Phenaleno[1,9-*cd*]dithiolyl: the First Example of a Monomeric, Coplanar, Carbon-based Free Radical

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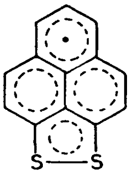
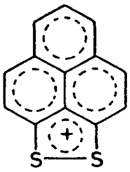
Summary The phenaleno[1,9-*cd*]dithiolyl radical has been prepared in solution by electrochemical and chemical reduction of phenaleno[1,9-*cd*]dithiolium hexafluorophosphate; it has been studied by e.s.r., mass, and electronic spectroscopy, and is monomeric in solution in the temperature range 19 to −95 °C.

Attention has been drawn to the potential of monomeric, planar, carbon-based radicals in the design of 'organic metals'.[1] We report here the first example of this class of compounds, the phenaleno[1,9-*cd*]dithiolyl radical (**1**), which may be prepared by chemical or electrochemical reduction of the hexafluorophosphate of (**2**).[2]

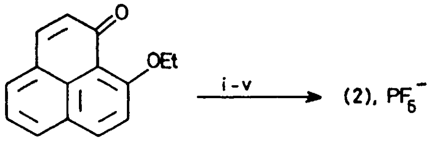


(1)



(2)

The cation (**2**) was prepared by the route in the Scheme, which is a modification of previous entries into the 1,2-dithiolium system.

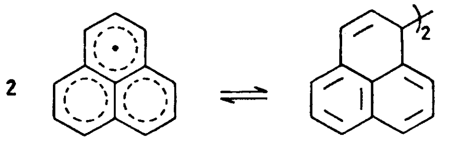


(**3**)

SCHEME. i P_2S_5, reflux in CS_2; ii solvent removal; iii 4N HCl, reflux; iv filtration; v addition of $NaPF_6$ solution to filtrate.

Most neutral organic radicals exist in equilibrium with a dimeric form.[3,4]† However, the dimerization of carbon-based radicals is inhibited by severe steric interactions (sometimes in conjunction with decreased electronic delocalization) in the dimer.[3,4] The relative importance of steric effects and delocalization in preventing dimerization of neutral, carbon-based radicals has been much debated, but current thought seems to favour steric arguments.[5]

Accordingly, the possibility of obtaining a monomeric planar carbon-based radical seemed rather remote. Although the phenalenyl radical (**4**) appeared to be a likely candidate,[1,6] this species has been observed to be in equilibrium with a diamagnetic dimer (**5**).[6,7] Since dimerization of (**4**)



(1)

(**4**) (**5**)

does not present particularly severe steric problems, the additional delocalization energy in the monomeric form (**4**) appears to provide the driving force favouring some degree of dissociation. There is evidence to suggest that chalcogens[8,9] are effective in stabilizing spin density, and we expected that incorporation of, *e.g.*, disulphide groups across the active positions[1] of (**4**) would stabilize the monomeric radical form while sterically interfering with dimerization.

We had expected that multiple substitution by disulphide groups would be required to inhibit the dimerization [reaction (1)] in derivatives of (**4**). However, surprisingly, solutions‡ of (**1**) prepared in various solvents§ showed no appreciable change in the concentration of monomer in the temperature range 19 to −95 °C. This behaviour is qualitatively similar to that noted for certain alkylated derivatives of (**4**)[6,7] and suggests that (**1**) is monomeric in solution. These results are substantially different, however, from those reported[7,8] for solutions of (**4**) in which e.s.r. signals are not observed below −25 °C.

The unique well resolved 36 line e.s.r. spectrum of (**1**) can be successfully computer-simulated assuming one set of three equivalent protons (a_H 1·49 G), and two sets of two equivalent protons (a_H 5·06 and 5·45 G). Essentially identical spectra were obtained when (**1**) was generated‡ by chemical (Zn) or electrochemical reduction of (**2**),PF_6^- in various solvents.§ Comparison of the observed hyperfine splitting constants for (**1**) with those for (**4**)[7] indicates that an appreciable amount of spin density (*ca.* 20%) is removed from the phenalenyl nucleus on disulphide substitution.

The electronic spectrum of (**1**) (red in solution), λ_{max} 420 nm, may be compared with that of (**3**) (blue in solution) which has an absorption maximum at 613 nm.[8] The mass spectrum of the solid left upon removal of carbon disulphide from a solution‡ of (**1**) showed a molecular ion at *m/e* 227 [$C_{13}H_7S_2^+$, assigned to (**2**)], with the expected isotope distribution.

The unusual stability of (**1**) toward dimerization is further demonstrated by its paramagnetism in the solid state. The temperature dependence of its magnetic susceptibility, together with the chemical and physical properties of (**1**) and (**2**) are being investigated.

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† For a discussion of heteroatom-based radicals, see ref. 3.

‡ Solutions of (**1**) were most conveniently prepared (under argon) by coulometric reduction of (**2**), PF_6^- (ref. 2) in acetonitrile, with subsequent extraction of the electrolyte with carbon disulphide.

§ Solvents used included methylene chloride–toluene (1 : 3, v/v), dimethoxyethane–toluene (1 : 3, v/v), methylene chloride, and carbon disulphide. Radical concentrations were in the range 10^{-6} to 5×10^{-4} M and were determined by measurement of the integrated e.s.r. signal intensity against a standard solution of 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-1-oxyl radical.

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[2] The cation (2) has been fully characterized and details will be published elsewhere: R. C. Haddon and F. Wudl, unpublished data.
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