deazetation are known,[7] this report is the first example, to our knowledge, of direct CT-mediated photodeazetation of an azoalkane complex. For efficient photochemistry to occur under these conditions, **1**[.+]'s deazetation reaction must compete with nonproductive back electron transfer (ET) within the photogenerated **1**[.+],TCNE[.−] contact ion pair. Since ET within such radical ion pairs is generally faster than diffusive cage escape of the ions,[8] we predict **1**[.+]'s deazetation rate constant to be on the order of 10^{10} s^{−1} or greater. This prediction suggests that **1**'s deazetation rate (4×10^{-8} s^{−1} at 0 °C)[9] is increased $\geq 10^{18}$-fold by electron loss, consistent with N_2 loss accelerations of 10^{18}−10^{22} found for other diazenes upon oxidation.[7c,10,11]

The issue of mechanism for the photoreaction is intriguing. Products **3** and **4** appear to derive from biradical **2** addition to TCNE in accord with **2**'s known reactivity toward electron deficient olefins.[12] Adduct **5**'s structure, however, is unprecedented in TMM biradical chemistry, and we suggest that **5** forms from direct ionic reaction of **2**[.+] with TCNE[.−]. That **3** and **4** derive from **2**, but **5** does not, is supported by the fact that thermolysis of **1**/TCNE mixtures in the dark gives **3** and **4** but no detectable **5**.[13] Furthermore, the lack of a significant solvent effect on the **3:4** ratio is consistent with these products deriving from biradical **2** addition to TCNE.

Of particular relevance to the photoreaction mechanism is the large medium dependence of the CC:CN product ratio, as shown in Table 1. These data require a differential solvent effect on the competing reactions at the bifurcation point for CC and CN product formation. We postulate a contact singlet **2**[.+],TCNE[.−] ion pair as the key common intermediate. This species can undergo either internal ion pair combination (cage combination) to form CN adduct **5** or ion pair separation (cage escape) to form, after reduction of **2**[.+] to **2**, CC adducts **3** and **4**. The rates of these competing reactions should be solvent dependent

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(4) Diaryl-substituted TMM[.+]'s have beem implemented in the photo electron transfer reactions of diarylmethylenecyclopropanes.[4a−c] These highly delocalized TMM[.+]'s show chemistry quite different from that reported here for an alkyl-substituted TMM[.+]. (a) Takahashi, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1983**, *105*, 6511−6513. (b) Miyashi, T.; Takahashi, Y.; Mukai, T.; Roth, H. D.; Schilling, M. L. M. *J. Am. Chem. Soc.* **1985**, *107*, 1079−1080. (c) Miyashi, T.; Kamata, M.; Mukai, T. *J. Am. Chem. Soc.* **1987**, *109*, 2780−2788.

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(13) The thermal reaction does not appear to activate an ET pathway between **1** and TCNE because **1**'s thermal decay rate is found to be first order and unchanged by added TCNE. This suggests that **1** deazetation is the rate-determining step under thermolysis conditions.

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Table 1. Products from CT Photolysis and Thermolysis of
1/TCNE Mixtures

conditns[a]	3[b]	4[b]	5[b]	CC/CN[c]	mb, %[d]
mc, $h\nu^e$	7.3	2.1	43	0.21	75
chl:an (97:3), $h\nu^e$	5.3	1.8	39	0.18	89
chl:an (95:5), $h\nu^e$	7.6	2.1	30	0.33	68
chl:an (75:25), $h\nu^e$	17	6.0	53	0.44	84
chl:an (50:50), $h\nu^e$	19	6.3	29	0.88	72
chl:an (25:75), $h\nu^e$	31	6.0	23	1.6	78
an, $h\nu^e$	26	5.3	8.0	3.9	93
an, LiClO$_4$,^{f} $h\nu^e$	16	3.1	3.6	5.3	89
an, Δ^g	62	1.0	h	>100	72
chl:an (95:5), Δ^i	65	trace	h	>100	80

^{a} **1**, TCNE at 30 mM, mc is CD$_2$Cl$_2$, chl is CDCl$_3$, an is CD$_3$CN. ^{b} Percent yield by ^{1}H NMR integration relative to added nitromethane. ^{c} (**3** + **4**)/**5**. ^{d} Mass balance based on combined **3**−**5** yields and unreacted starting material. ^{e} λ > 400 nm ($\leq$10 min) at 0−5 °C. ^{f} 0.17 M salt. ^{g} 6 h at 60 °C. ^{h} Not observed within detection limit of 0.5%. ^{i} 20 h at 40 °C.

Scheme 1
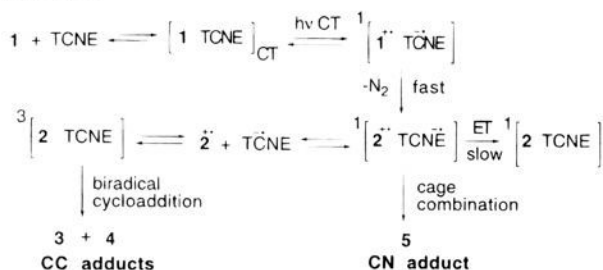
in a manner consistent with the observed data. A plausible mechanism is given in Scheme 1.

