

MEROSTABILISATION - A NEW PRINCIPLE GOVERNING THE STABILITY
OF ORGANIC FREE RADICALS

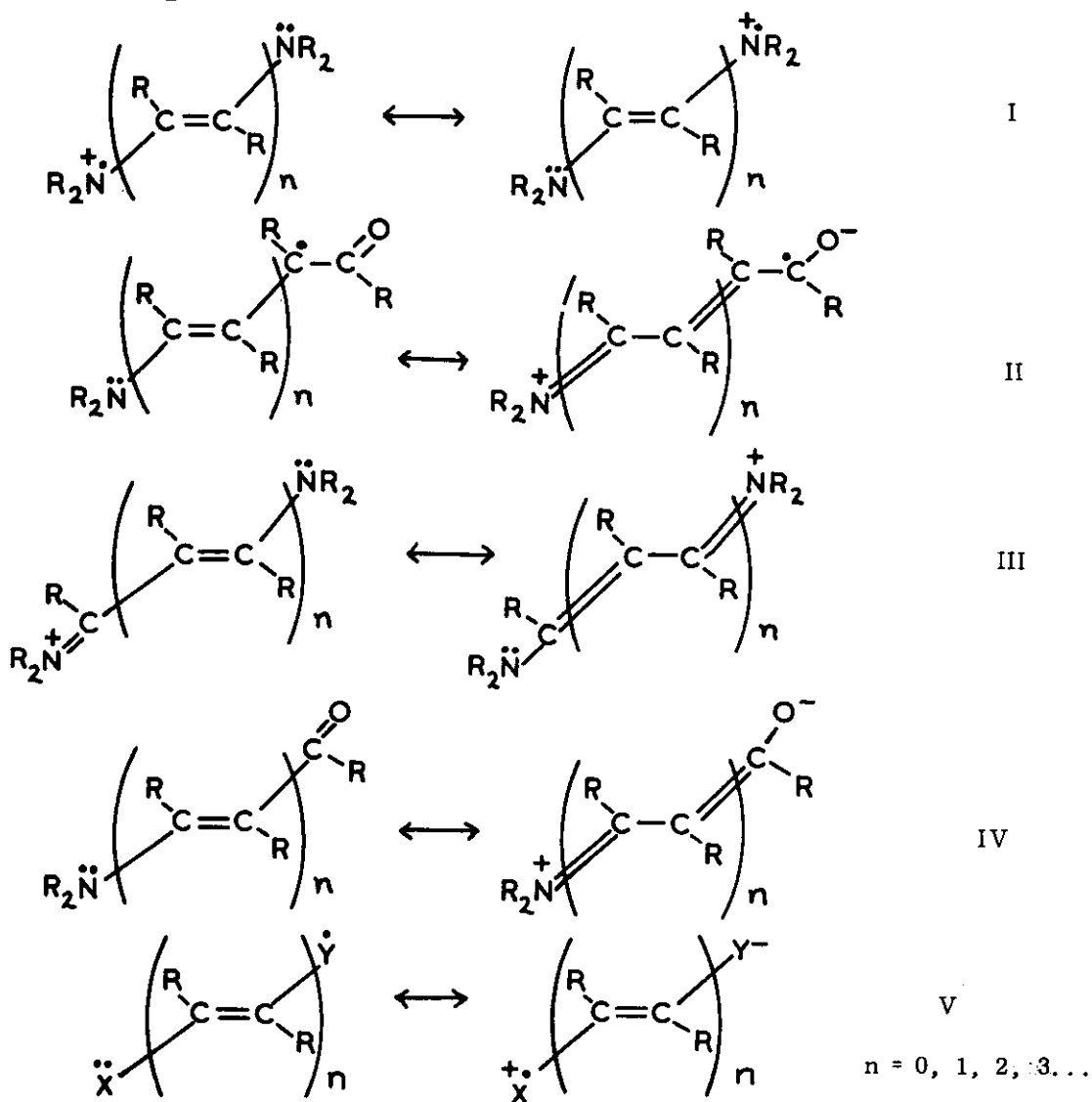
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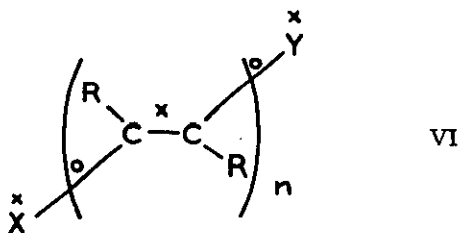
The concept of merostabilisation is discussed which predicts enhanced stability for those free radicals in which low energy zwitterionic canonical forms can contribute to the resonance hybrid. The principle has been used to predict the existence of several novel stable radicals which have been synthesised.

