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# A THEORETICAL EVALUATION OF THE SYNERGETIC CAPTO-DATIVE STABILISATION OF FREE RADICALS

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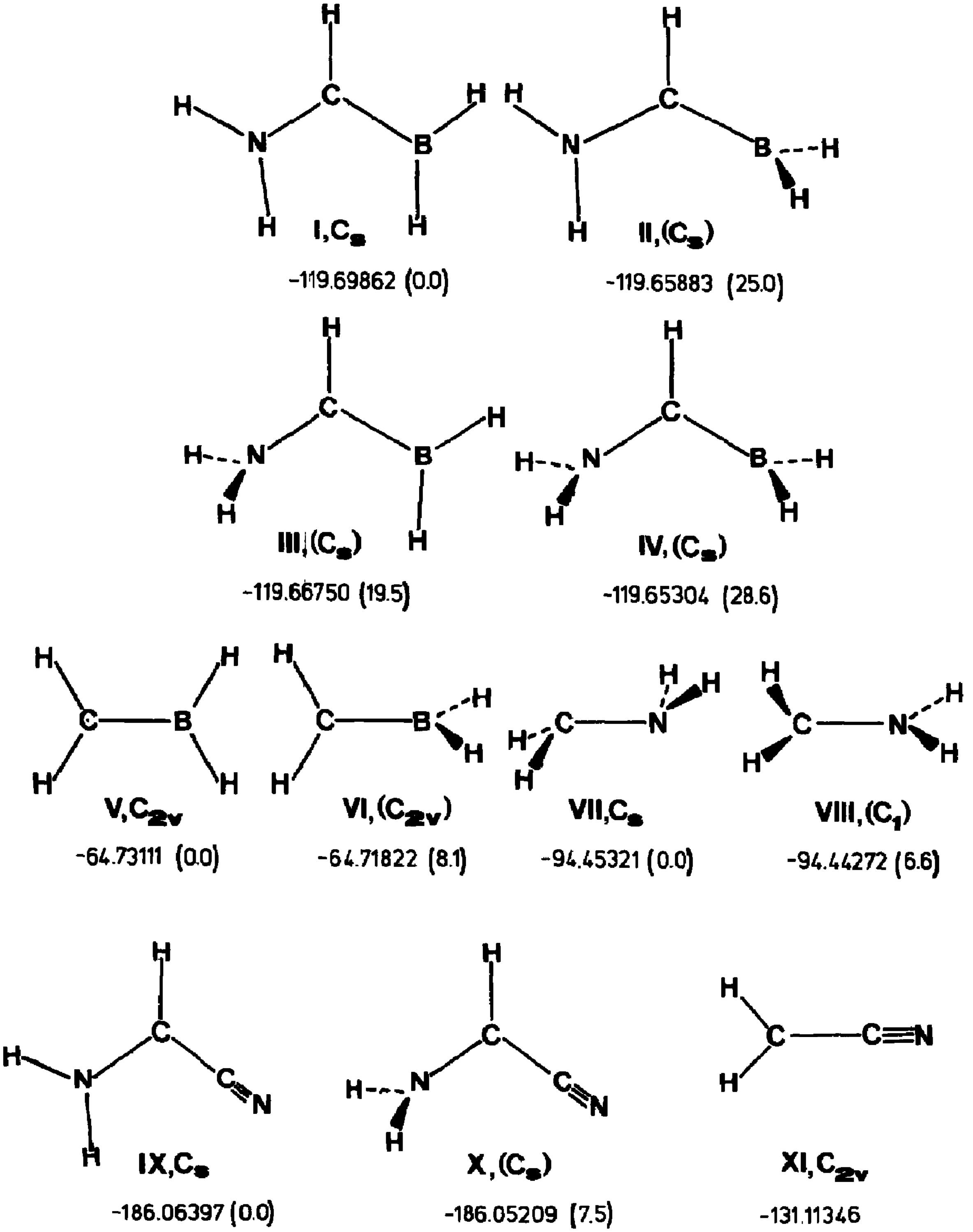
Summary: *Ab initio* molecular orbital calculations on the model capto-dative radicals, $BH_2$-$CHNH_2{}^{\cdot}$ and $H_2NCHCN^{\cdot}$, demonstrate that simultaneous stabilisation by pi-donor and pi-acceptor substituents is significantly greater than the additive substituent stabilisation energies of the individual groups.

