

TOPOLOGICAL DEFINITION OF DELOCALISATION ENERGY

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Recently, the exact topological formula for delocalisation energy has been obtained for alternant systems². Now, we have developed method valuable for alternant, nonalternant and radical molecules.

The idea of delocalisation energy /DE/ as a criterium for estimation of chemical stability is very old one. Hückel³ was the first who developed simple method for calculation of total π -electron energy of planar unsaturated organic molecules and who proposed the first model for estimation of DE. He stated that DE is the difference between the total π -electron energy of a molecule and total π -electron energy of hipotetic reference structure consisting of strongly localised double bonds where each of them has the energy of ethylene molecule. For example, benzene reference structure consists of three ethylene bonds. In general:

$$DE^{\text{Hückel}} = E_{\text{total}}^{\pi} - N/2 E_{\text{c=c}}^{\pi} / \text{ethylene} / \quad /1/$$

where N is the number of atoms. DE is evaluated in β -units:

$$DE^{\text{HMO}} = /E_{\text{total}}^{\pi} - N/\beta \quad /2/$$

inside Hückel molecular orbital /HMO/ theory.

From eq. /2/ it follows that DE is a function of number of atoms, only. This simple model have failed in the number of cases. Few examples are listed in the Table. The fact that reference struczure is baszd only on the number of atoms appeared to be the reason for its failures⁴.

In 1965 Dewar⁵ showed that there is no delocalisation energy in the case of acyclic polyenes. The total energy of such molecules is then sum of constant terms: energies of single and double bonds. These bonds can be used for construction of reference structure, so that:

$$DE^{\text{Dewar}} = E_{\text{total}}^{\pi} - N/2 E_{\text{C=C}}^{\pi}/\text{acyclic polyene}/ + \\ + \nu - N/2 E_{\text{C-C}}^{\pi}/\text{acyclic polyene}/ \quad /3/$$

where ν is the number of bonds in the molecule under consideration. All energy terms in eq./3/ had been obtained by modified Pariser-Parr-Pople SCF MO method which is much more sophisticated and complicated in comparison with HMO method. As it is seen from the Table there is very good agreement between DE^{Dewar} and observed properties of conjugated molecules. At first time it was supposed that the change in the MO method was crucial reason for the success of DE^{Dewar} but in 1971 Hess and Schaad⁷, and later, group from Zagreb⁶, independently applied Dewar's model of reference structure inside HMO theory and results were suprisingly good. / See Table where $DE^{\text{Hess, Schaad}}$ are listed for few molecules./ Obviously, the change in the reference structure was the reason for the success

of DE's defined in the manner of Dewar. It has been shown that the great part of correlation energy is taken into account when DE is defined in such manner⁴, that is: original molecule and its reference structure has the same number of bonds. It is important to notice: a/ there is no delocalisation in the case of acyclic polyenes, it means that delocalisation occurs only when at least one cyclic structural detail is present in the molecule, b/ DE is a function of topological parameters: number of atoms, bonds and rings. All of these parameters must differ from zero if delocalisation should occur.

From the above considerations we have conclude that the best form of topological energy of delocalisation /TED/ must fulfill these two conditions:

1. TED must contain all cyclic contribution to total π -electron energy, and
2. TED must not contain any acyclic contribution to total π -energy.

It is well known⁸ that characteristic polynomial of Hückel hamiltonian can be avaluated considering only the topology of a molecule by use of Sach formula⁹:

$$P(x) = \sum_{s \in S} (-1)^{c(s)} / 2^{r(s)} x^{N-N(s)} \quad /4/$$






where $\sum_{s \in S}$ presents a sum over all oriented Sach's graphs, and $c(s)$ and $r(s)$ are number of components and rings, respectively.

It is clear that above two conditions will be fulfilled if reference structure contains only acyclic

contributions to E_{total}^{π} . We have followed this idea in such a way that we evaluated "acyclic" characteristic polynomial of a molecule by use of eq./4/ neglecting term $2^{r/s/}$, that is neglecting all cyclic structural details in the molecule. The difference between HMO energy of a molecule and the sum of the first $N/2$ solutions of acyclic polynomial presents TED of a given molecule. Obviously, the exact separation in cyclic and acyclic parts is not possible because total energy is not additive function of simple topological parameters¹⁰.

Our method is valuable for all kinds of conjugated molecules and this is the main advantage in comparison with other methods appearing in this note. In the table we compare TED values with other methods and experimental facts.

TABLE

molecule	DE^{HMO}	DE^{Dewar}	$DE^{\text{Hess, Schaad}}$	TED	Exp. facts
	0.333	0.145	0.065	0.045	aromatic
	0.368	0.132	0.055	0.040	aromatic
	0.307	0.001	-0.018	-0.027	observed at -190°C
	0.298	0.054	-0.027	-0.050	never prepared
	0.244	0.008	-0.002	0.003	very reactive

All values in the Table are given per electron and in β -units except DE^{Dewar} which is given in eV.

References

- 1) Permanent address: "Pharmaceutical and Chemical Works PLIVA" Zagreb, I.L.Ribara 89, Yugoslavia.
- 2) I. Gutman, N. Trinajstić: J.Mol.Structure, submitted.
- 3) E. Hückel: Z.Physik, 70 (1931) 204.
- 4) I. Gutman, M. Milun, N. Trinajstić: Chem.Phys.Lett. 23 (1973) 284.
- 5) M.J.S. Dewar, G.J. Gleicher: J. Amer. Chem. Soc. 87 (1965) 692.
- 6) B.A. Hess, L.J. Schaad: J.Amer.Chem.Soc. 93 (1971) 305.
- 7) M. Milun, I. Sobotka, N. Trinajstić: J.Org. Chem. 37 (1972) 139.
- 8) I. Gutman, N. Trinajstić: Top. Curr. Chem. 42 (1973) 50.
- 9) H. Sachs: Publ.Math. (Debrecen) 11 (1963) 199.
- 10) I. Gutman: Theoret.Chim. Acta 35 (1974) 350.