TOPOLOGICAL METHODS OF QUANTUM CHEMISTRY FOR A STUDY OF CHEMICAL REACTIVITY

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In this paper all approximations are discussed which lead to a quantum chemical model which is adequate for structural formulas known in classical organic chemistry. Neglect of the energy differences caused by changes of valence and dihedral angles, *i.e.* neglect of all nonbonding interactions, leads to the separation of the Hartree–Fock matrix in blocks of core electrons, nonbonding electron pairs, two center blocks of σ-bonds and delocalized π-electronic structures. Such a procedure can be formulated at all levels of sophistication — from the one electron approximation to the MC–SCF method. Even on the one electron level, the average error in heats of atomization (35·9 kJ/mol) is lower than that of the more complicated geometrical methods MINDO/3 (52·1 kJ/mol) and MNDO (39·6 kJ/mol). The procedure suggested is about two orders of magnitude more efficient than geometrical ones of the same level and can be, therefore, used for a study of reaction mechanisms of medium size systems (30—50 atoms) without large expense.

At the beginning of exact chemical thinking[1] molecules were understood topologically as a set of atoms connected by formal chemical bonds. A reaction was interpreted as breaking of old bonds and formation of new ones. This conception was extremely useful in the utilization of structural formulas which contributed considerably to the formulation of principal chemical laws. The success of this structural chemistry indicates that information obtained using such formulas which are independent of the geometrical arrangement of atoms in the molecule are sufficient both to understand and explain even very complicated reaction mechanisms.

The view of organic chemists of reaction courses was dramatically changed by quantum chemistry which enabled objective calculations of interatomic interactions. According to the quantum chemical view geometrical relations are important, interactions between atoms not connected by chemical bonds are no longer vanishing and the difference between values of matrix elements between atoms connected or disconnected by the formal chemical bonds are only quantitative. The paper by Parr and Mulliken[2] where all integrals between π-electrons of *trans*-butadiene were evaluated can serve as an aid. It follows that values of resonance integrals between atoms 1—3 and 1—4 are 14% and 4% of the value of 1—2 integral. The more pronounced effect of nonbonding interactions can be found with electronic repulsion integrals. (11/33) and (11/44) integrals amount to 60% and 14% of the value of the (11/22) integral. From this viewpoint the neglect of nonbonding interactions can be regarded as a very crude approximation.

Quantum theory of chemical bonds appeared to be very successful in the interpretation and prediction of physical and chemical properties. Unfortunately, the most exact methods which avoid most of the quantum mechanical approximations (*ab initio*) as well as those which treat correctly energy hypersurfaces (full energy optimization, calculation of the correct reaction coordinate and the Hessian matrix analysis of stationary points) are too expensive and calculations of slightly complicated systems are quite unfeasible. The formulation of approximations which do not take into account unimportant information and neglect roughly constant though large contributions can be of importance and it is one of main streams in current theoretical chemistry. There are many attempts in the literature which are based on the utilization of topological information. In addition to papers dealing with the enumeration of isomers[3] or isomerization reaction paths[4] as well as to papers treating borane chemistry[5,6] and the formal topological treatment of reaction patterns[7], three purely topological quantum chemical methods are avaialble for the calculation of molecular properties. Particularly the HMO method should be mentioned[8] which appeared to be very important for the understanding of general principles which govern the properties of π-electronic systems[9,10]. Recently the well known results based on HMO theory have been systematically interpreted by formal graph theory[11]. Graph theory also promoted a suggestion of the so-called quantum chemical graph[12]. The topological version of the PPP method is the modification suggested by Heilbronner and coworkers[13]. Unfortunately none of these topological methods can be used for the analysis of energy hypersurfaces and for a study of reaction mechanism for which continuous changes of topological parameters during a reaction are typical. Moreover methods described in refs[8] and [13] are restricted to the π-electron approximation.

The aim of this paper is to suggest a quantum chemical model of the molecular system which avoids geometrical information and which enables one to discuss quantitatively reaction mechanisms which have been treated formally by the methods of classical structural chemistry.

