INTERACTION IN CARBOCATIONS AND HÜCKEL’S $4n + 2$ RULE

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The molecular orbital model of hyperconjugation was utilized in rationalizing some long range interactions in carbocations (1). Conveniently such interactions can be detected by measuring secondary kinetic deuterium isotope effects (2). Hückel’s $4n + 2$ rule can be extended to interactions between the cationic center and pseudo-π orbitals of CH$_3$, CH$_2$ and CH groups, respectively (3). Thus, in analogy to hyperconjugation one can envisage homohyperconjugation as the probable cause of normal $\gamma$-deuterium isotope effects (4). Results are presented of studies of these effects in the adamantane and norbornane system. The stability of the 1-adamantyl cation can be ascribed to a favorable $4n + 2$, configuration of $\sigma$-electrons comprising the $\beta,\gamma$-carbon carbon and/or $\gamma$-carbon hydrogen bonds. It is however not possible to distinguish between these alternatives since both could explain the observed $\gamma$-isotope effects. In contrast, the four CH$_2$ groups flanking C$_7$ in the 7-norbornyl cation form an antiaromatic $4n$ pseudo-π system which could explain the exceptional instability of this cation. Interactions of the empty $\pi$-orbital with the subjacent 4B$_2$ pseudo-π orbitals give rise to small normal $\gamma$-deuterium isotope effects of homohyperconjugative origin. In this system, due to symmetry constrains hyperconjugative interaction with the ribbon orbitals of the $\sigma$-framework is not possible.
REFERENCES


Abstractor: N. Trinajstić
By applying the Shannon equation (1) to the electron density matrix of a molecule, an information index is defined and used as the quantitative estimate of the ring (2) and total aromaticity of molecules in the ground and excited states. The approach is applicable within each LCAO-method. The index reproduces well the classification of molecules into aromatic, nonaromatic and antiaromatic, and correlates well with the results of other authors obtained by completely different approaches (3-6). Below is given a comparison with topological resonance energy per electron, T.RE(PE), index (5) for several conjugated molecules.

<table>
<thead>
<tr>
<th>Molecule(^a)</th>
<th>Information aromaticity index</th>
<th>T.RE(PE)</th>
<th>Status(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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</tr>
<tr>
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<tr>
<td></td>
<td>0.625</td>
<td>0.039</td>
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</tbody>
</table>
Graphs of studied molecules; \( \text{A} = \text{aromatic}, \text{NA} = \text{non-aromatic}; \)
\( \text{AA} = \text{anti-aromatic}. \)

A tendency is found for the aromaticity of aromatic molecules to decrease and of antiaromatic molecules to increase when the molecule is excited to the \( S_1 \)-state.

REFERENCES


Abstractor: N. Trinajstić
DO THE C–H BONDS CONTRIBUTE TO THE STABILIZATION ENERGY OF BENZENE?

Á. Furka and F. Sebestyén

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Stabilization energy of benzene (SE) has long been defined as the difference between the heat of formation ($\Delta H_f$) of benzene and that of a hypothetic reference compound: 1,3,5-cyclohexatriene. Since this compound does not exist, its $\Delta H_f$, of course, cannot be determined experimentally. The reference $\Delta H_f$ has usually been calculated from empirically or theoretically derived bond energies. In this way, for example, Klages (1) and Dewar (2) suggested 35.9 and 20 kcal/mol for SE, respectively.

In order to avoid uncertainties connected with the non-existence of the reference compound, the authors of the present paper suggest the definition and calculation of SE to be based on experimentally determined $\Delta H_f$-s of conjugated polyenes. From the $\Delta H_f$-s of the neighbouring members of the homologous series of linear open chain conjugated polyenes, $\Delta H_f$ increments can be derived. A $\Delta H_f$ increment may be considered as a contribution of two =CH– groups to $\Delta H_f$-s. Since benzene consists of six =CH– groups, a threefold value of the $\Delta H_f$ increment can well be accepted as reference $\Delta H_f$ for the calculation of SE.

This way 19.7 and 23.0 kcal/mole are derived for SE, when benzene is compared to trans and cis type polyenes, respectively. A comparison of the estimated C–C bond energy of benzene to that of olefins leads to the conclusion that C–C bonds are

Energy stabilization, of benzene,

Heat of formation of 1,3-butadiene, of ethylene, of trans-1,3,5-hexatriene,
responsible for only about 2/3 of SE. It is suggested that the rest of SE is connected with the difference in strength of the aromatic and olefinic C–H bonds.

REFERENCES


Abstractor: N. Trinajstić
WHY ARE THE PROPERTIES OF POLYCYCLIC HYDROCARBONS ADDITIVE OVER CONJUGATION CIRCUITS?

