

Correlation of the Energies of π -Bonds between Carbon and Other Elements with E.S.R. Hyperfine Coupling Constants

Christopher J. Rhodes

School of Chemistry, Thames Polytechnic, Wellington St., Woolwich, London SE18 6PF, U.K.

A linear correlation is found between C=A π -bond energies in compounds of the type $\text{H}_2\text{C}=\text{AR}_n$ (or $\text{HC}\equiv\text{AR}_{n-1}$) and β -proton hyperfine coupling constants for the corresponding radicals $\text{H}_3\text{C}-\dot{\text{A}}\text{R}_n$ (or $\text{H}_2\text{C}=\dot{\text{A}}\text{R}_{n-1}$): an empirical method is therefore available for either estimating π -bond energies from e.s.r. data or predicting hyperfine coupling constants from bond energy data.

We have found that a linear correlation ($r = 0.96$) exists between C=A π -bond energies (estimated as the difference $E(\text{C}=\text{A}) - E(\text{C}-\text{A})$; A is an element) and the β -proton hyperfine coupling constants in the corresponding radicals $\text{H}_3\text{C}-\dot{\text{A}}\text{R}_n$ (or $\text{H}_2\text{C}=\dot{\text{A}}\text{R}_{n-1}$). [We have taken the β -proton couplings of methyl groups as the maximum, on the basis of a $B\cos^2\theta$ dependence (*i.e.* as the value of B , since $\theta = 0$ for maximum coupling), in order to relate them directly to couplings in radicals of the type $\text{H}_2\text{C}=\dot{\text{A}}\text{R}_{n-1}$, where the geometry forces $\theta = 0$.] The data used in the correlation are collated in Table 1.

Our qualitative interpretation of this is that as the formation of a π -bond requires overlap between a singly occupied C(2p) orbital and a singly occupied A(np) orbital, so part of the hyperfine coupling mechanism for β -protons involves hyper-

conjugation, which, in the cases considered here, requires overlap between a doubly occupied carbon-based group orbital of π -symmetry and a single occupied A(np) orbital: a relationship between these processes therefore appears reasonable. We attribute the intercept on the plot to the fact that our simple difference method does not separate the strengthening of the C-A σ -bond due to the change in hybridisation between C(sp³)-C(sp³) and C(sp²)=C(sp²), which will therefore be included in the derived π -bond energies.

However, our main point is that this correlation may be used in a purely empirical way for predictive or interpretive purposes, by employing either equation (1) or (2), as illustrated by the following examples which relate to some areas of current interest.

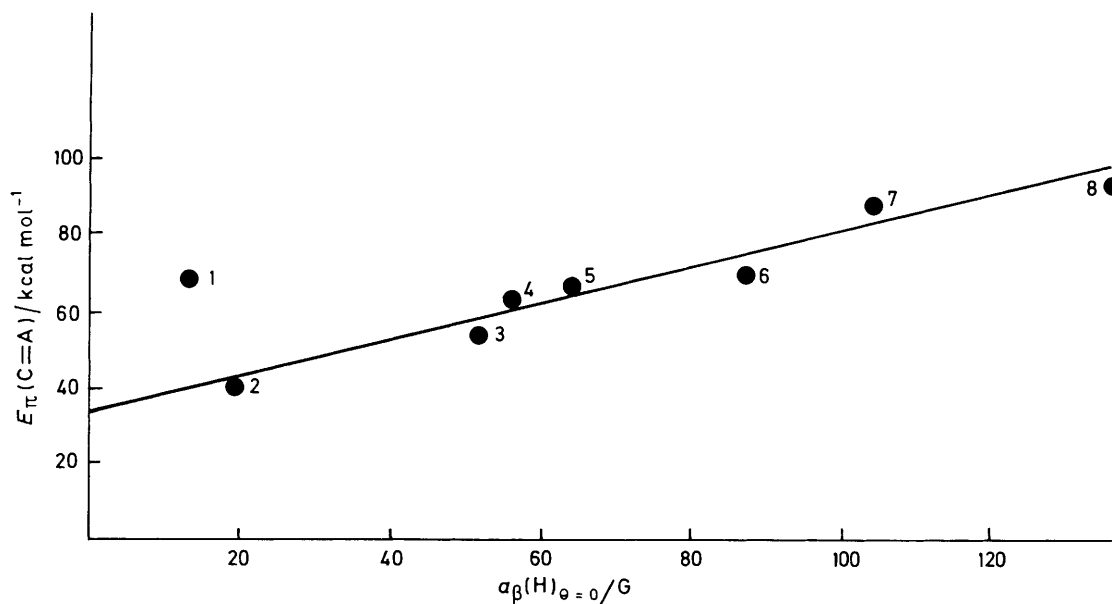


Figure 1. Plot of C=A π -bond energies for compounds $\text{H}_2\text{C}=\text{AR}_n$ (or $\text{HC}\equiv\text{AR}_{n-1}$) against β -proton hyperfine couplings in the corresponding radicals $\text{H}_3\text{C}-\dot{\text{A}}\text{R}_n$ (or $\text{H}_2\text{C}=\dot{\text{A}}\text{R}_{n-1}$) ($\theta = 0$).

