EPR studies of pyrazoline radical ions that are potential precursors to non-Kekulé polyene radical ions

Richard J. Bushby and Kai M. Ng

School of Chemistry, University of Leeds, Leeds, UK LS2 9JT

EPR spectra are reported for radical anion and (for the first time) radical cation derivatives of pyrazolines. The radical anion spectra are consistent with the unpaired electron being localized principally in the N=N π*-orbital and this agrees both with theoretical calculations and literature precedents. For the radical cations of 4-alkylidenepyrazolines, the near degeneracy of the N=N n⁻- and C=C π-orbitals makes the distribution of the unpaired electron difficult to predict. The spectra obtained indicate that the unpaired electron is chiefly associated with the N=N orbital. There is also significant density in the C=C bond. This is underestimated by UHF-INDO calculations. In principle, an elimination of (neutral) nitrogen from these radical ions would generate non-Kekulé polyene radical ions but so far this has not been achieved.

The planar acyclic polyenes with the general formula $C_{2n}H_{2n+2}$ containing $2n$ π electrons can be divided into two main groups: Kekulé and non-Kekulé.[1] For members of the former group we can write structures in which each π electron is 'paired' with one on a neighbouring carbon (as in butadiene, hexatriene, octatetraene, *etc.*) but for the non-Kekulé isomers (trimethylenemethane,† tetramethyleneethane,‡ pentamethyleneallyl, *etc.*) this is not possible. Most of the reactions of non-Kekulé polyenes parallel those of their Kekulé counterparts. They undergo cycloaddition,[2] dimerization,[3] electrocyclic[4] and sigmatropic[5] reactions and they form complexes with transition metals.[6] However, a major point of contrast is that the singlet state of a non-Kekulé polyene has a low unoccupied molecular orbital and as such it readily undergoes nucleophilic attack.[7] Also, since they are high 'HOMO', low 'LUMO' systems they should be more susceptible than Kekulé polyenes to one and two electron redox processes. Hence, as compared to butadiene 1 (a representative Kekulé polyene), trimethylenemethane 2 (a representative non-Kekulé polyene) should more readily form radical anion, dianion, radical cation and dication species (Fig. 1). A wide range of dianion (2-electron reduction) derivatives of non-Kekulé polyenes are known[8] but most of these were prepared by removal of two protons from the corresponding hydrocarbon rather than reduction of the polyene itself. The reason for this is obvious. Most non-Kekulé polyene are too short lived to 'trap' with a reducing agent. An interesting alternative route to non-Kekulé polyene redox products was recently outlined by Painter and Blackstock.[9] They showed that, after photo-oxidation, the pyrazoline radical cation 3 deazetizes to give (neutral) nitrogen and the trimethylenemethane radical cation 4. Their work also served to highlight another interesting contrast in behaviour between the radical ions of Kekulé and non-Kekulé systems. Whereas in Kekulé systems, such as the butadiene radical ion, the distribution of the 'charge' and the 'spin' are essentially the same, in non-Kekulé systems, such as radical cation 4, they are very different. In the ion 4, the spin resides mainly on the exocyclic position and the positive charge resides on the ring carbons. Such systems are termed 'distonic' and the separation of charge and spin distributions should have significant
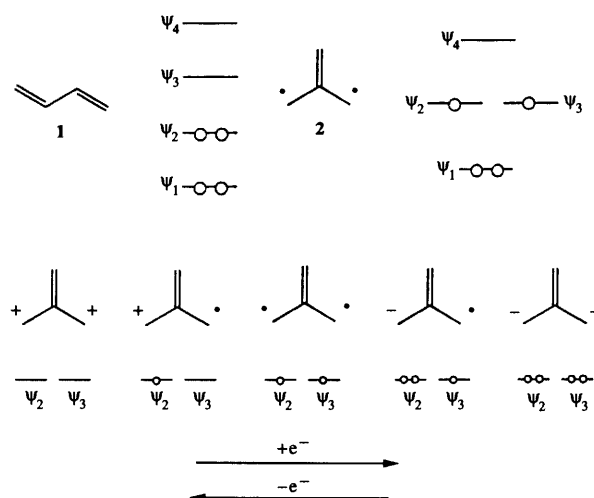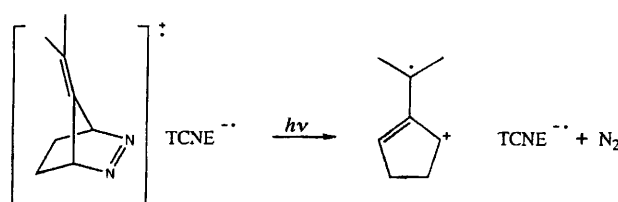