Topological Approximations

From both quantum chemical calculations and experiments available, the following facts indicate the possibility of introduction of topological approximations for a study of reaction mechanisms: *1*) The typical feature of chemical reactions is a bond breaking/bond formation; if the molecular geometry is expressed in inner coordinates the bond lengths will change considerably more than valence or dihedral angles. *2*) By the analysis of force constants of bond or angle stretching modes as well as of a height of a hindered rotation barrier it can be concluded that the energy difference caused by the bond length change is in an order of a magnitude larger than that caused by the change of angle variables. The displacements from the equilibrium positions of ethane, ethylene, and acetylene are presented in Table I which are responsive to an energy change 4 or 20 kJ/mol, resp. (1 or 5 Kcal/mol) considering the harmonic approximation. Experimental data were taken from refs[14-17] where the semisymmetric inner coordinate system was chosen[18]. It is seen from Table I that the bond length changes contribute more significantly to the energy difference than changes of valence or dihedral angles. Particularly the latter change has only negligible influence on the energy surfaces. *3*) The transferability of bonding parameters from one molecule to another was mentioned many times (see *e.g.* recent papers[19,20]). Data presented in Table I can also serve for the estimation of errors due to this approximation. The error limit 4 kJ/mol gives a tolerance from 6 (C≡C bond) to 11 (C—C bond) pm in the bond length, 18–26° in valence angle and 58° in dihedral angle. Such a tolerance is sufficiently large to cover experimentally detected secondary geometrical changes which are not directly engaged in chemical transformations. *4*) It was shown[21] that matrix elements between atoms not connected by chemical bonds almost vanish after a transformation of canonical orbitals in the orthogonal localized ones.

It follows from items *1*) and *2*) that energy differences caused by the bond angle changes can be neglected to a very good approximation. According to item *3*) the bond energy contributions are transferable from one molecule to another; these facts are believed to support the assumption of the low influence of geometrical parameters on the energy during the reaction course. According to item *4*) the energy of the molecule can be expressed only in terms of diagonal matrix elements and of off diagonal ones between orbitals connected by classical chemical bonds.

TABLE I

Changes of Inner Coordinates of Ethane, Ethylene and Acetylene, which Cause an Increase of a Bonding Energy in 4 or 20 kJ/mol, resp. Bond Lengths are Presented in pm, Angles in Degrees

Vibration	$E = 4$ kJ/mol		$E = 20$ kJ/mol		Ref.
	displacement	angle	displacement	angle	
C—C stretch	5·5		12·2		14
C═C stretch	3·8		8·3		15
C≡C stretch	2·8		6·5		16
C—H stretch (acetylene)	4·5		10·2		16
Ethane sym. bending	17	9	35	18	14
Ethylene sym. bending	18	10	41	21	15
Acetylene wag	24	13	57	30	16
Ethylene wag	24	13	57	30	15
Ethane int. rotation	—	29	—		17

The topological approach can be formulated by the following set of conventions and approximations: (*i*) A choice of a basis set which consists of orthogonal hybrid or localized atomic orbitals. (*ii*) Neglect of all interactions between orbitals located on the same atoms. (*iii*) Neglect of interactions between orbitals not connected by a chemical bond (*iv*) The utilization of conventional approximations for calculation of non-vanishing matrix elements, *i.e.* neglect of overlap, neglect of electron repulsion integrals, ZDO approximation, limited configuration interaction (LCI) *etc.* (*v*) Parametrization of resulting matrix elements directly in the basis of hybrid or localized orbitals.

The items (*i*)–(*iii*) are general for any type of the semiempirical or nonempirical method, items (*iv*) and (*v*) are specific for the semiempirical treatment.

