# Is the Radical Cation of Tetramethyl Urea Stable?

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An attempt is made to choose between the concept that the radical cation of tetramethylurea is stable, and has its SOMO confined to one nitrogen, and the concept that it decomposes to give $\cdot NMe_2$ radicals and $Me_2NCO^+$ cations.

Some time ago we obtained a well-defined e.s.r. spectrum from dilute solutions of tetramethylurea (TMU) in $CFCl_3$ after exposure to $^{60}Co$ γ-rays at 77 K. This spectrum comprised features readily assignable to a radical containing one coupled nitrogen nucleus and six equivalent coupled protons. The possibility that the parent cation had become deformed in such a way (**1**) that one of the $NMe_2$ groups had rotated so as to break the π-conjugation of the parent molecule, thereby confining the unpaired electron to the $Me_2\dot{N}$–C=O unit (**1a**) or to one $Me_2\dot{N}$– unit (**1b**), was considered, but was not favoured for reasons given previously for the open form of the $(CH_2)_3^{\cdot+}$ cation.[1,2] However, the spectrum (Figure 1 of ref. 3) proved to be virtually superimposable on that for $\cdot NMe_2$ radicals generated by other means, suggesting that the parent cations underwent a unimolecular breakdown, as in reaction (1).

$$(Me_2N)_2CO^{\cdot+} \rightarrow Me_2N\cdot + Me_2NCO^+ \qquad (1)$$

Qin *et al.*, however, object to this on chemical grounds and favour an 'orthogonal' structure (**1b**).[4] Their new experimental work, including photobleaching experiments, the observation of line broadening for genuine $\cdot NMe_2$ radicals in $CFCl_2CF_2Cl$, and results for the cyclic analogue, 1,3-dimethylimidazolidine-2-one (**2**) led Qin *et al.* to claim that there is 'strong *prima facie* evidence for a deconjugated TMU cation.'[4] The purpose of this note is to point out that although the new results and reasoning offer a reasonable alternative to my original interpretation,[3] they are not compelling.

Reaction (1) is not without precedent: there are now numerous examples in which unimolecular breakdown gives a cation of type $RCO^+$ as one product. These are particularly favoured when the radical product is stabilised, for example, by Me-substituents.[5,6] There is also evidence that these products remain as cage-trapped pairs. Thus, if $TMU^{\cdot+}$ does give $\cdot NMe_2$, this will remain adjacent to $Me_2NCO^+$ whilst the $\cdot NMe_2$ radical formed from $Me_2NH$ will probably remain hydrogen-bonded as in (**3**). (This structure is based on the expectation that the parent $Me_2NH$ molecules will be present as pairs or clusters at 77 K.)

These different local environments can subtly modify the e.s.r. spectra, so there is no compelling requirement that they be identical. Indeed, the spectrum for genuine $\cdot NMe_2$ radicals shown by Qin *et al.* (their Figure 1b) shows a broadening on the low-field side of the spectrum relative to the '$(TMU)^{\cdot+}$' spectrum (Figure 1a of ref. 4 and Figure 1 of ref. 3). However, spectra for $\cdot NMe_2$ radicals in the pure (H-bonded) material also show a low-field broadening.[7] Also, we have spectra for $\cdot NMe_2$ radicals generated in non-H-bonding media which superimpose almost exactly on that for the TMU species, with no low-field broadening.[8] It therefore seems quite reasonable that both spectra are due to $\cdot NMe_2$ radicals, the modification being caused by the presence or absence of H-bonds.

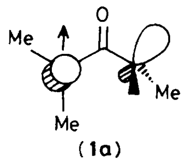
Furthermore, different environments can alter the photochemistry of the system. For the TMU system, given that dissociation has occurred, either $Me_2N\cdot$ or $Me_2NCO^+$ may be the photoactive species. It is not clear from ref. 4 what the paramagnetic photo-products are, but reaction between excited $Me_2N\cdot$ and $Me_2NCO^+$ (or *vice versa*) could explain the observed loss of signals that I have assigned to $Me_2N\cdot$ radicals. Indeed, the fragments may even form a charge-transfer complex, facilitating interaction in the excited state. The same reaction will not be available to the $Me_2NH$ system. Thermal reaction can still given an $R\text{–}\dot{C}H_2$ type radical, as in reaction (2), so this is understandable in either theory.

$$Me_2N\cdot + Me_2NCO^+ \rightarrow Me_2NH + H_2\dot{C}N(Me)CO^+ \qquad (2)$$

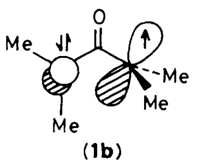
Results for 1-3-dimethylimidazolidine-2-one (**2**) are taken as further evidence for the twisted structure.[4] In this case, the e.s.r. spectra establish that the radical cation has a delocalised structure, with two equivalent nitrogen nuclei, six methyl protons, and four equivalent ring protons contributing to the spectrum. The results certainly show that, for the constrained ring system, reaction (1) doesn't occur. However, this is not unexpected. The results establish that delocalisation can, and does occur for this cation. I would not expect ring opening to occur because only 50% of the unimpaired electron density is associated with any one $Me_2N$ moiety. However, when twisting *can* occur, there is a shift of spin-density onto *one* nitrogen, and dissociation becomes possible. I view structure (**1b**) as a probable transition-state for reaction (1) as indicated in reaction (3). This does not require that (**1b**) should be the most stable structure, but simply that it should be accessible, which is not the case for the cyclic derivative. I conclude that these results accord well with my original postulate.