Fig. 1 Orbital occupancy for butadiene and trimethylenemethane, and for redox products of trimethylenemethane

chemical consequences,[9] particularly in polyenes where the NBMOs have a disjoint spatial distribution. This general strategy for producing radical-ions of non-Kekulé systems —producing the radical ion of a precursor that then eliminates a neutral fragment—has also been explored by Itoh *et al.* in the generation of radical anions and radical cations in the non-Kekulé quinodimethane series.[10] Therefore, it seemed of interest to reinvestigate the radical ions of some of the pyrazoline non-Kekulé polyene precursors that we have made.[11–13] In this paper we report the EPR spectroscopic observation and characterization of their radical anions and radical cations. These α-methylated pyrazoline TMM and TME precursors belong to the category of so-called 'reluctant' pyrazolines which are relatively difficult to deazetize both in the ground and excited state.[14] Unfortunately deazetization of

---

† TMM, trimethylenemethane. IUPAC preferred name: 2-methylidene-propane-1,3-diyl.
‡ TME, tetramethyleneethane. IUPAC preferred name: 2,3-dimethyl-idenebutane-1,4-diyl.

Table 1 EPR data for the radical ions derived from pyrazolines 5–8

Radical ion	Conditions	Hyperfine coupling constants[a]	g Factors	Fig.
5·⁺	DDQ, TFAH, hv, 260 K	a(2N) 12.80 G, a(6H) 1.0 G, a(12 H) 0.50 G and ΔH_{pp} 0.30 G	2.003 32	2(a), 2(b)
5·⁻	K, DME, 250 K	a(2N) 9.20 G, a(6 H) 0.11 G, a(12 H) 0.82 G and ΔH_{pp} 0.45 G	2.003 83	2(c)
6·⁺	DDQ, TFAH, hv, 260 K	a(2N) 12.87 G and ΔH_{pp} 0.85 G		3(a)
6·⁻	K, DME, 250 K	a(2N) 9.17 G, a(12 H) 0.87 G and ΔH_{pp} 0.40 G	2.003 82	3(b)
7·⁻	K, DME, 250 K	a(2N) 8.50 G and ΔH_{pp} 0.40 G		3(c)
8·⁻	K, DME, 250 K	a(2N) 8.85 G, a(12 H) 0.60 G, a(12 H) 0.50 G and ΔH_{pp} 0.25 G		3(d)

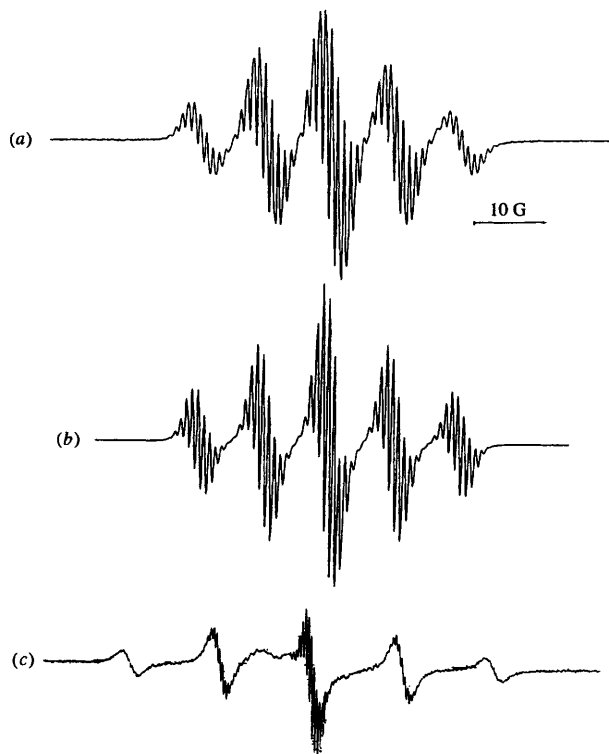[a] ΔH_{pp} = peak-to-peak width.