Table 1. π -Bond energies for C=A multiple bonds and coupling constants $a(\beta\text{-H})$ for $\text{H}_3\text{C}-\dot{\text{A}}\text{R}_n/\text{H}_2\text{C}=\dot{\text{A}}\text{R}_{n-1}$.

| No. | Radical | $a(\beta\text{-H})_{\theta=0}/\text{G}^a$ | $E(\text{C}=\text{A}) - E(\text{C}-\text{A})$ | |
|-----|---|---|---|-----------------|
| | | | kcal mol ⁻¹ | ^b |
| 1 | $\text{RCH}_2\text{S}^\cdot$ | 12.8 ^c | C=S | 68 |
| 2 | $\text{CH}_3-\dot{\text{S}}\text{i}(\text{SiMe}_3)_2$ | 18.72 ^d | C=Si | 39 ^e |
| 3 | $\text{H}_2\text{C}=\dot{\text{C}}\text{H}$ | 51 ^{f,g} | C=C | 53 |
| 4 | $\text{CH}_3-\dot{\text{C}}\text{H}_2$ | 53.8 ^f | C=C | 62 |
| 5 | $\text{CH}_3-\dot{\text{N}}\text{H}$ | 64 ^h | C=N | 70 |
| 6 | $\text{H}_2\text{C}=\dot{\text{N}}$ | 87 ⁱ | C=N | 69 |
| 7 | $\text{CH}_3-\dot{\text{O}}$ | 104 ^j | C=O | 87 |
| 8 | $\text{RHC}=\text{O}^{\cdot+}$ | 136 ^k | C=O | 92 |

^a 1 G = 10^{-4} T. ^b Taken from the sources in ref. 4, unless otherwise indicated. ^c Ref. 5. ^d Ref. 2. ^e Ref. 1. ^f J. K. Kochi, *Adv. Free Radical Chem.*, 1975, **5**, 189. ^g Average of *cis* and *trans* couplings. ^h S. G. Hadley and D. H. Volman, *J. Am. Chem. Soc.*, 1967, **89**, 1053. ⁱ I. S. Ginns and M. C. R. Symons, *J. Chem. Soc., Dalton Trans.*, 1972, 185. ^j M. Iwasaki and K. Toriyama, *J. Am. Chem. Soc.*, 1978, **100**, 1964. ^k L. D. Snow and F. Williams, *Chem. Phys. Lett.*, 1983, **100**, 198.

$$E(\text{C}=\text{A})/\text{kcal} = 33.95 + 0.456 a(\beta\text{-H})_{\theta=0}/\text{G} \quad (1)$$

$$a(\beta\text{-H})_{\theta=0}/\text{G} = 2.19 E(\text{C}=\text{A})/\text{kcal} - 74.45 \quad (2)$$

(a) The estimate of the C=Si π -bond energy obtained by Walsh¹ fits quite well with the rest of our data, when plotted against the B value derived from $a(\beta\text{-H})$ for the radical $\text{MeSi}(\text{SiMe}_3)_2$,² which is believed to be nearly planar. Previous estimates¹ of $E_{\pi}(\text{C}=\text{Si})$ appear to be too low on this basis. A value of 42 kcal mol⁻¹ is predicted by equation (1).

(b) From the $a(\beta\text{-H})$ value of 13.9 G for the $\text{Me}_2\text{P}^\cdot$ radical,³ we estimate that the π -bond energy of a C=P bond should be 47 kcal mol⁻¹.

(c) From our estimate of the π -bond energy of a C=S bond (68 kcal mol⁻¹),⁴ and using equation (2), we would predict that the β -proton coupling in the $\text{CH}_3\text{-S}^\cdot$ radical should be 37 G. Unfortunately, this radical does not appear to have been studied by e.s.r.; however, a B value of 12.8 G has been estimated from a single crystal study⁵ of a radical $\text{RCH}_2\text{-S}^\cdot$. This is plotted on Figure 1 (point 1) and is seen to deviate appreciably from the straight line, indicating that the value is far too low.

In fact, our prediction of the β -proton coupling of the $\text{CH}_3\text{-S}^\cdot$ radical is in accord with our recent assignment for $\text{R}_2\text{C}(\text{Mu})\text{-S}^\cdot$ radicals, studied by the muon spin rotation technique, which exhibit large muon hyperfine couplings in the range 40–50 G.⁶ (Temperature dependence studies indicate a weighting of conformations in which the muon is more strongly coupled than in a freely rotating case such as $\text{CH}_3\text{-S}^\cdot$). A previous e.s.r. assignment⁷ for $\text{RCH}_2\text{-S}^\cdot$ in the liquid phase, with $a(\beta\text{-H})$ ca. 9 G, also appears to be in error.

Received, 20th January 1988; Com. 8/00208H

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