The Radical Cation of Tetramethylurea: $Me_2N\text{-}CONMe_2{}^{+\bullet}$

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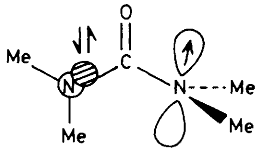
The radical formed from ^{13}CO labelled tetramethylurea in $CFCl_3$ solutions on exposure to ^{60}Co γ-rays at 77 K exhibits a nearly isotropic ^{13}C coupling of *ca.* 10 G in its e.s.r. spectrum, and hence it must be the parent radical cation $Me_2N\text{-}(CONMe_2)^{+\bullet}$ as suggested by Williams and his co-workers.

The study of radical cations formed by radiolysis of dilute solutions of many neutral compounds in Freon solvents at low temperatures by e.s.r. spectroscopy has revealed a variety of unexpected results.[1] In certain cases, these have been interpreted with alternative structures, one of the most novel being the 'orthogonal' structure for the ring-opened form of the cyclopropane radical-cation, in which the spin is confined to one carbon and the positive charge to the other $(H_2\overset{+}{C}CH_2\overset{\bullet}{C}H_2)$.[2] One of us has felt that the loss of 'delocalisative stabilisation' caused by the 90° twist required to generate such a structure from the conjugated π-alternative makes such orthogonal forms unlikely, unless the asymmetry is stabilised by, for example, bonding to a solvent molecule.[3]

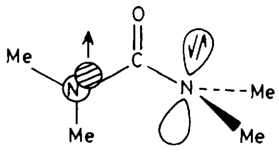
Recently, Williams and co-workers have suggested that the radical-cation of tetramethylurea (TMU) has such an orthogonal structure; that shown in (I) being favoured over (II) for a variety of reasons.[4] However, its e.s.r. spectrum (Figure 1) is essentially identical with that for $Me_2N^\bullet$ radicals, and so one of us has favoured the idea that reaction (1) occurs, the orthogonal structure (I) being a necessary reaction intermediate.[5,6] It was pointed out that Me_2NCO^+ is isoelectronic with Me_2NCN, and hence should be reasonably stable.

$$(Me_2N)_2CO^{+\bullet} \longrightarrow Me_2N^\bullet + Me_2NCO^+ \qquad (1)$$

Arguments for[4] and against[6] the orthogonal structure (I) have been presented in depth and need not be repeated herein. Suffice it to say that although Qin *et al.* stated that they were reasonably convinced that this structure is correct,



(I)



(II)

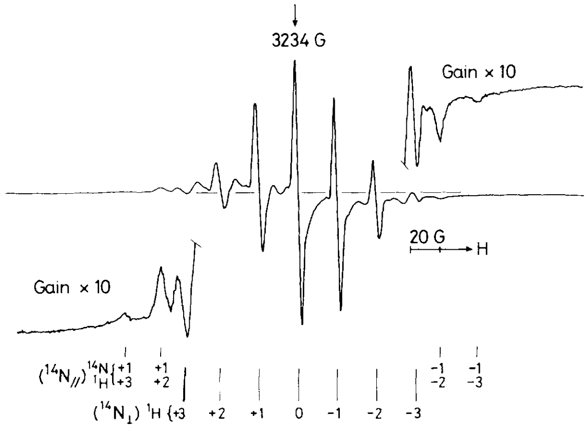


Figure 1. E.s.r. spectrum of $Me_2NCONMe_2{}^{+\bullet}$ cations in $CFCl_3$ at 77 K.

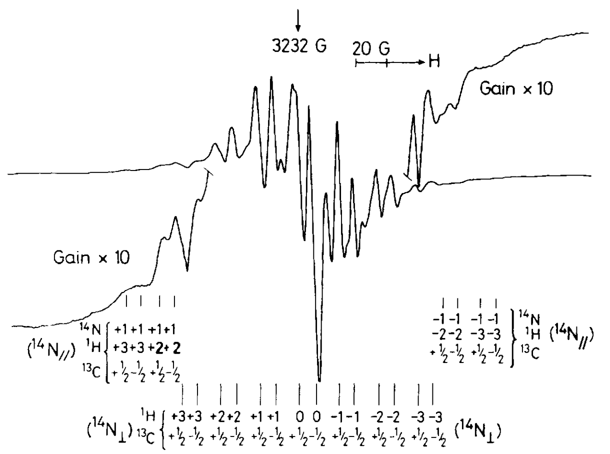


Figure 2. E.s.r. spectrum of $Me_2N^{13}CONMe_2^{+\cdot}$ cations in $CFCl_3$ at 77 K, showing additional 10.3 G ^{13}C doublet splittings of all features present in the spectrum of the ^{12}C derivative (Figure 1).

various alternative arguments have been proposed, which, in our view, left the issue quite open.[6]

It was therefore decided to attempt to resolve the issue by studying $(Me_2N)_2{}^{13}CO$ in $CFCl_3$, since $Me_2N^\cdot$ radicals would not be expected to show any significant ^{13}C hyperfine coupling. The results are, in fact, definitive, and seem to us to establish structure (I) unambiguously. For this structure there is no direct delocalisation of the unpaired electron onto the carbonyl carbon, but spin polarisation of the N–C σ-bonding electrons induced by the N(2p) electron is expected to give *ca.* 3% negative spin density on carbon. This would require an isotropic coupling close to 10 G ($G = 10^{-4}$ T). The ^{13}C hyperfine anisotropy is expected to be small due to cancellation of small dipolar interactions of opposing sign: one arising from the dipolar coupling between the ^{13}C nucleus and the N(2p) spin density, the other arising from the induced negative spin density in the N–C bonding orbital. In fact, 10.3 G splittings of all features were obtained (Figure 2) with no clear difference between parallel and perpendicular values. Thus the results agree with expectation for (I), and rule out the fragmentation reaction (1) as being of significance at 77 K. Even on annealing to the matrix softening point (*ca.* 160 K) we could not detect the loss of the ^{13}C coupling which would be expected to accompany the fragmentation (1).

This means that the novel concept that deconjugation can occur in a π-system on electron loss[4] is supported. We note that long established ideas regarding stabilisation *via* π-delocalisation have recently been called into question as a broad generalisation in a much wider context.[7]

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