The question of how TMM biradical **2** forms under the photoreaction conditions is an important one. We expect this to occur by ET from TCNE$^{·-}$ to **2**$^{·+}$ within a triplet ion pair complex and not within the initially formed singlet **2**$^{·+}$,TCNE$^{·-}$ ion pair. If ET occurred in the singlet **2**$^{·+}$,TCNE$^{·-}$ ion pair to yield **2**,TCNE (and ultimately CC adducts) in competition with ion pair combination to give a CN adduct, then a large medium effect on the CC:CN product ratio would not be expected because these two competing processes (ET and ion combination) would have similar solvent dependencies: both would be faster in less polar solvents. Furthermore, ET within the singlet **2**$^{·+}$,TCNE$^{·-}$ contact pair would give, by spin conservation, singlet TMM (**2-s**),TCNE in the solvent cage, which would lead to exclusive formation of f-CC **3** and no b-CC **4** adduct because of the regiospecificity of **2-s**'s trapping reaction.[14] However, the observed **3**:**4** ratio in the photoreaction is generally 3−5, suggesting that the CC products derive primarily, if not solely, from the less regioselective reaction of triplet **2** (**2-t**) with TCNE (as in Scheme 1).[15]

We conclude that the **2**$^{·+}$,TCNE$^{·-}$ ET reaction must be unusually slow and does not contribute significantly to product formation in the **1**,TCNE photolysis. This ET step is slow

presumably because it gives singlet (excited state) TMM **2-s** and thus lacks sufficient driving force to compete with other facile reactions such as cage escape and ion pair collapse.[16] Once out of the cage, **2**$^{·+}$ may diffuse to a TCNE$^{·-}$ of like spin to form a triplet ion pair. This ion pair apparently undergoes facile ET to give triplet (ground state) **2-t**[17] and TCNE, which then add to yield a mixture of fused and bridged CC adducts **3** and **4**.

Finally, there is the issue of the electronic ground state of the distonic TMM radical cation **2**$^{·+}$. Two configurations are possible:[18]
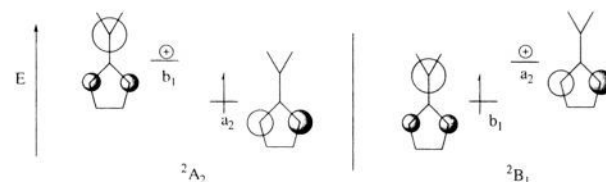
Calculations by AM1[19] indicate that these states are close in energy. In fact, the predicted ground state depends on the type of calculation employed. The AM1/UHF method predicts a ^{2}B$_1$ ground state for optimized C_{2v} **2**$^{·+}$, while the AM1/π-CI treatment of the same finds the states to be within ~3 kcal/mol of each other, the energy ordering being dependent on the CI reference configuration used. Given our data, we look to the observed regiochemistry of the f-CN adduct **5** for a clue about the electronic nature of **2**$^{·+}$. Assuming that product **5** derives from direct reaction of **2**$^{·+}$ and TCNE$^{·-}$ as postulated, the observed regioselectivity is most consistent with a matching of the electrophilic character of the TMM cation and the nucleophilic character of the TCNE anion if a ^{2}B$_1$ state of **2**$^{·+}$ is the reactive species. It is also true that the NBMO ordering in a ^{2}B$_1$ radical cation is consistent with that in the neutral singlet biradical **2** which best accounts for **1**'s thermal and photochemical reactivity[14a] and which best fits the dipolar character of **2-s**.[20] We hasten to add, however, that no direct experimental evidence currently allows conclusive identification of the TMM **2**$^{·+}$ ground state, although studies to provide such information are in progress.

In summary, we have observed the first direct photochemistry of an azoalkane CT complex and report the generation of a localized TMM radical cation whose chemistry is strongly solvent dependent. We postulate that spin control of the reaction dynamics plays an important role in the reaction outcome and that a ^{2}B$_1$ distonic state of TMM **2**$^{·+}$ is the key reactive intermediate.

(14) Thermal reaction of **1** and TCNE in an O$_2$-saturated medium, where O$_2$ selectively scavenges **2-t**,^{5a} yields as the only CC adduct **3** (with no **4**), showing that **2-s** reacts with TCNE regiospecifically. In addition, Berson and co-workers have shown that TMM diyl-trapping reactivity parallels dienophilicity for olefinic traps and that maleic anhydride is one of the fastest diyl traps, probably reacting at the diffusion-controlled limit.^{14a} Because TCNE is an even stronger dienophile than maleic anhydride,^{14b} we expect TCNE's reaction with **2-s** to be diffusion-controlled, so that if the two were formed in a solvent cage, quantitative formation of adduct **3** would result. (a) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446−453 and references therein. (b) Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183−3207.

(15) The regiochemistry of **2-t**'s reaction with TCNE is not known independently, but because the reaction must be stepwise, it is expected to be less regioselective than **2-s**'s reaction with TCNE, which is probably concerted. We note that **2-t** reacts with acrylonitrile to give a f:b adduct ratio of ~3 while the corresponding **2-s** reaction is completely regiospecific for fused cycloadduct formation.^{12}

(16) It is also possible that a torsional geometry change between **2**$^{·+}$ (planar) and **2-s** (bisected) may contribute to a significant ET barrier in this case.

(17) Reduction of **2**$^{·+}$ to **2-t** should be thermodynamically easier than reduction to **2-s** by an energy equal to the singlet, triplet (S, T) energy gap for **2**, which has been measured to be 13 ± 4 kcal mol^{-1}. Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 2681−2683. The S, T gap we calculate for **2** by AM1/UHF^{19} is 12.8 kcal mol^{-1} and by AM1/π-CI is 14.5 kcal mol^{-1}.

(18) The parent TMM$^{·+}$ is predicted by AM1/UHF (our work) and by ab initio methods^3 to prefer a planar (not bisected) geometry. AM1/UHF calculations suggest that alkyl-substituted TMM **2**$^{·+}$ will also prefer a fully conjugated π system.

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