The concept of "capto-dative" radical stabilisation, in which the synergetic effect of donor and acceptor substituents on the same radical centre lead to an enhanced stabilisation over that expected from the sum of the stabilisation energies of the individual substituents, has been developed and experimentally verified principally by Viehe and his coworkers, although others have made significant contributions.[1] This effect, also known as "merostabilisation"[2] was anticipated by Dewar in 1952[3] in one of a series of papers on radical stabilisation. However, a recent general, theoretical study of radical substituent effects failed to reveal any extra stabilisation in capto-dative radicals.[4] We have now used unrestricted Hartree-Fock *ab initio* molecular orbital theory[5] at the fully geometry optimized split valence 4-31G[6] basis set level to investigate the interaction of a pi-donor and a pi-acceptor bound to the same radical centre. As a model system, the $HN_2CHBH_2$ radical can be compared with $NH_2CH_2{}^{\cdot}$ and $BH_2CH_2{}^{\cdot}$. The $NH_2$ and $BH_2$ groups have the advantage that the $\pi$-effects can be "turned off" by $90^{\circ}$ rotation. We have also considered the $NH_2CHCN$ radical, which is closely related to species studied experimentally.[1,7] The results are shown in the Scheme and in the Table.

The $BH_2CHNH_2$ radical is most stable in the planar $\underline{C}_s$ conformation, I. Both the $BH_2$ and $NH_2$ groups in I show larger rotation barriers than in the monosubstituted radicals, V and VII. Rotation of the $BH_2$ group (I $\rightarrow$ II) requires 25.0 kcal $mol^{-1}$, compared with 8.1 kcal $mol^{-1}$ in $CH_2BH_2{}^{\cdot}$ (V $\rightarrow$ VI). Similarly $90^{\circ}$ rotation of the amino group (I $\rightarrow$ III) requires 19.5 kcal $mol^{-1}$ (compared with 5.6 kcal $mol^{-1}$ for the monosubstituted radical (VII $\rightarrow$ VIII)). Simultaneous rotation of both substituents (I $\rightarrow$ IV) requires 28.6 kcal $mol^{-1}$. These rotation barriers, which are roughly equivalent to pi stabilisation energies, indicate that $NH_2CHBH_2{}^{\cdot}$ has 13-17 kcal $mol^{-1}$ <u>extra</u> stabilisation arising from the capto-dative interaction of the two substituents. The stabilisation energy relative to $CH_3{}^{\cdot}$ for $BH_2CHNH_2{}^{\cdot}$ (defined by Equation 1)[8] is 33.4 kcal $mol^{-1}$, compared with 10.2 and 10.9 kcal $mol^{-1}$ for the $NH_2CH_2$ and the $BH_2CH_2$ radicals, respectively (Table). The extra (capto-dative) stabilisation in I is thus 33.4 - (10.2 + 10.9) or 12.3 kcal $mol^{1}$. This value fortuitously is similar in magnitude to the resonance energy



Scheme. Substituted methyl radicals. Total energies (hartrees) from UHF/4-31G//4-31G calculations; relative energies (kcal/mol$^{-1}$) of various conformations are given in parentheses. Point groups resulting from complete geometry optimization are shown; point groups in parentheses indicate that some geometrical constraints were imposed.

of the allyl radical,[9] which is isoelectronic and isostructural with I. Both the allyl radical and I benefit from $\pi$ delocalisation of three electrons over three centres.

$$NH_2CH_2BH_2 \quad + \quad CH_3^{\cdot} \quad \rightarrow \quad NH_2CHBH_2^{\cdot} \quad + \quad CH_4 \qquad (1)$$

Similarly, the $NH_2CHCN$ radical, IX, shows a slightly higher rotation barrier (IX → X, 7.5 kcal $mol^{-1}$) than $NH_2CH_2$ (VII → VIII, 6.6 kcal $mol^{-1}$). The total stabilisation of IX relative to $CH_3^{\cdot}$ (Table) is 26.1 kcal $mol^{-1}$; this is 3.4 kcal $mol^{-1}$ more than the sum of the stabilisations of $NH_2CH_2^{\cdot}$ (10.2) and $NCCH_2^{\cdot}$ (12.5 kcal $mol^{-1}$).[10] The capto-dative effect therefore can lead to significant extra stabilisation of disubstituted radicals. (The earlier failure to find extra stabilisation [4] in IX was due to incomplete geometry optimizations.)