Fig. 2 (a) EPR spectrum for the radical cation of 5 (TFAH, 260 K). (b) Simulation using the parameters for **5·⁺** given in Table 1. (c) EPR spectrum for the radical anion of 5 (K⁺ salt, DME, 250 K).

Fig. 3 (a) EPR spectrum for the radical cation of 6 (TFAH, 260 K). (b) EPR spectrum for the radical anion of **6** (K⁺ salt, DME, 250 K). (c) EPR spectrum for the radical anion of **7** (K⁺ salt, DME, 250 K). (d) EPR spectrum for the radical anion of **8** (K⁺ salt, DME, 250 K).

their radical ions has also proved to be difficult. However, the work has led to the first EPR characterization of pyrazoline radical cations and other interesting observations.

Results and discussion

The main results of our EPR studies are summarized in Table 1 and typical EPR spectra are shown in Figs. 2 and 3. The radical anions were easy to prepare by reducing the pyrazoline with potassium mirror in dimethoxyethane (DME).[15] The EPR spectra of radical cations of pyrazolines have not been reported previously. Their EPR spectra were obtained by photolysis within the cavity of the EPR spectrometer of a solution of the pyrazoline in trifluoroacetic acid (TFAH) containing 2,3-dichloro-5,6-dicyanoquinone (DDQ).[16] The radical cation spectra only seemed to persist as long as the illumination continued and had totally disappeared within 15 s of turning off the lamp.

As can be seen from Figs. 2 and 3 all of the EPR spectra are dominated by coupling to two equivalent nitrogen nuclei giving a 1:2:3:2:1 quintet. In most cases, many smaller splittings are also seen which are attributed to coupling with hydrogen nuclei. A somewhat unusual feature is the broadening of the outer lines of the spectra, which is seen particularly clearly in Fig. 2(c).
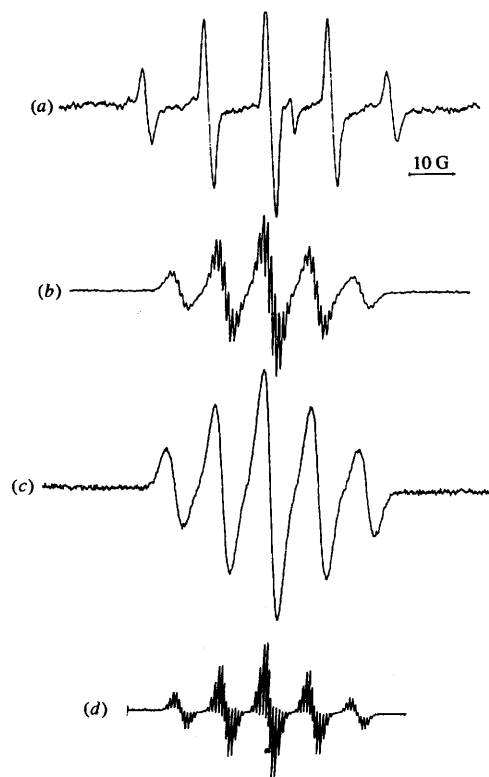
This has been noted for radical anions of other organic azo compounds and is attributed to the differences in the quadrupolar relaxation terms for the transition associated with the inner and outer lines.[15] This broadening effect made it a little difficult to simulate the spectra but as can be seen by comparing Fig. 2(a) and 2(b), the inner line(s) of the spectra could be simulated in a satisfactory manner. The results of the simulations are summarized in Table 1.

