

The Electronic Configuration of 1,3-Dialkyltriazenyl Radicals

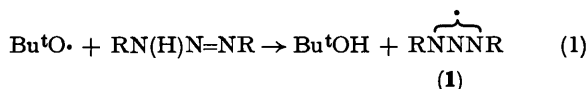
By JOHN C. BRAND and BRIAN P. ROBERTS*

(Christopher Ingold Laboratories, University College London, 20 Gordon Street, London WC1H 0AJ)

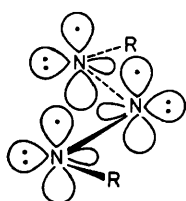
Summary It is concluded from the e.s.r. spectra of $\overset{\cdot}{\text{R}}\text{N}=\text{N}\overset{\cdot}{\text{N}}\text{R}$ (R = Me or Bu^t) that these species are σ radicals, rather than π radicals as proposed previously.

THERE has been much interest recently in the electronic configurations of nitrogen-centred free radicals and particular attention has been given to theoretical and experimental studies of π and σ states of amidyl and imidyl radicals.^{1,2}

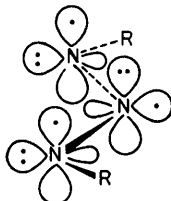
In 1978 Lunazzi and coworkers³ reported that photolysis of di-*t*-butyl peroxide in the presence of 1,3-dimethyltriazenes gave rise to an e.s.r. spectrum which they assigned to the 1,3-dimethyltriazenyl radical [equation (1; R = Me)].



These authors analysed the spectrum which they obtained at 173 K in terms of $a(1\text{N})$ 3.9, $a(2\text{N})$ 7.7, and $a(6\text{H})$ 11.6 G and thus concluded that (1; R = Me) is a π -radical [see (2)] in which the unpaired electron occupies a non-bonding allyl-type molecular orbital and is centred mainly on the two terminal nitrogen atoms. The σ electronic state (3) (analogous to the ground states⁴ of the isoelectronic NO_2 and N_3^{2-}) was rejected, since smaller proton and larger central nitrogen splittings would be expected if the unpaired electron were to occupy the anti-bonding three-centre σ molecular orbital.³



(2)



(3)

However, we have pointed out that the g -factor (2.0020) of (1; R = Me), reported by Lunazzi *et al.*, is difficult to reconcile with the π electronic configuration (2). Furthermore, we have shown that addition of trialkylsilyl radicals to alkyl or trialkylsilyl azides gives 1,3-triazenyl radicals [equation (2)] and we have proposed that these have σ ground



states analogous to (3).⁵ For example, the e.s.r. spectrum of $\text{Et}_3\text{SiN}=\text{N}\overset{\cdot}{\text{N}}\text{Me}$ shows $a(1\text{N}_{\text{central}})$ 17.1, $a(1\text{N})$ 3.6, $a(1\text{N}')$ 1.8 G, g 2.0009 at 260 K.

† Made by reaction of *t*-butyl-lithium with *t*-butyl azide, followed by hydrolytic work-up; satisfactory spectroscopic data and elemental analysis were obtained for this new compound (b.p. 64 °C at 45 Torr).

‡ The solvent was cyclopropane-benzene (4:1 v/v). Weaker spectra of (1; R = Me or Bu^t) were obtained when the appropriate triazene was photolysed in the absence of di-*t*-butyl peroxide. Photolysis of 1,3-dimethyltriazenes, either alone or with the peroxide, gave rise to a weak spectrum of the methyl radical in addition to that of (1; R = Me).

We now report that u.v. photolysis in the temperature range 160–260 K of a cyclopropane solution containing di-*t*-butyl peroxide and 1,3-di-*t*-butyltriazenes,† whilst the sample was in the cavity of an e.s.r. spectrometer, gave rise to a spectrum showing splitting by three ¹⁴N nuclei and which we assign to the triazenyl radical (1; R = Bu^t). Thermal generation of *t*-butoxyl radicals, from di-*t*-butyl hyponitrite⁶ at 335 K, in the presence of the triazene also afforded the spectrum of (1; R = Bu^t) (see the Figure).