The Choice of Methods

As follows from the preceding discussion, the main feature of the passage from a geometrical theory to the topological one is the expression of the energy on a hypersurface spanned by the HF matrix elements instead of a treatment of energy as a function of coordinates of atomic nuclei. Moreover, it is assumed, that such matrix elements or atomic integrals are transferable from one molecule to another. From the topological viewpoint, one difficulty is encountered with this description. The N-atomic nonlinear molecule is unambiguously described by $3N$-6 inner coordinates. The MO-LCAO description in the basis of n AO's ($n \geqq N$) requires $1/2\ n(n + 1)$ matrix elements which are, therefore, not mutually independent. (This holds particularly for a quantum chemical graph suggested by Polansky[12].) The introduction of topological approximations (*i*) to (*iii*) from the preceding paragraph greatly reduces the number of geometry-dependent nondiagonal elements as only the elements between atoms connected by a chemical bond are considered. These are about N with common molecules. It follows that in the framework of the topological approach most of $3N-6$ inner coordinates are in fact redundant. By the inclusion of the approximations included in item (*iv*) of the preceding paragraph, the following classification of topological methods can be made:

1) *Neglect of overlap, empirical parametrization of whole elements of the* HF *matrix*. It is in fact an HMO approach for π- and δ-bonds with empirical energy contributions for σ-bonds and for the strain in small rings. The accuracy of the total energy is roughly given by the accuracy of the bond energy additivity assumption. As the average bonding energies vary considerably in different papers the proper estimation was done in this paper. Using the ΔH_f^{298} data for ethane, ethylene and cycloalkanes with $n = 3$ to 6 the set of recommended values was obtained and is presented in Table II. The bonding energy ΔH^{bond} was evaluated using the relation

$$\Delta H^{\text{bond}} = 0{\cdot}715\ .\ n_c + 0{\cdot}218\ .\ n_H - \Delta H_f^{298} \quad [\text{MJ/mol}]\,, \qquad (1)$$

where n_c and n_H is the number of C and H atoms in a molecule. The bonding energy can be expressed by means of data from Table II as a sum of contributions, namely

$$\Delta H^{\text{bond}} = 0{\cdot}413 \,.\, k_{\text{C-H}} + 0{\cdot}346 \,.\, k_{\text{C-C}} + 0{\cdot}252 \,.\, k_{\text{C=C}} - 0{\cdot}202 \,.\, k_3 - \\ - 0{\cdot}11 \,.\, k_{34} - 0{\cdot}028 \,.\, k_5 \,, \qquad (2)$$

where $k_{\text{C—H}}$, $k_{\text{C—C}}$, $k_{\text{C=C}}$ are the numbers of corresponding bonds, k_3 is the number of cyclopropene rings, k_{34} is the sum of all cyclopropane, cyclobutane and cyclobutene rings, k_5 is the number of five-membered rings in the molecule. With conjugated systems, $k_{\text{C=C}}$ is half of the total π-electron energy.

Calculated heats of formation are presented in Table III for hydrocarbons of various structural types and compared with those obtained by the more sophisticated semiempirical methods MINDO/2 (ref.[22]) and MNDO (ref.[23]). The only real failure of the simplest topological method was found with 1,3-butadiyne (error 168 kJ/mol). The standard deviation for all 55 members of this set amounts to 35·9 kJ/mol and decreases to 29·1 kJ/mol (6·9 kcal/mol) on exclusion of 1,3-butadiyne. The MINDO/3 method gives a standard deviation of 52·1 kJ/mol (12·5 kcal/mol), the MNDO method 39·6 kJ/mol and 29·5 kJ/mol (7·1 kcal/mol) when cubane is removed from the set. This comparison seems to be favorable for the topological method at the HMO-level if its is kept in mind that the calculations with aliphatic molecules can be performed by a "pen and paper" method and with aromatic systems with negligible

TABLE II

Empirical Bonding and Strain Energies E for ΔH_f^{298} under the Bond Energy Additivity Assumption (all values in kJ/mol)

Component	Taken from	E
H—H	H_2	436
C—H	C_2H_6, C_6H_{12}	413
C—C	C_2H_6, C_6H_{12}	346
C=C	C_2H_4, C—H, C—C	252
	C_3H_4, C—H, C—C, C=C	−202
  	C_3H_6, C_4H_8, C—H, C—C	−110
 	C_5H_{10}, C—H, C—C	− 28

computing time expense. The utilization of this method for a study of topological energy hypersurfaces will be discussed in the paper V of this series.

