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CALCULATION OF GRAPH DISTANCE MATRIX FOR HETEROAROMATIC SYSTEMS

Pavel Tvarůžek and Jaro Komenda

Department of Theoretical and Physical Chemistry
J.E.Purkyně-University
Kotlářská 2, 61137 Brno, Czechoslovakia

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ABSTRACT
The elements of the graph distance matrix of heteroatom molecules have been calculated from the electronegativity values for hybridized atomic orbitals of different structure. The electronegativities belonging to all the atoms of the periodic system are calculated semiempirically with carbon C(sp^3) as standard.

INTRODUCTION

Topological indices are applied for analysing the relations between structure and properties of molecules. The topological distance[1] is one of the methods generally used for calculation of topological indices. Calculation of the elements of a distance matrix associated with a hydrocarbon molecule proceeds without problems. The presence of a heteroatom in the molecule requires the development of special procedure for evaluation of vertices and edges of the multigraph which belongs to the molecule.

This evaluation can be carried out by using coulombic and resonance integral values of Hückel molecular orbital theory[2] or according to Barysz[3]. The latter method uses for the calculation of diagonal d_{ii} and offdiagonal d_{ij} elements of distance matrix D the proton number of atoms and multiplicity of bonds[3]. Numeric values are in this way easily available, for carbon atoms these values are identical with those which are used for the

definition of matrix elements of homoatomic molecules. However, for the elements with the proton number lower then 6 is $d_{ii}<0$. Semiempirical electronegativity values of atoms calculated on the basis of the known covalent diameters of atoms and their belonging to groups in the periodic system are used by Balaban for calculation of his topological index J[4].

We devise here a molecular multigraph edges and vertices evaluation to come out of orbital electronegativities values of atoms joined through a bond.

DEFINITION

In the chemical bond between two atoms each atom participates in the first approximation by one (in the case of single bond) till three (in the case of triple bond) hybridized atomic orbitals (HAO). It is not difficult to find the types of HAO participating in each bond of the molecule under study. In this case it is possible to use electronegativity values dependent on the valence state of atoms to characterize the bond. The corresponding electronegativity values of HAO can then be estimated acording to Pancir[5].

The diagonal elements of matrix D are determined as the mean electronegativity of the i-th atom:

$$d_{ii} = 1 - 816.3 / \left(\prod_i |E_i|\right)^{1/n_A} \qquad (1)$$

where n_A is the number of valence orbitals of atom A and E_i is the electronegativity of the i-th orbital.

The evaluation of edge H which corresponds to the bond between atoms A and B is the following:

$$H = K / \left(\prod_{i\in A} E_i \cdot \prod_{j\in B} E_j\right)^M \qquad (2)$$

The E_i and E_j are electronegativities of HAO of atoms A and B which are taking part in the chemical bond. The values of K and M constants are:

bond	K / kJ.mol^{-1}	M
single	816.3	1/2
double	400.6	1/4
triple	266.9	1/6
aromatic	534.2	1/4

Some of the most frequently used electronegativity values are presented in TABLE 1.

TABLE 1. Electronegativities of HAO and nonhybridized p-AO and diagonal elements of distance matrix for various atoms and their hybridization

atom	hybridization	AO	electronegativity (- kJ.mol^{-1})	d_{ii}
H				-0.0312
H (in hydrogen bond)				-0.0150
C	sp^3	sp^3	816.3	0
C	sp^2	sp^2	830.9	-0.0005
		p	772.5	
C	sp	sp	860.1	-0.0287
		p	772.5	
N	sp^3	sp^3	868.4	-0.0638
N	sp^2	sp^2	888.1	0.0592
		p	809.2	
N	sp	sp	927.3	0.0251
		p	809.2	
O	sp^3	sp^3	927.0	-0.1356
O	sp^2	sp^2	952.3	
		p	851.2	
F	sp^3	sp^3	1272.9	0.3587
Cl	sp^3	sp^3	890.7	0.0835
Br	sp^3	sp^3	869.5	0.0612
I	sp^3	sp^3	863.9	0.0551

The electronegativity values of HAO can be calculated for practically all the elements of the periodic system.

DISCUSSION

The values of diagonal elements d_{ii} have a similar property as the diagonal elements defined in ref.3 : for carbon atom in sp^3 hybridization d_{ii} equals zero and if the mean electronegativity of the i-th atom is higher than the mean electronegativity of carbon atom C(sp^3) then $d_{ii}<0$. In the case when the d- and f-orbitals participate in the hybridization of the atom, too, the values of electronegativities and distance matrix elements depend on the structure type of the HAO. FIGURE 1 shows the situation of vanadium atom in sp^3d hybridization and two structure types.

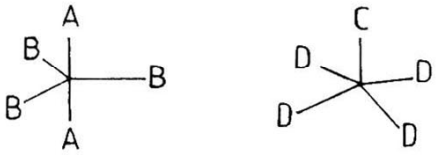

FIGURE 1. Orbital electronegativity of vanadium
Electronegativity values ($kJ.mol^{-1}$):
A -737.8, B -727.8, C -734.7, D -719.6.

The values of H from equation (2) are consistent with evaluation of edges in graphs associated with hydrocarbon molecules acording to Balaban and co-workers[14]. The evaluation of edges of molecular multigraph through electronegativity values of HAO is here derived from the feature of the chemical bonds and not exclusively from the feature of atoms joined through bonds. The structure of HAO is incorporated in the constructed distance matrix, therefore, it includes the maximum of information which can be read from the structure formula of the molecule. The elements of this distance matrix are defined for systems with the intramolecular hydrogen bond, too. The distance

matrix used to calculation of topological indices[1] and distance matrix calculated on the basis of the HAO electronegativities are identical for hydrocarbon molecules.

Comparison of topological indices J calculated by Balaban[4] and indices J calculated from distance matrix constructed by the method described in this paper is given in TABLE 2.

TABLE 2. Topological indices J

molecule	J1	J2
ethanol	1.5986	1.7057
1-propanol	1.9000	2.0164
2-propanol	2.2294	2.3841
1-butanol	2.1323	2.2177
2-methyl-1-propanol	2.4728	2.5755
2-butanol	2.4625	2.5787
t-butyl alcohol	2.9314	3.0791
isobutylamine	2.5030	2.5571
sec. butylamine	2.4971	2.5586
N-methylisopropylamine	2.4540	2.5524
N,N-dimethylethylamine	2.4057	2.6166

J1 - topological index calculated on the basis of relative electronegativities of atoms

J2 - topological index calculated on the basis of HAO electronegativities.

AVAILABILITY:

Electronegativity values of HAO for other the elements are available upon request from our laboratory.

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