Returning to the e.s.r. parameters, the comparison between those for the TMU system and for established amide cations,[7,8] was the reason why I originally concluded that the species was *not* the primary cation. The key comparisons are (i) for structure (**1a**), for $(DMF)^+$ (DMF = dimethylformamide), $A(^{14}N)_\parallel \approx 39$ G† whilst for the TMU radical, $A(^{14}N)_\parallel \approx 42$ G. Given that $A_\perp \approx$ zero for both, this means there is a clear fall in spin density on nitrogen on going from the TMU radical to normal amide cations. In marked contrast, $A$(Me) for the amide cations (*ca.* 33 G) is much greater than that for the TMU radical (*ca.* 26.5 G). I can find no explanation for these reverse changes if the species has structure (**1a**), but the result is to be expected if the TMU species is $Me_2N\cdot$. This is because the spin is more localised on nitrogen for $Me_2N\cdot$ and hence $A(^{14}N)_\parallel$ is increased, but *despite* this, $A$(Me) is greater for the amide cations because of the well established positive charge effect which increases hyperconjugative electron release. These results show that for the TMU radical, the spin-density on nitrogen is higher than expected for an amide cation, and there is no positive charge enhancement.

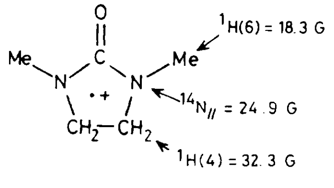
Qin *et al.* also consider that structure (**1a**) is unlikely, and have decided in favour of (**1b**). Now the comparison is not with amide cations but with, say, $Me_2\dot{N}H^+$. This has $A_\parallel(^{14}N) \approx 50$ G and $A$(Me) $\approx 37$ G.[7] These values are both



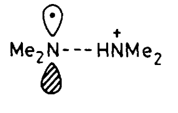
(**1a**)



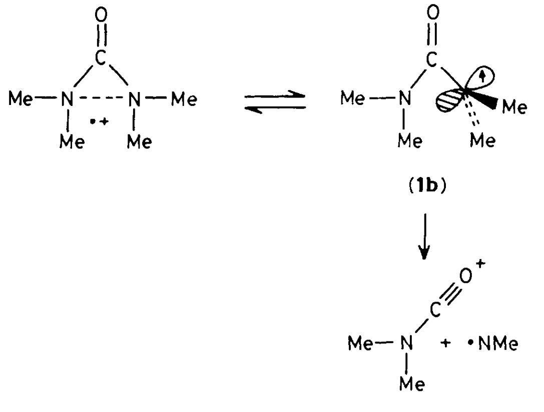
(**1b**)



(**2**)



(**3**)



(3)

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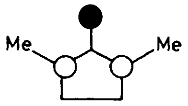
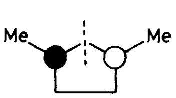
† 1 G = $10^{-4}$ T.



$(\pi_1)$

**(4a)**



$(\pi_2)$

**(4b)**

considerably greater than those assigned[4] to the $TMU^{\cdot+}$ cation [$A$(Me) = 27 G; $A_{\parallel}$ ($^{14}N$) = 42 G], but this difficulty has been overcome by postulating a novel interaction between the 2p orbital on N and the in-plane $n_O$ orbital on the carbonyl oxygen atom.[4] Although they do not suggest that this interaction is the *reason* for the preference of a 90° twist (**1b**), I can see no other reason for this unexpected preference (as opposed to the delocalised planar structure). I accept that this is a possible reason for the unexpected parameters. However, I still consider that the concept that the C–N bond then breaks to give $\cdot NMe_2$ is equally probable, the key point remaining that the e.s.r. spectra for non-hydrogen-bonded $\cdot NMe_2$ radicals and that from irradiated TMU are effectively identical.

Now that e.s.r. data for the delocalised cation are available, one can attempt to choose between the alternative SOMO's, ($\pi_1$, **1a**), (**4a**) and ($\pi_2$, **1b**), (**4b**). In my view, the data strongly support $\pi_2$ as the SOMO. Thus, if $A_{\perp}$($^{14}N$) is close to zero, the calculated 2p spin-density is *ca.* 0.5 on each nitrogen. Furthermore, the proton hyperfine coupling constants are very large compared with expectation based on data for the amide cations.[9,10] This suggests that there is no delocalisation onto the carbonyl group, as required for $\pi_2$.

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