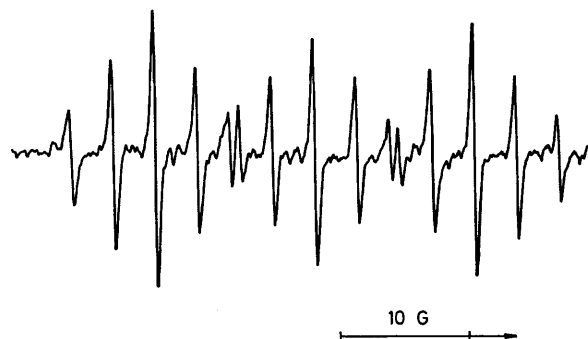


FIGURE. E.s.r. spectrum of (1; R = Bu^t) obtained during thermolysis of di-*t*-butyl hyponitrite (*ca.* 0.5 M) in the presence of 1,3-di-*t*-butyltriazenes (*ca.* 1 M) in benzene at 335 K.

The e.s.r. parameters are $a(1\text{N})$ 12.4, $a(2\text{N})$ 3.3 G, g 2.0019 at 335 K and, since the larger splitting is presumably from the central nitrogen, these imply that (1; R = Bu^t) adopts the σ electronic configuration (3).

In order to resolve the apparent discrepancy between our result and that reported previously, we generated the 1,3-dimethyltriazenyl radical by the published method [equation (1)]. Our spectrum (g 2.0021) at 190 K was essentially the same as that reported by Lunazzi *et al.*, but computer simulation using $a(1\text{N})$ 11.6, $a(2\text{N})$ 3.9, $a(6\text{H})$ 7.7 G resulted in equally good agreement with the experimental spectrum as was obtained using the values given previously³ (see above). At 170–200 K all the coupling constants are almost exact multiples of 3.9 G, leading to line superposition and hence to an apparently simple spectrum of equally-spaced lines (see the figure in ref. 3). However, slight temperature dependence of the coupling constants and a decrease in line-width at higher temperatures permits much more fine structure to be resolved in the spectrum of (1; R = Me) obtained at 226 K [$a(1\text{N})$ 11.5, $a(2\text{N})$ 4.0, $a(6\text{H})$ 8.0 G].‡

Our analysis was confirmed by generating the 1,3-bis-(trideuteriomethyl)triazenyl radical (1; R = CD₃) by hydrogen abstraction from the parent triazene. The spectrum obtained at 225 K was analysed and computer simulated using $a(1\text{N})$ 11.5, $a(2\text{N})$ 4.0, and $a(6\text{D})$ 1.2 G, whereas simulation of the experimental spectrum based on

the coupling constants given by Lunazzi *et al.*³ for the protio-analogue was not possible.

We conclude that the 1,3-dialkyltriazenyl radicals (1; R = Me or Bu^t) are σ radicals (3) rather than π radicals (2) as previously³ reported. The energy difference between σ and π configurations may be relatively small and recent *ab initio* molecular orbital calculations² have predicted that

for HNNNH these states are very close in energy with the σ radical more stable by only 6.7 kJ mol⁻¹.

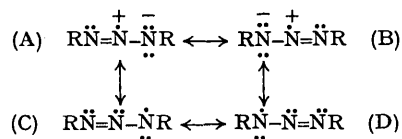
The unpaired electron in (1; R = Me or Bu^t) occupies a three-centre molecular orbital composed primarily of an

anti-bonding combination of nitrogen σ atomic orbitals, as shown in (3), and the largest coupling constant arises from the central ¹⁴N nucleus. § Both of these nitrogen-centred radicals have *g*-factors less than the free-spin value (2.0023), implying (for each) mixing-in by spin-orbit coupling of an excited state in which the unpaired electron is promoted to the empty π^* molecular orbital.

We thank the S.R.C. for financial support and we are grateful to Mr. C. J. Cooksey for preparing t-butyl azide.

(Received, 16th April 1981; Com. 452.)

§ In valence bond terms, the triazenyl radicals may be represented as a hybrid of the canonical structures (A)–(D), in which σ electrons are shown above the formulae.



¹ P. S. Skell and J. C. Day, *Acc. Chem. Res.*, 1978, **11**, 381; T. Clark, *J. Am. Chem. Soc.*, 1979, **101**, 7746; J. Lessard, D. Griller, and K. U. Ingold, *ibid.*, 1980, **102**, 3262; Y. Apeloig and R. Schreiber, *ibid.*, p. 6144.

² N. C. Baird and K. F. Taylor, *Can. J. Chem.*, 1980, **58**, 733.

³ F. Bernardi, M. Guerra, L. Lunazzi, G. Panciera, and G. Placucci, *J. Am. Chem. Soc.*, 1978, **100**, 1607.

⁴ P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967; G. W. Neilson and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 1772.

⁵ B. P. Roberts and J. N. Winter, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1353.

⁶ H. Kiefer and T. G. Taylor, *Tetrahedron Lett.*, 1966, 6163.