Semiempirical All-valence-electron Calculations on the Reactivity of Azulene and Benzofuran

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Calculations by the CNDO/2 method on the σ-complex energy in the protonation of azulene and benzofuran show that, when the molecule has rings with different numbers of atoms, the use of all-valence-electron methods results in substantial modifications in the order of reactivity compared with that obtained by considering only π-electrons.

THE reactivity of aromatic molecules has been studied using all-valence-electron methods in order to calculate the relative energies of the σ-complex.[1-5] Although from a mathematical point of view the all-valence-electron methods are more satisfactory than the π-electron ones, the computer time used by the former is much larger. Murrell [5] concludes that the all-valence-electron SCF theories do not necessarily lead to improved correlation with chemical reactivity and that the greater cost in computer time is thus not justified.

Heilbronner [6] suggested that an important reason why the 1-azulenium cation is the most stable protonated azulene is that the rehybridized carbon atom fits best into a five-membered ring (internal angle 108°) as such a ring will accommodate the sp^3 hybrid (optimal angle 109° 28′) with less angle strain than a seven-membered ring, with its internal angles of *ca.* 124°. This different angular distortion can at present be taken into account by means of methods which include the σ-electrons.

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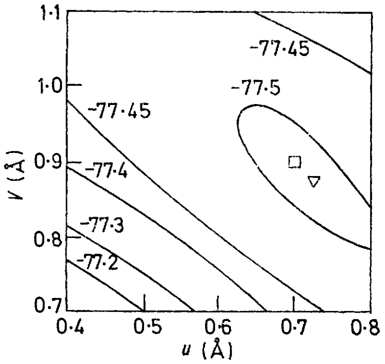
It thus seems that the use of all-valence-electron methods in studying the relative order of reactivity of centres belonging to different membered rings would cause substantial modifications in the structure and stability of the σ-complex. Azulene and benzofuran have been taken as examples in the protonation process. Using the CNDO/2 method,[7] the energy of symmetrical Wheland intermediates [3] has been calculated for the different positions of both molecules.

As the C–H distance and $\widehat{HCH}$ angle are varied in each reaction centre, the minimum energy of all the centres of azulene and benzofuran corresponds always to a C–H distance of 1·14 Å and a $\widehat{HCH}$ angle of 105°.

CNDO/2 Studies made of the σ-complex in the $(C_6H_7)^+$ cation [8-10] give an optimum C–H distance of 1·135 Å and an $\widehat{HCH}$ angle of 101°. These results are slightly different from those previously given for azulene and benzofuran. In order to discover the reason for this difference, a new minimization was made by using smaller variations of the parameters in the *uv* plane (the plane perpendicular to the molecule which contains the C–H bond of the initial compound) in the neighbourhood of the minimum previously found. This has been done for two positions belonging to the different azulene rings. The Figure shows the isoenergetic lines of the 1-azulenium σ-complex. It can be observed that the new minimum (triangle) is slightly shifted with respect to the previous one (square). The C–H distance is found to be 1·136 Å and the $\widehat{HCH}$ angle 100·6°. These values agree with those obtained for the $(C_6H_7)^+$ cation.



Conformational energy map of 1-azulenium σ-complex

For position 6 of azulene the contours are almost exactly those obtained for position 1 except for a vertical shift of the surface. This is the most significant result concerning the structure of the σ-complex. Its geometry seems to be independent of the ring angle of the centre under consideration. Studies made with a partial relaxation of the geometry [8,9,11] indicate that the ring angle is modified in the reaction centre. Before this conclusion can be confirmed it is necessary to allow a complete relaxation of the σ-complex geometry.

Tables 1 and 2 show the minimum energy values which correspond to each of the respective positions of azulene and benzofuran. The relative orders of reactivity which can be deduced from them are for azulene: $1 > 2 > 5 > 4 > 6$ and for benzofuran: $2 > 6 \geqslant 3 > 4 > 5 > 7$.

TABLE 1

Minimum energy values for different positions of azulene

Position	Energy (a.u.)
1	−77·5031
2	−77·4509
4	−77·4054
5	−77·4482
6	−77·4047

TABLE 2

Minimum energy values for different positions of benzofuran

Position	Energy (a.u.)
2	−80·2803
3	−80·2715
4	−80·2706
5	−80·2659
6	−80·2717
7	−80·2634

The localized model gives the following order of reactivity for azulene: $1 > 5 > 2 > 4 > 6$.[12] It should be pointed out that position 1 is shown to be the most reactive even more clearly when using the all-valence-electron method. Furthermore position 2, the other possible reaction centre in the five-membered ring, is the second most reactive, replacing position 5 which is in the seven-membered ring.

The following order of reactivity for benzofuran is obtained from the localization energies calculated by a SCF π method: $2 > 4 > 6 > 7 > 5 > 3$.[13] This order is noticeably different from the one obtained when using the CNDO/2 method. The increase in reactivity of position 3, belonging to the five-membered ring, stands out clearly when all-valence-electrons are considered. The experimental order of reactivity for benzofuran with an electrophilic reagent is $2 > 3 \geqslant 6 > 4 > 5 > 7$.[13] The order obtained from the energies of the σ-complex, calculated by the CNDO/2 method, agrees with the experimental values. A more quantitative correlation of calculated and experimental values is not possible because we could not find the latter in the literature.

In sum, when the molecule has rings with different numbers of atoms, the use of all-valence-electron methods results in substantial modifications in the order of reactivity compared with that obtained when considering only the π electrons. An attempt to

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optimize the energy of the system as a function of the C–H distance and $\widehat{HCH}$ angle indicates that these parameters remain constant for all molecules and positions studied, making this (partial) optimization of the geometry unnecessary in the applications of all-valence-electron methods to the study of electrophilic substitution reactions in aromatic compounds.

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