Radical anions

Fig. 4 shows schematically the ordering of the energies of the molecular orbitals for a 4-alkylidenepyrazoline. The lowest unoccupied molecular orbital is the π^* orbital associated with the nitrogen-nitrogen double bond. This is expected to be singly occupied in the corresponding radical anion. Such a radical anion is expected to be associated with a relatively large g value and relatively small nitrogen hyperfine splitting, because of its 'low s, high p' character. The values given in Table 1 are close to those reported for related *cis* azo radical anions [a(2N) 8.00–8.10 G and g values 2.0041–2.0042].[15,17] An INDO calculation[18] on the radical anion **5·⁻** using a geometry optimized for the neutral molecule at the MNDO level showed
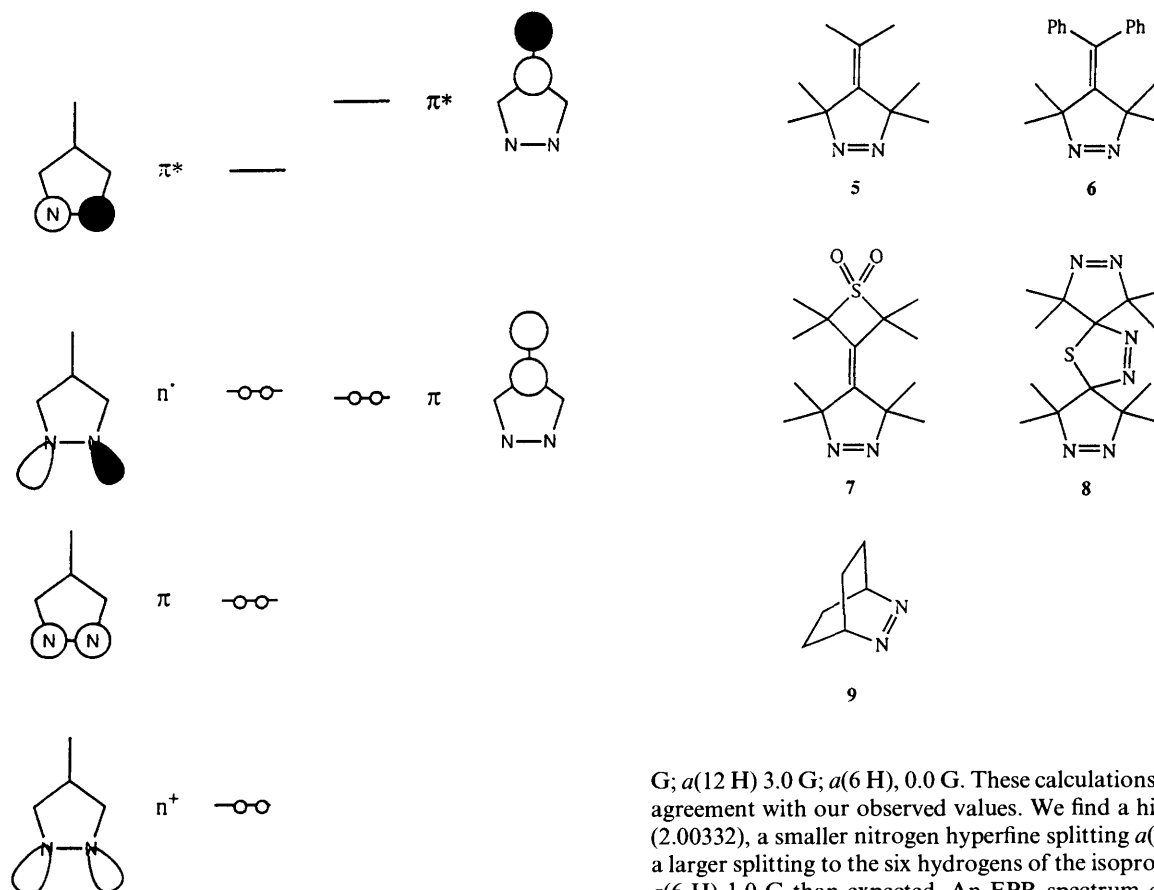
Fig. 4 Schematic representation of the significant occupied and unoccupied orbitals of a 4-alkylidenepyrazoline (see text)

that the unpaired electron was indeed associated with the nitrogen–nitrogen π^*-orbital. It gave predicted hyperfine splittings of $a(2N)$ 7.7 G; $a(12 H)$ 0.5 G; $a(6 H)$ 0.1 G which is in quite good agreement with that observed. Unlike some related systems,[15,17] we did not find it necessary to include splittings due to the metal cation nucleus. In the case of the radical anion derived from compound **8**, it is not clear *a priori* which of the three five-membered rings should bear the unpaired electron and whether there will be exchange between nitrogen π^*-orbitals. The observed EPR spectrum was temperature independent between 233 K and 298 K and could only be simulated in a satisfactory manner by including all 24 H with similar hyperfine splittings. It is most simply interpreted in terms of a spin more-or-less localized on the central thiadiazoline ring.

