Formation of Three- and Two-electron σ-Bonds by removal of Lone Pair Electrons from a Diamine†

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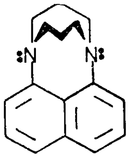
Summary 8,9,10,11-Tetrahydro-7*H*-7,11-propanonaphtho[1,8-*bc*][1,5]diazocine (**1**) is reversibly oxidised to (**2**) and (**3**); spectroscopic data for (**2**) and (**3**) suggest that simple two-centre 3- and 2-electron σ-bonds are formed in the oxidation.

The preparation, solid-state structure, and photoelectron spectrum of (**1**) have been reported.[1] Cyclic voltammetry of (**1**) in MeCN (Pt anode, 0·2M Et_4NBF_4 supporting electrolyte) shows two reversible waves at +0·11 and +0·72 V *vs.* SCE. The second wave is only reversible at scan speeds $> 1\ V\ s^{-1}$ and then only when the special drying technique of Hammerich and Parker[2] is used. These oxidation potentials are exceptionally low for a non-conjugated amine and are similar to those for *NNN′N′*-tetramethyl-*p*-phenylenediamine (+0·01 and +0·60 V *vs.* SCE). Tetra-alkylhydrazines have[3] similar first oxidation potentials (oxidations to dications are not reversible); their cation radicals have 3-electron π-bonds and are of moderate stability ($t_{\frac{1}{2}}$ several hours).

Solutions of (**2**) in MeCN (prepared by oxidation with $AgBF_4$ or PhN_2PF_6) appear to be indefinitely stable, though we have been unable to obtain a crystalline salt from (**2**). Acidic aqueous solutions of (**2**) are also quite stable, with maximum stability near pH 2 where the characteristic visible absorption persists for months in dilute solution. The e.s.r. spectrum of the BF_4^- salt of (**2**) in MeCN can be simulated with the following parameters: $2 \times a_N$ 1·41 mT, $4 \times a_H$ 2·25 mT, linewidth 0·6 mT. The spectrum is unchanged up to 75 °C (in AcOH) and fits a structure for (**2**) with nearly planar equivalent nitrogen atoms. The relatively large value for a_N is consistent with

† No reprints available.

σ* character in n_- (the spin-bearing orbital), which will cause the nodes to lie inside the nitrogen nuclei.[4] The interpretation of the a_H values appears to depend on the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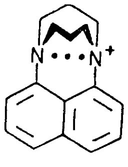
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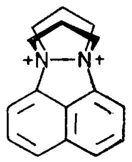
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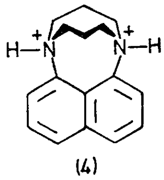
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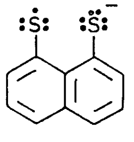
(5)

conformation of the alicyclic ring in (**2**) and this could be boat-chair, chair–chair, or boat–boat (or a mixture).‡ However, models of all these conformations (with planar nitrogen atoms) show one proton of each α-CH$_2$ group making a dihedral angle, ϕ, of *ca.* 20° with the axis of the spin-bearing orbital (the other α-proton has ϕ *ca.* 90°). From $a_H = B\cos^2\phi$, taking $B = 5{\cdot}0$ mT and allowing for spin distribution between two nitrogen atoms, one calculates $a_H = 2{\cdot}21$ mT for these protons. The remaining 14 protons should have small hyperfine couplings ($< 0{\cdot}1$ mT), the sum of their effects presumably causes the large linewidth of the spectrum.

The cation radical is brown-red (λ_{max} 480 nm, log ϵ_{max} 3·1 in MeCN) with a smoothly declining absorption into the near i.r. (log ϵ 0 at 1050 nm), the whole band having an oscillator strength of *ca.* 0·02). We suggest this band is a result of the excitation of an electron from n_+ to n_-. The broadness of the band fits a large change in equilibrium N–N distance between the two states (Figure). The u.v. spectrum of (**2**) closely resembles that of (**1**) and points to the non-involvement of the naphthalene portion of the molecule in the oxidation.

Treatment of (**1**) with SbF$_5$ in SO$_2$ClF at −80 °C, followed by addition of HSO$_3$F and evaporation of SO$_2$ClF, gives a solution (stable at room temperature) which we believe contains (**3**) and (**4**) in *ca.* 2 : 1 ratio. (**4**) arises from protonic acid impurities present during the SbF$_5$ oxidation, and can be separately observed by dissolving (**1**) in HSO$_3$F. The peaks due to (**3**) can be analysed as an aromatic ABX system [ν_A (*ortho*) δ 1·89; ν_B (*meta*) δ 1·82; ν_X (*para*) δ 1·55; $J_{o,m}$ 7·5; $J_{o,p}$ 0·6; $J_{m,p}$ 8·4 Hz) and an (approximate)§ C$_2$D$_2$YZ spectrum for the alicyclic protons (ν_C δ 4·95; ν_D δ 4·85, ν_Y δ 3·38; ν_Z δ 2·92; J_{CD} 12; $J_{CX} = J_{DX} = J_{DY}$ 6; J_{CY} 7, J_{XY} 15 Hz). Three features of this spectrum call for comment. (i) Absorptions for both α- and β-CH$_2$ groups of (**3**) are substantially downfield of those for (**4**) (α-CH$_2$ δ 4·25, β-CH$_2$ δ 2·4—2·7). This accords with a greater average proximity of positive charge centres to these protons in (**3**). (ii) $J_{o,p}$ is small for (**3**) but large (1·9 Hz) for (**4**). We have always found that, in 1,8-disubstituted naphthalenes, $J_{o,p}$ is large if the 1- and 8-substituents are splayed apart ($J_{o,p}$ 1·7 Hz for 1,3,6,8-tetra-t-butylnaphthalene)[5] but is small if the 1- and 8-substituents are bonded together (0·6 Hz in acenaphthylene).[6] This suggests (**3**) contains a N–N σ bond of fairly normal length. (iii) The coupling constants among the alicyclic protons are consistent[7] with the presence of 5-membered rings in (**3**). (**3**) appears to be the first recorded fully substituted hydrazinium dication.

