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Free Valence Numbers of Carbon

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The free valence number F_r has been defined by COULSON [2] as

$$F_r = N_{\max}(sp^2) - N_r$$

where N_r is the sum of the bond orders formed by a carbon atom r and $N_{\max}(sp^2)$ is the maximum value of N_r for an sp^2 hybridized carbon atom. BURKITT, COULSON and LONGUET-HIGGINS [1] proposed to use different values of $N_{\max}(sp^2)$ for different types of carbon atoms namely $(3 + \sqrt{1})$, $(3 + \sqrt{2})$ and $(3 + \sqrt{3})$ for primary, secondary and tertiary carbon atoms respectively. Free valence numbers F_r defined in this way are related to the energy required to localise one π-electron at the carbon atom r. Usually, however, only the largest value $(3 + \sqrt{3}) = 4.732$ as calculated by MOFFITT [5] for trimethylenemethane is taken for $N_{\max}(sp^2)$.

Recently CRAWFORD et al. [3] and DOWD [4] presented evidence for the occurrence of trimethylenemethane as an intermediate; DOWD [4] states that the compound is important in theoretical chemistry by virtue of the fact that the central atom of the molecule attains the maximum π bond order possible for any carbon atom. From discussions of the free valence index in recent textbooks [6, 7] one may infer that this statement is correct.

However a calculation of N_r for the central sp hybridized carbon atom of $[\mathrm{H{-}C{=}C{=}C{-}H}]^{00}$, or one of its singly or doubly charged ions leads to a value of $(2 + 2\sqrt{2}) = 4.830$ which is slightly larger than $N_{\max}(sp^2)$ considered till now.

Literature

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