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Comment on the Paper by T. P. Živković "Heats of Atomization of Conjugated Hydrocarbons by a New Semiempirical Method"

Wolfgang Gründler

Department of Chemistry, Martin Luther University Halle-Wittenberg, DDR-4020 Halle/Saale, Weinbergweg 16, German Democratic Republic

In the abovementioned paper [1] the author claimed to formulate a new theoretical approach combining features of *MO* and *VB* or resonance theory by using a linear combination of nonorthogonal configurations built from bond orbitals according to the resonance structures. But with the same intention a quite similar description was proposed by us in 1978 [2*a*], consisting in a linear combination of nonorthogonal closed-shell configurations, using bond orbitals. It was applied within the Hückel model to a series of problems in the following years [2*b* – *j*] and extended to some broader fields of chemistry, as condensed hydrocarbons, carbenium ions and carbanions, pi radicals and transition states of pericyclic reactions, including systems containing heteroatoms [3–5]. In this way, the $4n+2$ rule of Hückel for neutral and charged monocyclic systems [2*c*, *f*, *h*], the selection rules for thermal pericyclic reactions [2*e*, *h*], the directing effect of donor and acceptor substituents on pericyclic reactions [2*j*], the regioselectivity of the electrophilic attack to unsaturated hydrocarbons and heterocycles [4] and stability rules for condensed benzenoid hydrocarbons [5] were derived. A first resumé may be found [3]. The configurations were called "significant electron structures" (SES).

Only one difference exists between the two approaches: Živković used in fact a mixture of closed and split-shell configurations. In contrast to our original method of significant electron structures, which has been ignored by Živković, the clear correspondence between the structural formula like one of the Kekulé structures of benzene and a single configuration is lost. In the approach of Živković, the two Kekulé structures of benzene symbolize four configurations, but only two in our approach.

No advantage seems to be reached by the formalism of Živković. Because of more delocalization introduced by the inclusion of split-shell configurations, there is a larger resonance energy (we prefer the notion mesomerism energy). For benzene, Živković calculated a change in energy of 1,2β, leading to $\beta = -0{,}7$ eV, whereas a mesomerism energy of $6/17\beta$ results in our approach [2c, 3], giving $\beta = -2{,}6$ eV as the mean value for a series of unsaturated hydrocarbons. This value of β is consistent with those derived from optical transitions and ionization potentials. It seems, that the main drawback of the HMO description, which overemphasizes the extent of delocalization, is retained partly in the approach of Živković.

Some examples of mesomerism energy including all important interactions between closed-shell configurations corresponding to the Kekulé structures are compared with the SCF MO resonance energy defined by Dewar [6]:

	ME	*RE* [6] (in eV)
Benzene	0.92	0.87
Naphthalene	1.32	1.32
Anthracene	1.53	1.60
Phenanthrene	1.97	1.93
Pyrene	2.07	2.10
Perylene	2.64	2.62
Triphenylene	2.75	2.65
Benzo(c)phenanthrene	2.47	2.49
Chrysene	2.47	2.48
1,2-Benzanthracene	2.25	2.29
Azulene	0.10	0.17
Pentalene	0	0.006

(details will be given elsewhere [7]). Also with our treatment, the agreement with the completely different SCF MO description is very satisfactory. The case of azulene offers no difficulties, the interaction integrals of the two structures are $S_{12} = 1/256$ and $H_{12} = 5/64\beta$, resulting in the small mesomerism energy $10/257\beta$.

The conceptual and practical usefulness of the theory of significant electron structures was shown by us in the papers cited [2–5]. The formalism of Živković offers in our opinion no more practical possibilities, at least at the level of the Hückel model.

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