The stability of organic free radicals is usually rationalised in terms of (a) the electron delocalisation in the radical and/or (b) the steric shielding of the centres of highest electron density and/or (c) the destabilising effect of steric interactions in a possible dimer. In valence bond terms, for a hydrocarbon radical such as triphenylmethyl, low energy canonical forms can be drawn in which the unpaired electron is placed on the 2, 4 and 6 carbon atoms of the phenyl rings. The unpaired electron can be placed on the 1, 3 and 5 positions of these rings only in canonical forms involving formal positive and negative charges on carbon atoms. In some radical cations¹ of generalised structure I, the odd electron can be placed on any of the atoms in the carbon/nitrogen skeleton of the radical without involving canonical forms of unreasonably high energy. In a neutral free radical, complete delocalisation of this type is only feasible if low energy zwitterionic forms can contribute to the resonance hybrid. It is our suggestion that radicals in which this type of delocalisation is possible, which will be those in which an electron donating group and an electron withdrawing group interact with the same radical centre, as in II, will show enhanced stability. Comparison of the structures I and II

with the generalised structures of the cyanine and merocyanine dyes,² III and IV, leads us to describe radicals of structure II as merostabilised. Generalising further, we would expect to find enhanced stability due to merostabilisation in any radical of formula V, where, for example, X could be $R_2\ddot{N}^+$, RS^{\cdot} , or RO^{\cdot} and Y could be \dot{O} or $\dot{N}R$.



This proposition correlates well with certain conclusions which arise out of Linnett's double quartet theory of molecular structure.³ Linnett considers radicals in two classes: those such as triphenylmethyl in which the odd electron is in a non-bonding orbital and those, which we would describe as merostabilised, in which he considers the odd electron to be in a bonding orbital. Using Linnett's conventions we can write the structure VI, involving half-integral bond orders and half-integral formal charges, as one of the major contributing structures for a merostabilised radical. This formula clearly illustrates the bonding nature of the unpaired electron.

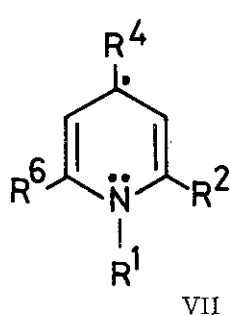


Many known stable free radicals can be seen to comply with our criteria for merostabilisation and to fit our generalised formula V, e. g. pyridinyls ($n = 2$), hydrazyls ($n = 0$) and nitroxides ($n = 0$).

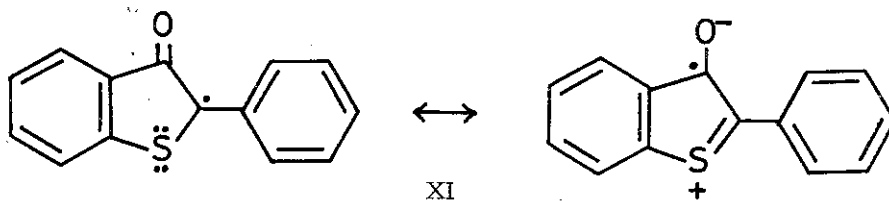
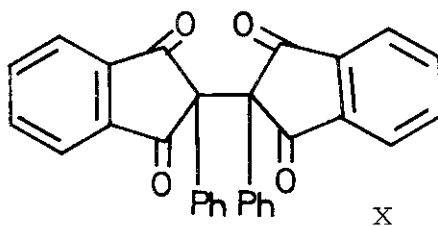
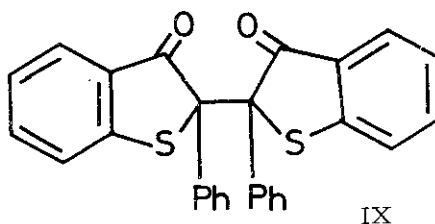
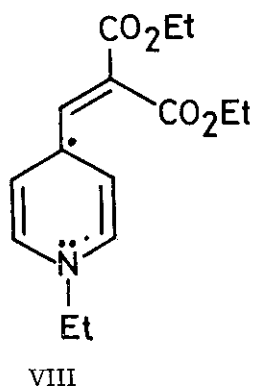
Recently, Balaban⁴ has published a classification of nitrogen radicals based on this principle and has successfully employed similar ideas to predict the existence of new stable radicals.⁵

We have also used our principle to predict the existence of novel stable radicals, several of which have been prepared, particularly in the pyridinyl field. Of the new radicals VII (a)-(d), VII (c) is stable indefinitely under nitrogen. Preliminary investigations indicate that VIII is also rather stable. These results demonstrate that the previously known pyridinyls⁶ are part of a larger class of merostabilised radicals. We have also investigated by e. s. r. the dissociation⁷ of IX into free radicals. Radicals are readily detectable in solutions of IX in mesitylene at 40° . This compares with the temperature of

$100^{\circ 8}$ required to produce radicals from X and is evidence for the importance of merostabilisation in the radical XI.



	R ¹	R ²	R ⁴	R ⁶
(a)	Et	Me	CN	Me
(b)	Et	CN	H	CN
(c)	Et	CN	Me	CN
(d)	Me	CO ₂ Me	H	CO ₂ Me



Further work to delineate the applicability of the principle of merostabilisation is in progress.

ACKNOWLEDGEMENT This work was carried out during the tenure of postgraduate studentships from the D. S. I. R. (to R. W. Baldock) and the S. R. C. (to P. Hudson). We are grateful to the Royal Society and the Hungarian Academy of Sciences for a Fellowship (to F. Soti).

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Received, 20th August, 1973