Capto-dative Stabilization in Nitrogen-centred Push–Pull Radicals: an *Ab initio* SCF–MO Study

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Capto-dative stabilization in the title radicals may take two forms, allylic and allenic, in which the π-systems are coplanar and perpendicular, respectively, and may be more effective than in carbon-centred analogues.

The simultaneous stabilization of free radicals by both donor and acceptor groups is a well established phenomenon. Such radicals, which have been variously referred to as 'push–pull,[1] 'merostabilized,'[2] or more recently as 'capto-dative,'[3] appear to have relatively long lifetimes owing to this stabilization although in many cases steric factors appear to play a role in decreasing reactivity. While the long known stable free radical diphenylpicrylhydrazyl has been considered as a characteristic example of such systems,[4] recent theoretical[5,6] as well as experimental[3] efforts have focused attention on carbon-centred free radicals substituted with donor and acceptor groups. It is our purpose to point out that the nitrogen-centred free radicals (push–pull aminyls) are different in character from the carbon-centred free radicals. As a result the theoretical treatment applied to capto-dative radicals may not be appropriate for nitrogen-centred radicals. We present two alternative models for capto-dative interactions: the allylic and allenic systems. The MO features of the models are discussed and supported by UHF–SCF–MO calculations.

The traditional treatment of capto-dative stabilization assumes coplanarity of the nodal planes of the three participating π-systems: those of the central atom, and the donor and acceptor groups. We refer to this arrangement as the allylic type, since the MOs bear a strong resemblance to those of the allyl radical.‡ While this description suffices for the treatment of carbon-centred radicals, the nitrogen-centred analogues have two alternative MO descriptions, since the central

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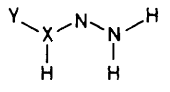
‡ Indeed one may view the allyl radical as an extreme example of a carbon-centred capto-dative free radical, in which the donor is CH_2^- and the acceptor CH_2^+.

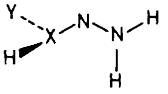
Table 1. Calculated energies and geometries of push–pull aminyls.

Compd.	Relative energy/ kcal mol^{-1}	Bond length/Å[a]				Bond angle/°[a]		
		N–N	N–X	C=O	C–H	N–N–X	N–C–O	N–C–H
(**1a**)	4.98	1.32	1.44			117.8		
(**2a**)[b]	3.75	1.30	1.35			180.0		
(**3a**)	0.00	1.31	1.37			144.8		
(**4a**)	29.42	1.27	1.41			180.0		
(**1b**)	0.00	1.33	1.35	1.26	1.08	116.4	120.7	119.6
(**2b**)	11.70	1.34	1.41	1.20	1.08	115.6	124.4	113.8
(**3b**)	20.58	1.30	1.34	1.21	1.09	134.1	126.1	111.8
(**4b**)	32.97	1.28	1.29	1.29	1.08	180.0	123.3	120.0
(**5b**)	32.02	1.30	1.33	1.22	1.08	180.0	126.7	112.0

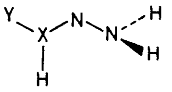
[a] The following values were kept constant: N–H, 0.99; B–H, 1.18 Å; angles: N–N–H, 121.0; N–B–H, 122.0°. [b] Since (**2a**) optimized to a linear structure, (**2a**) and (**5a**) are identical.



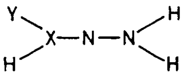
(**1**) (allylic)



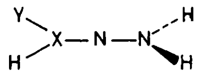
(**2**) (allenic)



(**3**) (allenic)



(**4**) (allylic)



(**5**) (allenic)

a; X = B, Y = H
b; X = C, Y = O

nitrogen atom has two orbitals which can engage in π-bonding: a p-orbital perpendicular to the N–N–A plane (A represents the π-acceptor group), and a hybrid orbital lying within that plane. These alternatives are best visualized by reference to the appropriate geometries of borylhydrazyl and formylhydrazyl radicals, which were chosen as model push–pull aminyl systems suitable for *ab initio* calculations. In geometry (**1**) (allylic), the donor and acceptor groups both conjugate with the p-orbital on nitrogen; the hybrid orbital lies in the nodal plane of the π-system, and hence remains out of conjugation. By contrast, in structures (**2**) and (**3**) only one of the substituent groups is conjugated with the p-orbital, while the other is able to conjugate with the hybrid orbital which lies in the N–N–A plane. This situation is analogous to the π-MO structure of the allene system, and we refer to it as the allenic type.

