# (3-Nitrenophenyl)methylene: a Ground State Quintet Molecule having Both Carbenic and Nitrenic Atoms

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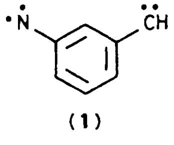
(3-Nitrenophenyl)methylene (**1**), a non-Kekulé molecule with quintet ground state, has been generated photochemically from (3-azidophenyl)diazomethane in organic matrix at cryogenic temperatures.

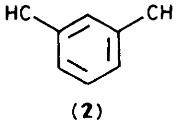
Intramolecular interaction between radical centres in organic polyradicals is of great interest in current theoretical, physical, and preparative organic chemistry. In work guided by Longuet-Higgins' theory[1] on π-non-bonding molecular orbitals in alternant hydrocarbons, a number of diradicals[2] and polyradicals have been generated that have high-spin ground states. Most of them are, however, hydrocarbon radicals, for which this theory applies rigorously. In this paper, we report the generation and spin-state of the nitreno carbene (**1**), a mixed analogue of *m*-phenylenebis(methylene) (**2**) and *m*-phenylenebis(nitrene) (**3**) that were shown[3] 20 years ago to be in quintet ground states. The ground-state spin multiplicity of this new non-Kekulé molecule cannot be predicted straightforwardly because the non-bonding molecular orbitals are far from degenerate. As a result of the different electronegativities of carbon and nitrogen, zwitterionic singlet or triplet states could be more stabilized than those of (**2**) and (**3**).

Thermolysis (70 °C; 5 min) of the sodium salt of 3-azidobenzaldehyde tosylhydrazone in ethylene glycol gave (3-azidophenyl)diazomethane (**4**) as a thermolabile orange-red oil.† Irradiation (500 W Hg lamp; Pyrex-filtered; 13 min) of freshly sublimed (**4**) in 2-methyltetrahydrofuran at 18 K produced material exhibiting a set of e.s.r. signals due to a quintet species together with a signal characteristic of the $X,Y$-transition (at 0.6862 T, $|D|/hc = 1.011\ \mathrm{cm}^{-1}$, $|E|/hc = 0\ \mathrm{cm}^{-1}$) of a triplet mononitrene (Figure 1). Signals due to the $|\Delta m| = 1$ transition of triplet arylmethylene were not detected.

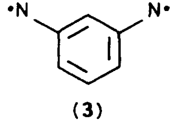
The observed resonance fields, in particular the signal at 0.7295 T assigned to the $Z$-transition of $|\Delta m| = 1$ for a quintet, were best reproduced by a third-order perturbation calculation[4] with $|D|/hc = 0.124\ \mathrm{cm}^{-1}$ and $|E|/hc = 0.002\ \mathrm{cm}^{-1}$. A few signals observed at lower fields (0—0.1 T and 0.27 T) cannot be explained by the calculation at this level, but they may be assigned to the quintet state.[4c] The $D$ value lies between those of (**3**) ($|D|/hc = 0.156\ \mathrm{cm}^{-1}$) and (**2**) ($|D|/hc = 0.0844\ \mathrm{cm}^{-1}$). This is reasonable because the dipolar interaction tensor of a quintet species[4] is expressed as the sum of the dipolar tensors of the individual triplet species; a dominant factor governing the $D$ value of the quintet species constructed from two triplet sites is the sum of the $D$ values for the triplet sites [–CH: and –N: in the case of (**1**)], and a secondary factor is the angle between the principal axes of the triplet centres. The intensities of all signals appearing below 0.8 T obeyed the Curie law in the temperatrue range 17—69 K. Irreversible decrease of the quintet signals was observed at 77 K (within a few min). When the material was cooled to 16 K after 10 s at 84 K, no quintet signals were regenerated; the triplet signal remained unchanged. These observations indicate that the



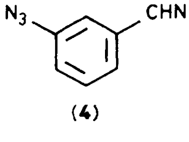
(**1**)



(**2**)



(**3**)



(**4**)

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† Spectroscopic data for (**4**): $\nu_{\mathrm{max.}}$ (neat) 2060 and 2120 cm$^{-1}$; $\lambda_{\mathrm{max.}}$ (2-methyltetrahydrofuran) 480 nm; $\delta_H$ (400 MHz; $CDCl_3$) 7.25 (t, $J$ 7.9 Hz, 1H), 6.70 (ddd, $J$ 7.9, 1.8, and 1.0 Hz, 1H), 6.68 (ddd, $J$ 7.9, 1.8, and 1.0 Hz, 1H), 6.52 (t, $J$ 1.8 Hz, 1H), 4.93 (s, 1H); $\delta_C$ (100 MHz; $CDCl_3$) 140.98, 132.23, 130.32, 117.86, 114.36, 111.49, and 47.48.

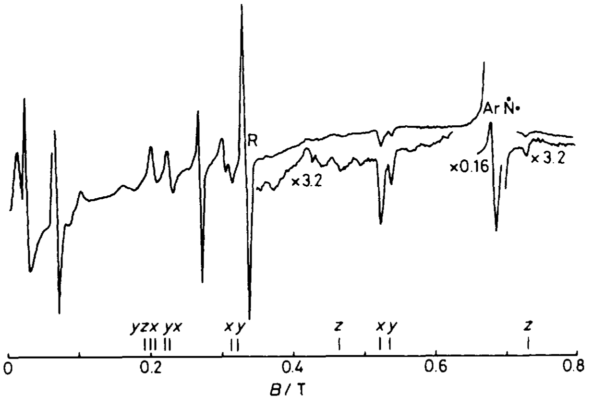

**Figure 1.** E.s.r. spectrum (*X*-band, 9.33149 GHz) of (3-nitrenophenyl)methylene (**1**) obtained by u.v. irradiation of (**4**) in 2-methyltetrahydrofuran at 22 K; R and ArN denote doublet and triplet impurities, respectively. Bars at the bottom indicate calculated resonance fields for the quintet with $|D|/hc = 0.124$, and $|E|/hc = 0.002\ \text{cm}^{-1}$.

quintet is the ground state of (3-nitrenophenyl)methylene (**1**) and the observed triplet peak does not correspond to a thermally populated state or to a state degenerate with the quintet of (**1**) but to (3-diazomethylphenyl)nitrene or other arylnitrenes.

An *ab initio* calculation (3-21G basis set) for the quintet species (**1**) shows the lack of degeneracy of non-bonding molecular orbitals and alternation of α- and β-spins over the whole molecule. It is interesting that Hund's first rule is inviolate in (**1**) (e.s.r. experiments) even with this lack of degeneracy of NBMOs. The finding is consistent with data on mixed diradicals given by Platz[5] and Berson.[6] All the results demonstrate that ground-state spin multiplicities of alternant non-Kekulé molecules are subject not to splitting of energy levels of NBMOs due to substitution by heteroatoms, but to good connectivity[6] or topological symmetry.[7]

These results may point the way to the construction of high-spin molecules and organo-ferromagnets by combinations of open-shell centres.

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