The origin of this extra stabilisation is most easily seen using a stepwise perturbational (PMO) approach.[11] Figures 1(a) and 1(c) show the orbital interactions responsible for stabilisation of a radical centre by a pi-acceptor and a pi-donor, respectively. A one electron interaction of the unperturbed radical SOMO with an acceptor orbital (A) results in stabilisation (Fig. 1(a)). A donor, on the other hand, stabilises via a three electron interaction (Fig. 1(c));[12] the resulting singly occupied orbital (labelled $\psi_2$ in Fig. 1) is higher in energy than the unperturbed radical SOMO. Consequently, such a donor substituted radical is a more effective one-electron donor than its unsubstituted counterpart. Figure 1(b) shows the interaction of the donor substituted radical orbital $\psi_2$ with the acceptor orbital, A. Since the energy gap between $\psi_2$ and A in Fig. 1(b) is smaller than that between SOMO and A in Fig. 1(a), stabilisation by the acceptor in the captodative radical (Fig. 1(b)) is more effective than in the monosubstituted radical (Fig. 1(a)). The perturbation argument can be recast: the lower lying singly occupied MO of an acceptor substituted radical interacts more favorably with a donor substituent (the interacting orbital energy levels are closer together).[1 Capto-dative stabilization is of importance, not just with free radicals, but in many other contexts.[1-3]

Table. Stabilisation Energies[a] of Radicals

| Radical | Conformation | Stabilisation Energy, kcal/mol[a] | Capto-Dative Stabilisation[b] |
|---|---|---|---|
| $H_2C\text{-}BH_2$ | V | 10.9 | - |
| $H_2C\text{-}NH_2$ | VII | 10.2 | - |
| $H_2C\text{-}CN$ | XI | 12.5[c] | - |
| $H_2NCHBH_2$ | I | 33.4 | 12.3 |
| $H_2NCHCN$ | IX | 26.1[c] | 3.4[c] |

[a] Based on $CH_3^{\cdot}$; see Equation 1. [b] Stabilisation in excess of the sum of the stabilisations of the individual substituents. [c] See footnote 10.

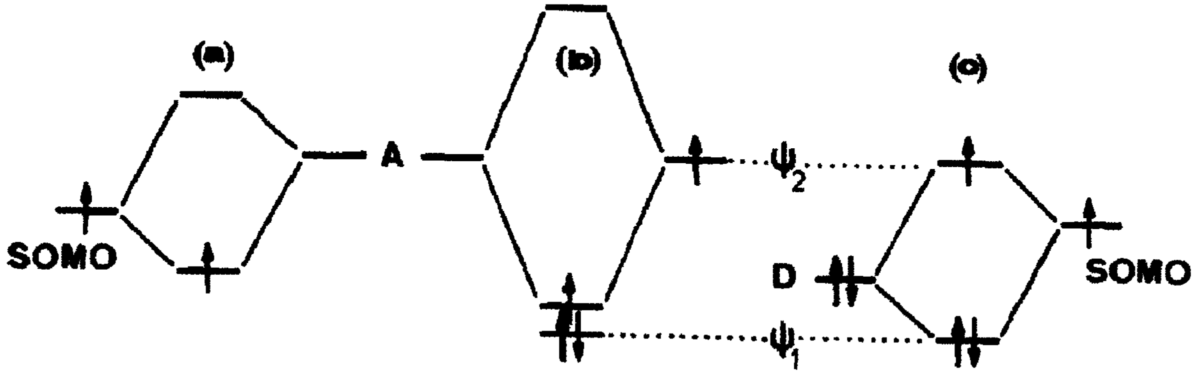


Figure 1. Interaction of an unperturbed radical orbital (SOMO) in (a) with a vacant acceptor orbital, A, and in (c) with a filled donor orbital, D. The latter results in a new singly occupied orbital, $\psi_2$. Capto-dative stabilization by interaction of $\psi_2$ with A is shown in (b).

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10. All cyano-substituted radicals examined exhibit considerable spin contamination at UHF/4-31H//4-31G ( $S^2$ values are about 1.0 instead of the ideal 0.75 value found for the other radicals). However, this spin contamination may not affect conclusions based on comparisons between cyano-substituted species.
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