2) *Explicit treatment of γ-integrals, inclusion of correlation energy.* The conventional π-electronic PPP method is "topological" in the estimation of core integrals (tight binding approximation) and "geometrical" in the calculation of γ-integrals. In all valence electron semiempirical methods described so far all atomic integrals are a function of geometry. Using explicit formulas for energies of ground and excited states of benzene in the PPP approximation, Salem and Longuet-Higgins[24] showed that excitation energies can be reasonably expressed in terms of the difference $\gamma_{1,i} - \gamma_{1,i-1}$ and that these differences approach zero faster with increasing interatomic distances than γ-integrals themselves. This piece of knowledge was used for formulation of a purely topological π-electronic method by Heilbronner and coworkers[13]. From the viewpoint of a chemical reactivity study, this method suffers from neglecting the σ-parts of a system, neglect of doubly excited configurations and a purely empirical choice of parameters which complicates calculations of heterocyclic compounds and derivatives. The solution of these difficulties is more complicated and the topological method suggested will be discussed in Part III of this series.

3) *Study of excited singlet and triplet states.* Within the framework of a topological approximation of electronic repulsion integrals two different approaches can be suggested. Either the convenient closed-shell calculation in $\sigma + \pi + \delta \ldots$ approximation can be performed followed by a limited CI method or a restricted/unrestricted type of an open shell method can be used. For a study of reaction mechanisms one would undoubtedly prefer the first approach. Crossing or avoided crossing of adiabatic hypersurfaces as well as the energy transfer between reacting molecules are of great importance[25,26] in the study of mechanisms of photochemical reactions. The CI method is clearly the proper choice for such a study. The topological approximation within the CI procedure has also another advantage. The most cumbersome task with all CI-calculations is the evaluation of molecular integrals from the basis of atomic integrals. The time needed is proportional to the 5th power of a number of orbitals with nonempirical methods and to the 2nd power under ZDO approximation. With the topological method, this time is almost linearly proportional to the number of orbitals which enables one to calculate even large systems without considerable expense.

4) *Topological* SCF *method.* With exception of the reduction of the number of nonzero matrix elements, the topological approach from an economical point of view has no advantage. The approximation used will be thoroughly discussed in a paper dealing with problems of electronic repulsion.

5) *Multiconfiguration* SCF *method.* The convenient CI method is one of the important tools for calculation of correlation energy of reactants and products.

TABLE III

Experimental Heats of Formations $(\Delta H_f^{298})_{exp}$, Experimental and Calculated Bonding Energies $(\Delta H^{bond})_{exp}$ and $(\Delta H^{bond})_{th}$ of the Representative Set of Hydrocarbons (all values in MJ/mol)

The error of a simplest topological calculation as well as that of MINDO/3 and MNDO semiempirical methods are presented in kJ/mol. Experimental data are taken from ref.[23].

Hydrocarbon	$(\Delta H_f^{298})_{exp}$	$(\Delta H^{bond})_{exp}$	$(\Delta H^{bond})_{th}$	Error (topol.)	Error (MINDO/3)	Error (MNDO)
CH_4	−0·0749	1·6619	1·6520	−9·9	48·5	25·1
C_2H_6	−0·0845	2·8225	2·8240	1·5	1·7	2·1
C_2H_4	0·0523	2·2497	2·2500	0·3	28·5	11·7
C_2H_2	0·2272	1·6388	1·6760	37·2	14·5	12·6
$CH_3CH_2CH_3$	−0·1038	3·9928	3·9960	3·2	−7·1	−0·4
$CH_3CH{=}CH_2$	0·0205	3·4325	3·4220	−10·5	6·7	0·0
$CH_3C{\equiv}CH$	0·1858	2·8312	2·8480	16·8	−38·9	−14·6
Ketene	0·1908	2·8262	2·8480	21·8	−16·3	−7·5
n-Butane	−0·1272	5·1672	5·1680	0·8	0·0	2·9
i-Butane	−0·1356	5·1756	5·1680	−7·6	31·4	23·4
1-Butene	−0·0008	4·6048	4·5940	−10·8	5·0	2·1
t-2-Butene	−0·0126	4·6166	4·5940	−22·6	−13·8	−8·8
2-Me-1-propene	−0·0180	4·6220	4·5940	−28·0	−15·9	9·2
Methylketene	0·1623	4·0057	4·0200	14·3	—	−22·6
Butadiene	0·1088	4·0592	4·0795	20·3	24·3	12·1
1-Butyne	0·1653	4·0027	4·0200	17·3	—	−16·3
2-Butyne	0·1452	4·0228	4·0200	−2·8	−94·6	−43·1
1-Buten-3-yne	0·3046	3·4274	3·5055	78·1	−46·4	−32·6
1,3-Butadiyne	0·4728	2·8232	2·9909	167·7	91·6	−45·2
n-Pentane	−0·1469	6·3379	6·3400	2·1	−4·2	2·9
Neo-pentane	−0·1686	6·3596	6·3400	−19·6	107·5	65·7
t-1,3-Pentadiene	0·0757	5·2433	5·2515	8·2	4·2	2·5
1,4-Pentadiene	0·1059	5·2131	5·1920	−21·1	6·3	2·5