Radical cations

The case of the radical cations is much less straightforward. Molecular orbital calculations and the results of the vapour phase photoionization studies[19] show that there are two high energy MOs that are almost degenerate, the n^--orbital (the out-of-phase combination of the nitrogen 'lone pair' orbitals) and the carbon–carbon π-orbital. In the strictly symmetrical planar[20] molecule these are orthogonal to each other. Results obtained by Williams[21] and calculation by Gerson[22] and Gescheidt[17] on the *cis*-azo radical cation of the diazine **9**, in which an electron has been removed from the n^--orbital, leads to a relatively small g factor (2.0022) and a relatively large nitrogen hyperfine splitting $a(2N)$ 31.4 G. An INDO calculation on **5**[·+] (using the MNDO optimized geometry for the neutral molecule) leads to the prediction that the unpaired electron is mainly associated with the n^--orbital but with some spin-density in the C=C bond (apparently showing some mixing between n^- and π-orbitals) and gives a prediction of $a(2N)$ 19.9

5

6

7

8

9

G; $a(12 H)$ 3.0 G; $a(6 H)$, 0.0 G. These calculations are in a poor agreement with our observed values. We find a higher g factor (2.00332), a smaller nitrogen hyperfine splitting $a(2N)$ 12.80 G, a larger splitting to the six hydrogens of the isopropylene group $a(6 H)$ 1.0 G than expected. An EPR spectrum of the radical cation of compound **5** predeuteriated in the exocyclic isopropylene[23] confirmed that the splitting for six hydrogens in the radical cation **5**[·+] is indeed due to this group. When the geometry was optimized at the MNDO level for the *ion* it was found that the exocyclic isopropylene group twisted out-of-plane, and the charge became almost localized in the carbon–carbon π-orbital leading to INDO predicted values $a(2 N)$ 0.3 G; $a(12 H)$ 15.2 G; $a(6 H)$ 2.5 G. Still not in good agreement with the observed values. The problems of the interpretation undoubtedly arise from the near degeneracy of the n^- and π-orbitals. It seems either that the unpaired electron is undergoing rapid exchange (on the EPR timescale) between the nitrogen–nitrogen and carbon–carbon bonds but that the spin is predominantly associated with the N=N moiety or that we have a single species in which the spin is delocalized between the two centres and that the INDO calculation underestimates the spin density in the C=C double bond.

Experimental

The preparation of compounds **5–8** has been described previously.[11,12,23] Solvents were redistilled or of HPLC grade and reagents were used as supplied.

A potassium mirror was used for reduction of **5–8** and prepared by sublimation of small potassium metal chips. The apparatus and method employed have been described previously.[24]

EPR spectra were recorded on either Varian E-line or Bruker ER200 system, while g values were determined on Varian E-109 instrument equipped with a gaussmeter and using pyrene radical anion as the calibration standard.

Continuous photolysis within the cavity of the spectrometer was performed using a previously descibed 1 kW high pressure capillary mercury lamp and focusing system.[25]

Geometry optimization for closed shell species were performed at the RHF MNDO level. UHF INDO calculations have been used for the prediction of the hyperfine splittings of the radical ions.

References

1 R. J. Bushby and C. Jarecki, *Tetrahedron Lett.*, 1988, 2715; *J. Chem. Soc., Perkin Trans. 1*, 1990, 2335; G. Allinson, R. J. Bushby and J.-L. Paillaud, *J. Mater. Sci.: Mater. Electron.*, 1994, **5**, 67.