Clearly, since carbon radicals have a C–H bond in place of the nitrogen nonbonding electron pair, only the allyl-type conjugation can apply. Thus calculations on carbon-centred capto-dative radicals may not be pertinent to discussion of push–pull aminyls.

The donor HOMO will prefer to conjugate with the radical orbital on the central nitrogen, resulting in energy lowering of the doubly occupied π-combination. The π* combination, which increases in energy, is singly occupied, and thus the overall three-electron interaction is stabilizing. Overlap with the lone pair involves a destabilizing four-electron interaction and can be excluded. By contrast, the π-interaction of the acceptor LUMO with either the lone pair or the radical orbital should lead to stabilization. The choice is between an interaction with a lower-energy doubly occupied orbital [as in (**2a**), (**2b**)], and one with a higher-energy singly occupied π* orbital [resulting from the aforementioned donor–radical interaction as depicted in (**1a**), (**1b**)]; or one with a pure p-type lone pair, [(**3a**), (**3b**)], in which the resulting π-orbital is lower in energy than the in-plane orbital, and hence doubly occupied. Unrestricted Hartree–Fock SCF–MO calculations have been employed to determine which of these possibilities prevails.§

Calculations were carried out for structures (**1a**)—(**3a**) and (**1b**)—(**3b**), as well as the corresponding N–N–A linear structures [linear-allylic, (**4**); linear-allenic, (**5**)], and are summarized in Table 1. The difference between nitrogen- and carbon-centred radicals is immediately apparent from these results. In the BH_2 substituted radical the most stable structure is the allenic (**3a**), while with the less powerful π-acceptor, the formyl group, the allylic structure (**1b**) is found to be most stable. In both these ground-state structures the singly occupied MO (SOMO) involves the donor group NH_2, but in only one of them, (**1b**), is the acceptor group also conjugated with the radical. Depending on the π-electron-withdrawing power of the acceptor group the π-orbital resulting from interaction of the acceptor and the nitrogen p-orbital may either be singly occupied, (**1b**), or doubly occupied, (**3a**). This demonstrates the flexibility in nitrogen-centred capto-dative radical structures, which is lacking in carbon-centred analogues.

We conclude that capto-dative stabilization can be more effective in nitrogen-centred radicals than in carbon radicals, since the allenic stabilization may in some systems be more effective than the allylic type. Formylhydrazyl serves as a better model for those capto-dative systems in which carbonyl groups or aryl rings substituted with electron-withdrawing substituents function as the acceptor. On the other hand, borylhydrazyl represents a system with a much more effective acceptor, and is probably a good model for such systems as the hydrazone radical cations in which BH_2 is replaced by a carbocation.[8]

It is interesting to note that attempts to optimize bond lengths and angles at the (**2a**) structure resulted in the linear (**5a**). BH_2 is such an effective π-acceptor that the loss in energy due to promotion of the hybrid lone pair to pure p is more than offset by the gain due to better overlap and π-bond formation.

The calculations may also offer an insight into the process

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§ UHF-SCF calculations were carried out using the GAUSSIAN-76 system of programs and the built in 4-31G basis set.[7] Geometry optimization was performed except for the B–H and N–H bond lengths and the associated angles N–N–H and N–B–H (see Table 1).

(topomerization) responsible for the observed temperature dependence in the e.s.r. spectra of 1-benzoyl-2,2-diarylhydrazyls.[9] Exchange of the two diastereotopic hydrogen atoms in (**1b**) can be achieved either by torsion about the N–N bond (T_A)[10] or by planar inversion (I_A)[10] *via* an N–N–C linear structure. Table 1 reveals that the T_A barrier, *via* (**3b**) as transition state, is 20.6 kcal/mol (1 cal = 4.184 J), while inversion through any of the linear structures (**4b**) or (**5b**) involves a substantially higher I_A barrier (33 and 32 kcal/mol, respectively). While these calculated barriers cannot reproduce the exact experimental results in solution, the large difference does seem to reflect the lowest energy path of the topomerization.

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