Cyclopropane	0·0531	3·3999	3·4060	6·1	−16·7	− 6·3
c-1,2-Dimethylcyclopropane	0·0054	5·7496	5·7500	0·4	−13·8	− 13·0
Cyclopropene	0·2770	2·7400	2·7400	0·0	−28·5	8·4
1-Methylcyclopropene	0·2435	3·9245	3·9120	−12·5	−66·9	− 19·2
1,2-Dimethylcyclopropene	0·1941	5·1249	5·0840	−40·9	—	− 30·5
Methylenecyclopropane	0·2004	3·9676	4·0040	36·4	−58·6	− 42·3
Cyclobutane	0·0285	4·5755	4·5780	2·5	−49·8	− 78·2
Cyclobutene	0·1569	4·0111	4·0040	− 7·1	−18·0	− 27·2
1,2-Dimethylcyclobutene	0·0828	6·3872	6·3480	−39·2	−41·8	− 56·1
Methylenecyclobutane	0·1218	5·1972	5·1760	−21·2	−54·0	− 76·1
Cyclopentane	−0·0770	5·8320	5·8320	0·0	−39·7	− 50·6
Cyclopentene	0·0343	5·2847	5·2580	−26·7	−10·9	− 36·0
Cyclopentadiene	0·1335	4·7495	4·7715	21·9	36·9	0·4
Fulvene	0·1987	5·3993	5·4667	67·5	86·6	25·5
Cyclohexane	−0·1234	7·0294	7·0320	2·6	−29·7	− 22·2
Cyclohexene	−0·0046	6·4746	6·4580	−16·6	4·2	− 37·2
Cyclohexadiene	0·1063	5·9277	5·9435	15·7	—	− 46·0
Benzene	0·0828	5·5152	5·5620	46·8	37·7	5·9
Toluene	0·0502	6·6988	6·7340	35·2	48·1	6·3
Ethylbenzene	0·0301	7·8699	7·9060	36·1	—	5·9
Styrene	0·1477	7·3163	7·3854	69·1	—	9·2
Cycloheptatriene	0·1837	6·5653	6·6065	41·2	−27·6	− 43·1
Bicyclobutane	0·2171	3·9509	3·9880	37·1	−8·8	72·0
Spiropentane	0·1854	5·1336	5·1600	26·4	−64·9	− 44·4
Dicyclopropyl	0·1293	6·3407	6·3320	− 8·7	−29·7	− 9·6
Bicyclo[2,1,0]pentane	0·1561	5·1629	5·1600	− 2·9	—	− 29·7
Norbornane	−0·0519	7·6729	7·6680	− 4·9	87·0	8·8
Norbornadiene	0·2498	6·4992	6·5200	20·8	103·8	12·1
Propellane	−0·1008	8·8728	8·8960	23·2	58·6	− 9·2
Naphthalene	0·1510	8·7430	8·8342	91·2	88·7	8·4
Adamantane	−0·1335	10·7715	10·7600	−11·5	146·9	23·0
Cubane	0·6222	6·8418	6·7960	−45·8	−37·2	−207·5

