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Free Valence Indices of Carbon in Heterocyclic Compounds

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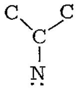
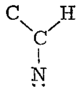
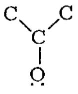
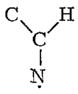
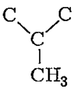
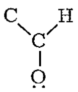
The free valence index (F_r) has been introduced and defined by Coulson [1] as:

$$F_r = N_{\max} - N_r$$

where N_r is the sum of the π-bond orders of all bonds attached to the atom r, and $N_{\max}$ represents its highest possible π-bonding capacity. $N_{\max}$ is usually taken as $\sqrt{3}$, being the sum of bond orders for the central carbon atom in the hypothetical molecule trimethylenemethane [2]. Burkitt, Coulson and Longuet-Higgins [3], however, proposed different values for $N_{\max}$ in hydrocarbons, depending on the number of carbon atoms bonded to the atom in consideration. In other words, the following values have been suggested for $N_{\max}$: $\sqrt{3}$, $\sqrt{2}$, and $\sqrt{1}$ for tertiary, secondary and primary carbon atoms, respectively.

It is natural to extend the idea of Burkitt and coworkers to heterocyclic compounds and consider $N_{\max}$ of the carbon atom dependent on heteroatoms attached to it. If one calculates $N_{\max}$ for a particular example in the same way as was carried out for trimethylenemethane [2], one obtains the results presented in Table 1.

Table 1. *$N_{\max}$ calculated for various hypothetical models*[a]

Hypothetical model	$N_{\max}$	Hypothetical model	$N_{\max}$
	1.679		1.335
	1.628		1.396
	1.589		1.257

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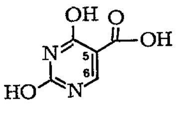
[a] We have used Hückel molecular orbital theory. The choice of parameters for heteroatoms is the same as recommended by Pullman and Pullman [4]. For methyl group the heteroatom model and the parameters from Streitwieser's book [5] were used.

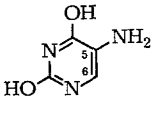
In the majority of cases the values for $N_{\max}$ are close to those obtained for carbon atoms in pure hydrocarbons. But this difference might be rather important in considering the reactivities of conjugated systems, particularly if a methyl group or a oxygen two electron donor is attached to the carbon.

The free valence concept is considered as a molecular orbital version of THIELE's residual affinity and it correlates roughly with reactivity of an atom in the molecule with respect to the free radical attack [3—6].

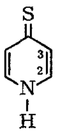
We shall consider the following examples: uracil-5-carboxylic acid (I), 5-aminouracil (II) and 4-thiopyridone (III). Free valence indices for the positions of interest for these compounds are presented in Table 2. It is not difficult to see that if one uses the standard procedure to calculate free valence indices, the predicted probability for the radical attack in uracil compounds is much greater for the position 6 than for the position 5. Also, in the case of 4-thiopyridone the position 2 is more favoured. It has been observed, however, that in compound (I) the position 5 is the site of the attack of radical-like particles [7]. In compound (II) both positions are approximately equally probable [7]. In 4-thiopyridone, the position 3 is the most reactive site towards substitution reagents [8]. In all these cases a prediction based on the standard procedure gives wrong results. However, a prediction based on the approach described above (see results in the last column of Table 2) is fully in agreement with experimental data.



(I)



(II)



(III)

Table 2. *Free Valence Indices*

Compound	Position of attack	F_r $(N_{\max} = \sqrt{3})$	F_r ($N_{\max}$ from Table 1)
I	5	0.183	0.183
	6	0.429	0.093
II	5	0.150	0.097
	6	0.488	0.112
III	2	0.544	0.148
	3	0.490	0.172

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