2 J. A. Berson, in *Diradicals*, ed. W. T. Borden, Wiley, New York, 1982; R. D. Little, *Chem. Rev.*, 1986, **86**, 875.

3 J. A. Berson, R. J. Bushby, J. M. McBride and M. Tremelling, *J. Am. Chem. Soc.*, 1971, **93**, 1544.

4 F. Weiss, *Q. Rev. Chem. Soc.*, 1970, **24**, 274; P. Dowd, *Acc. Chem. Res.*, 1972, **5**, 242; J. A. Berson, *Acc. Chem. Res.*, 1978, **11**, 446.

5 R. J. Bushby and S. Mann, *Tetrahedron Lett.*, 1986, 2057; *J. Chem. Soc., Perkin Trans. 1*, 1987, 2497.

6 M. D. Jones and R. D. W. Kemmitt, *Adv. Organomet. Chem.*, 1987, **27**, 279; B. M. Trost, *Pure Appl. Chem.*, 1988, **60**, 1615; A. J. Deeming, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 4.

7 R. D. Little, L. M. Brown and M. R. Masjedizadeh, *J. Am. Chem. Soc.*, 1992, **114**, 3071.

8 R. B. Bates, in *Comprehensive Carbanion Chemistry*, Part A, eds. E. Buncel and T. Durst, Elsevier, Amsterdam, 1980; J. Klein, *Tetrahedron*, 1983, **39**, 2733.

9 S. L. Painter and S. C. Blackstock, *J. Am. Chem. Soc.*, 1995, **117**, 1441.

10 M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita and K. Itoh, *J. Am. Chem. Soc.*, 1992, **114**, 7470; *Bull. Chem. Soc. Jpn.*, 1993, **66**, 1333.

11 R. J. Bushby and M. D. Pollard, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2401.

12 R. J. Bushby, M. V. Jesudason and S. Mann, *Tetrahedron Lett.*, 1983, 4743; *J. Chem. Soc., Perkin Trans. 1*, 1984, 2457.

13 R. J. Bushby, M. V. Jesudason, M. D. Pollard and K. F. Shuhaibar, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2647; R. J. Bushby,

M. V. Jesudason and M. D. Pollard, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2655.

14 M. F. Mirbach, M. J. Mirbach, K.-C. Liu and N. J. Turro, *J. Photochem.*, 1978, **8**, 299; P. S. Engel, C. J. Nalepa, R. A. Leckonby and W.-K. Chae, *J. Am. Chem. Soc.*, 1979, **101**, 6435; P. S. Engel, L. R. Soltero, S. A. Baughman, C. J. Nalepa, P. A. Cahill and R. B. Weisman, *J. Am. Chem. Soc.*, 1982, **104**, 1698; P. S. Engel, *Chem. Rev.*, 1980, **80**, 99.

15 C. H. Ess, F. Gerson and W. Adam, *Helv. Chim. Acta*, 1991, **74**, 2078.

16 A. G. Davies and K. M. Ng, *Aust. J. Chem.*, 1995, **48**, 167.

17 G. Gescheidt, A. Lamprecht, C. Ruchardt and M. Schmittel, *Helv. Chim. Acta*, 1991, **74**, 2094.

18 J. A. Pople, D. L. Beveridge and P. A. Dobosh, *J. Am. Chem. Soc.*, 1968, **90**, 4201.

19 K. N. Houk, Y.-M. Chung and P. S. Engel, *J. Am. Chem. Soc.*, 1975, **97**, 1824.

20 R. J. Bushby, S. Mann and W. S. McDonald, *Tetrahedron Lett.*, 1982, **23**, 573.

21 F. Williams, Q.-X. Guo, P. A. Petillo and S. F. Nelsen, *J. Am. Chem. Soc.*, 1988, **110**, 7887.

22 F. Gerson and X.-Z. Qin, *Helv. Chim. Acta*, 1988, **71**, 1498.

23 R. J. Bushby, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1211.

24 R. J. Bushby and G. J. Ferber, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1688; G. Allinson, R. J. Bushby, J.-L. Paillaud and M. Thornton-Pett, *J. Chem. Soc., Perkin Trans. 1*, 1995, 385.

25 P. B. Ayscough, T. H. English and D. A. Tong, *J. Phys. E*, 1976, **9**, 31.