In a paper[27] it was shown that potential energy hypersurfaces can be incorrectly analyzed as discontinuous even on a CI level of calculation. (This artifact is not effective with the HMO-CI calculation.) Moreover, derivatives of energy with respect to SCF expansion coefficients do not vanish with the CI wave functions. From the paper[28] it can be assumed that this error is small. On the MC-SCF level of a calculation both these artifacts are eliminated. The problem with a MC-SCF approach in the topological approximation is similar to that in the PPP method[29,30]. Detailed discussion of the molecular integrals in the MC-SCF method as functions of topological rather then geometrical parameters will be discussed in paper III of this series.

The Pattern of a Molecule in the Topological Approximation

Within topological approximations (*i*)–(*iii*) (*vide infra*) the HF matrix is factorized in all approximations to:

1. Blocks including core electrons.
2. 2 × 2 blocks of single bonds localized in straight lines.
3. π-Electronic polycentric blocks localized in planes.
4. δ-Electronic blocks delocalized in space *etc.*

Here these blocks are named elementary components. A chemical reaction is then considered topologically as an interaction of two or more elementary components. If various components localized in one molecule interact, a monomolecular reaction proceeds. In the case of an interaction of elementary components of two, three, ... molecules we speak about bimolecular, termolecular, ... reactions. From a formal topological viewpoint, there is no difference between monomolecular and multimolecular reactions but there is a difference between monocomponent and polycomponent reactions with respect to the number of elementary components which interact. During a reaction course elementary components which interact are no longer factorized and the pertinent electrons are delocalized similarly as with aromatic compounds. The remaining components are factorized in any reaction stage, therefore, it is possible to neglect their approximately constant contributions for a calculation of activation and/or reaction parameters. This reduces considerably the size of the matrix in all levels of sophistication – from an HMO to MC-SCF level.

This idea can be illustrated in the case of the butadiene molecule. Butadiene has 10 atoms and 30 electrons. The topological HF matrix will be factored into:

1. Blocks of 1s electronic pairs on carbon atoms.
2. Six 2 × 2 blocks of C—H σ-bonds.
3. Three 2 × 2 blocks of C—C σ-bonds.
4. One 4-center block of delocalized π-electrons.

The treatment of any monomolecular reaction of butadiene is a problem of the 26th order in a nonempirical study using a minimal basis set and it is a problem of the

22nd order with a semiempirical study on a CNDO/2 level but also using a simple EHT method. With the topological method only elementary components which take part in the reaction can be considered, namely:

(*i*) C—H bond dissociation: one component of the type *2.*; second order problem.

(*ii*) C—C bond dissociation: one component of the type *3.* and one of the type *4.* 6th order problem.

(*iii*) Sigmatropic hydrogen shift: one component of the type *2.* and one of the type *4.* Problem of the 6th order.

(*iv*) *Cis–trans* isomerization: one component of the type *4.* Problem of the 4th order.

(*v*) Electrocyclic reaction: one component of the type *4.* Problem of the 4th order.

(*vi*) Dimerization of butadiene. Two components of the type *4.* Problem of the 8th order. (Compare with the problem of the 44th order in the CNDO/2 approximation.)

(*vii*) As an example of a reaction of two different molecules the Diels–Alder reaction between butadiene and ethylene can be presented. Topologically, it is problem of the 6th order.

If we take into account that the HF matrix diagonalization is proportional to the 2nd to 3rd power of the size, than the topological treatment of *e.g.*, reaction (*iii*) will be 13 to 49 times faster, with reaction (*iv*) 30 to 166 times faster than the geometric calculation of the same level of a sophistication. The inclusion of advanced procedures such as a full energy optimization, calculation of the real energy path on a multidimensional energy hypersurface and a Hessian matrix analysis of all stationary points is feasible even for molecules of a medium size (30–50 atoms). Transformation of topological variables to geometrical ones can by made by several procedures. Let us mention here well known bond energy – bond length relationships (*e.g.*, using the Morse curve, empirical potentials *etc.*). The more detailed discussion on this topic will be presented in Part V of this series.

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