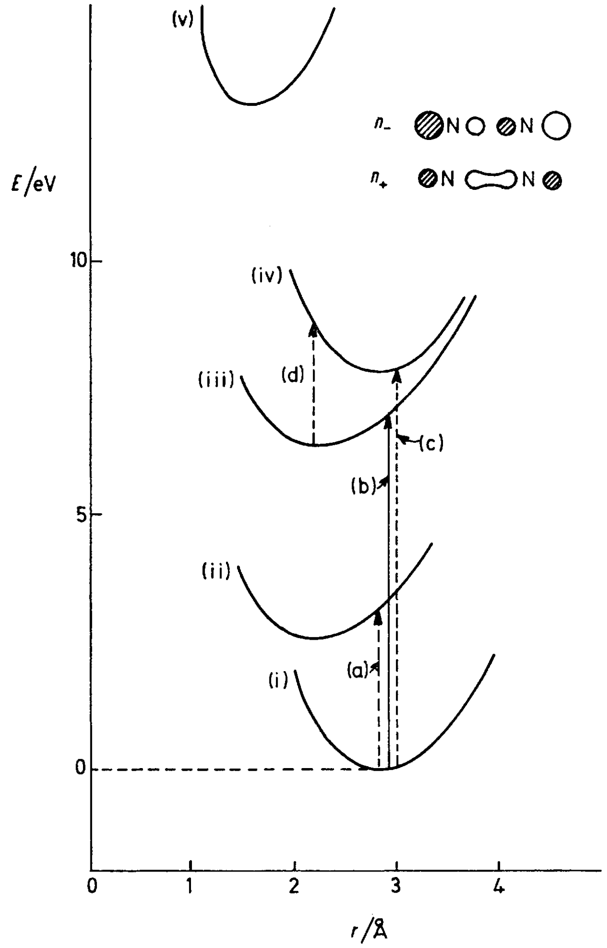

FIGURE. Schematic representation of energy *vs.* N–N distance (r; other co-ordinates relaxed to minimise energy). (i) Amine (**1**), ground state, n_+ (⇅) n_- (⇅). (ii) First excited state of amine, probably n_+ (⇅) n_- ( ) σ* (↓). (iii) Ground state of (**2**), n_+ (⇅) n_-(↑). (iv) First excited state of (**2**), n_+ (↑) n_- (⇅). (v) Dication (**3**), n_+(⇅) n_-(0), energy arbitrary. (a) Visible absorption of (**1**), 3·25 eV. (b) First vertical I.P. of (**1**), 6·90 eV. (c) Second vertical I.P. of (**1**) 7·75 eV. (d) Visible absorption of (**2**), 2·58 eV. The first adiabatic I.P. of (**1**) is <6·4 eV from the cut-off in the photoelectron spectrum. A figure of *ca.* 6·3 eV may be estimated from the correlation of oxidation potential and I.P. given by V. D. Parker, *J. Amer. Chem. Soc.*, 1976, **98**, 98, assuming (**2**) is solvated like an alternant aromatic hydrocarbon radical cation. The (questionable) application of the same correlation to the second oxidation wave would place the minimum for (**3**) *ca.* 13 eV above that for (**1**).

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‡ Although (**1**) is in a boat-chair conformation in the solid (ref. 1), low-temperature ^{13}C n.m.r. spectra indicate a conformational mixture (*ca.* 1 : 1) in solution, probably of the boat-chair and chair–chair forms.

§ Overlapping absorptions from (**4**) in the region of the β-CH$_2$ absorptions prevent more precise analysis.

The system (**1**) $\rightleftharpoons$ (**2**) $\rightleftharpoons$ (**3**) is experimentally convenient for studying some of the fundamental features of σ-bond formation. The molecular geometry of bicyclo[3.3.3]-undecane is probably close to ideal for the formation of species like (**2**). The He_2^+–H_2 bond length ratio of 1·46 leads one to expect an optimum bond length of about 2.2 Å for a 3-electron N–N σ-bond. The natural 'bite' of both naphthalene and $[CH_2]_3$ bridges is *ca.* 2·4 Å. (**2**) is a member of a growing class of species containing 3-electron σ-bonds,[8] but the only other example which is stable in solution and whose redox chemistry is fully established is (**5**).[9]

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