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"Conjugated" Nitronyl-nitroxide and Imino-nitroxide Biradicals

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Summary The new biradicals (**3**), (**5**) and (**6**) have low lying triplet states having perpendicular conformations in solution.

Controversy exists concerning the nature of so-called conjugated organic biradicals.[1] A non-conjugated structure for porphyrindene has recently been suggested,[2] and the Chichibabin-type biradicals are reported to associate in complex ways in solution.[3] Bis-verdazyls,[4] bis-galvinoxyl[5] and the Yang biradical[6] are the best characterized stable biradicals that are potentially conjugated. The relatively small electron–electron dipolar interactions in these compounds suggest that interactions within the π-electron systems may be hindered due to non-planarity, although direct evidence concerning their conformations in solution is lacking. We report here evidence concerning the geometries of a new class of stable, potentially conjugated biradicals which show particularly strong dipolar interactions.

Zero field splitting parameters (*Gauss*)[a]

	Calculated[b]						
Biradical	Perp.		Planar		Found		1/2 Field line
	D	*E*	*D*	*E*	*D*	*E*	
(**3**)	159	0	710	50	215	$\sim$5[c]	1622
(**5**)	198	15	685	54	267	21	1622
(**6**)	214[d]	7	544[d]	70	422	$\sim$12[c]	1611

[a] Measured in methyltetrahydrofuran at 77° K at 9·12 GHz. [b] Each unpaired electron was assumed to be localized at points within a single ring, either midway between the O- and N-atoms of an NO group or directly on the imino-nitrogens. In the imino-nitroxide rings 67% of the spin density was assigned to the NO group. Angles and distances were estimated from Dreiding models. [c] Estimated by taking the separation of the inner pair of lines as equal to $D-3E$. See text for description of spectra. [d] Calculated D-values for (6) are low since no spin density was assigned to the trigonal carbons. M.O. calculations predict spin density on these atoms in the imino-nitroxide ring but not in the nitronyl-nitroxide ring.

The unsubstituted nitronyl-nitroxide (**1**) ionizes with potassium t-butoxide in dimethyl sulphoxide to the radical-anion (**2**).[7] Treatment of solutions of (**2**) with oxygen or potassium ferricyanide yielded the light purple bis-nitronyl-nitroxide (**3**) [m.p. 220—222°, m/e, 312 (M^+)]. Alternatively, biradical (**3**) was formed by treatment of the iodonitronyl-nitroxide (**4**)[7] with copper in dimethylformamide. Treatment of biradical (**3**) with sodium nitrite in dimethylformamide containing *ca.* 0·5% acetic acid yielded two additional biradicals (**5**) [brown solid, m.p. 195—196°, m/e, 296 (M^+)]‡ and (**6**) [orange solid, m.p. 206—209°, m/e, 280 (M^+)].‡

Ether solutions of each of the biradicals (**3**), (**5**), and (**6**) displayed very broad e.s.r. signals at room temperature with poorly resolved hyperfine coupling, difficult to interpret. Bulk magnetic susceptibility measurements[8] of the biradicals at 35° in methylene chloride gave values indicative of 49%, 67%, and 63% triplet character respectively for (**3**), (**5**), and (**6**). These values are low relative to the 75% triplet character expected of biradicals with weakly interacting free spins. By comparison, the unconjugated trimethylene-bis-nitronyl nitroxide‡ derived from glutaraldehyde and 2,3-dimethyl-2,3-bis-(hydroxylamino)-butane[9] displayed 75% triplet character. The absence of concentration dependence of the magnetic susceptiblities rules out molecular association as a cause of the reduced spin concentrations.

When the temperature of methylene chloride solutions of (**3**) and (**5**) were lowered from 35° to −35°, the magnetic

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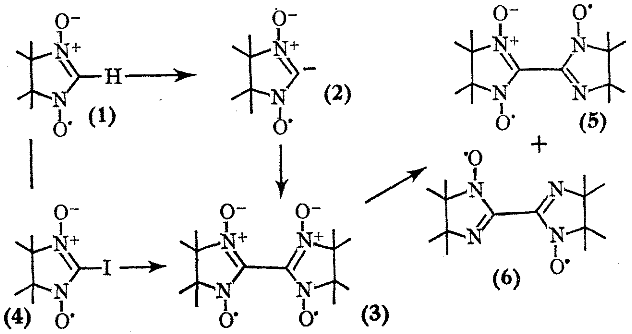
‡ Satisfactory elemental analysis obtained.

susceptibilities decreased. The singlet states of (**3**) and (**5**) are thus less energetic than the triplet states; $\Delta H(\mathbf{3}) = 750$ and $\Delta H(\mathbf{5}) = 280$ cal., $\Delta S(\mathbf{3}) = 2{\cdot}2$ and $\Delta S(\mathbf{5}) = 2{\cdot}3$ eu. These entropy differences agree with the value expected from the statistical 3 : 1 triplet : singlet ratio predicted from quantum mechanics.

The triplet character of the biradical (**6**) increased on lowering the temperature from 35° to −14°. The triplet state thus *appears* to lie below the singlet, $\Delta H(\mathbf{6}) = -850$ cal, but the singlet state is statistically preferred, $\Delta S(\mathbf{6}) = -1{\cdot}7$ eu. These data together with the appearance of $<75\%$ triplet character in (**6**) demand that the singlet and triplet states must be geometrically non-equivalent with the singlet conformationally the more mobile. The possibility of conformational isomerism introduces an uncertainty in the above thermodynamic data. Since conformationally similar molecules will have a statistical 3 : 1 triplet : singlet preference, the entropy contribution arising from the conformational mobility of the singlet can be eliminated by combining the theoretical entropy, $\Delta S(\mathbf{6}) = 2{\cdot}19$ eu., with the largest observed equilibrium constant, $K = 2{\cdot}2$. Since this gives a maximum possible enthalpy which is positive, $\Delta H(\mathbf{6}) = 160$ cal., the multiplicity of the ground state of any one fixed conformation of (**6**) remains uncertain.



The e.s.r. spectra of (**3**) and (**6**) at 77°K display two lines and (**5**) displays three lines on either side of weak monoradical signals. Zero-field splitting parameters are summarized in the Table together with calculated parameters. Despite only rough numerical agreement due to the approximations used, the relative magnitudes of the zero-field splitting parameters clearly suggest nearly perpendicular conformations for the triplet states of all three biradicals. Since in (**3**) and (**5**) the singlet and triplet states must have similar conformational mobility to account for the "normal" entropy values, the simplest interpretation of the data assigns preferred perpendicular conformations to both states of (**3**) and (**5**). However the conformation of the singlet of (**6**) remains indeterminate.

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[8] Measured by the n.m.r. method of D. F. Evans, *J. Chem. Soc.*, 1959, 2003.

[9] *Cf.* ref. 7 for the method of synthesis of nitronyl nitroxides.