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Properties as different as resonance energies and magnetic ring-currents are investigated and a non-empirical system of increments is proposed. It is shown that the π-electron properties of conjugated, polycyclic hydrocarbons are additive over all conjugation circuits that can be identified in the molecule. The contribution from each individual conjugation circuit is calculated non-empirically on a simple, free-electron model for the associated annulene. Within a special form of the resonance theory, it is shown that all conjugation circuits should contribute with equal weight, and not only the ‘independent circuits’ as proposed earlier by Randić (1,2) or certain lower circuits as postulated by Herndon (3). Contributions from higher circuits turn out quite naturally, however, to be small.

Results for a wide variety of polycyclic hydrocarbons, alternant and non-alternant, are presented. Both for resonance energies and for magnetically-induced ring currents, satisfactory agreement with conventional calculations has been obtained (4).
REFERENCES


Abstractor: N. Trinajstić
Recently structural features which characterize the energy gap in polymeric conjugated hydrocarbons (1) within the framework of the simple Hückel MO theory have been specified using graph-theoretical methods (2). It has been shown that molecules of interest as potential units in polymers with zero energy gap have to satisfy certain structural conditions which relate the number of selected 'excited' valence structures to that of the Kekule structures for the system. As in the previous work units separated by essentially single bonds are considered.

The search for benzenoid systems which can satisfy the requirement is now elaborated. A necessary condition that a system may have zero energy gap is that the repeating benzenoid unit has a non-prime number (K) of Kekule valence structures. Then K could be factored: $K = K_1 \cdot K_2 \ldots K_m$. (Generally, there are more factorizations of K and the procedure needs to be carried out over all of them.) Fragments $F_i$ that have the number of Kekule structures given by $K_i$ are recognized, and we try to superimpose all of them over the skeleton of monomer unit. (The procedure needs to be carried out for all possible factorizations corresponding to a given factorization.) If it is possible to cover the monomer unit with all the fragments leaving at least two positions available for linking the units in polymer form, then the energy gap of such a polymer is zero.
In a number of examples it is illustrated how the actual search is performed. A list of benzenoid systems of interest as units in a polymer with the zero energy gap is given. The search is quite efficient and speedy as it requires the enumeration of Kekulé valence and related structures of monomer unit under consideration only.

REFERENCES


Abstractors: A. Graovac and N. Trinajstić
EFFECT OF CYCLES ON TOPOLOGICAL RESONANCE ENERGY

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Topological resonance energy, TRE, a new concept in theoretical organic chemistry introduced by the Zagreb group (1), is defined as follows (2),

\[ \text{TRE} = \sum_{j=1}^{N} (g_j x_j - h_j x_j^R) \]  

which for \( g_j = h_j \) reduces (1,3) to

\[ \text{TRE} = \sum_{j=1}^{N} g_j (x_j - x_j^R) \]  

where \( x_j \) and \( x_j^R \) (\( j = 1, 2, ..., N \)) are the zeros of the characteristic (Hückel) and acyclic (reference, matching) polynomial, respectively, of a conjugated molecule, whilst \( g_j \) (and \( h_j \)) is (are) the pertinent occupation number(s).

The author has analysed some general mathematical properties of TRE. Three basic properties of TRE are established:

1. TRE represents the joint effect of all cycles on total \( \pi \)-electron energy (E) of conjugated system.
2. The effect of a particular cycle on TRE is equal to the effect of the same cycle on E.

3. An approximate formula enables one to express TRE as a linear combination of contributions of single cycles,

\[ \text{TRE} \approx \sum_{C} I(G,C) \]  

(3)

where

\[ I(G,C) = -2(-1)^{|C|/2} <(G-C)> \]  

(4)

Symbol C stands for cycle. The validity of formula (3) was tested on a number of conjugated systems, to the alternant and non-alternant, monocyclic and polycyclic. The relation between the approximation (3) and the exact TRE is not linear. The correlation is good for systems having positive and small negative values of TRE, but considerably high violations occur in the case of anti-aromatic molecules, especially [4N]-annulenes.

REFERENCES


Abstractor: N. Trinajstić
ON TOPOLOGICAL RESONANCE ENERGY OF COUMARIN AND ITS DERIVATIVES

P. Ilić, A. Jurić, and N. Trinajstić

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Topological resonance energies (TREs) of coumarin and the following derivatives: 3-hydroxycoumarin, 4-hydroxycoumarin, 3,4-dihydroxycoumarin, 4,5,7-trihydroxycoumarin, 3-carboxy-4-hydroxycoumarin, 3-bromo-4-hydroxycoumarin, and 6-bromo-4-hydroxycoumarin, are reported.

The following TRE formula is used for the numerical work (1-4)

\[ \text{TRE} = \sum_{j=1}^{N} g_j (x_j - x_j^{ac}) \]  

(1)

where \( x_j \) and \( x_j^{ac} \) represent the Hückel spectrum of a given structure and the spectrum of the corresponding acyclic polynomial (1,2), respectively, while \( g_j \) (\( j = 1, 2, \ldots, N \)) are the orbital occupancy numbers.

The heteroatomic parameters are taken from the work by Hess and Schaad (5). In order to compare aromatic stability of coumarin and related compounds the normalized form of TRE, TRE per electron, TRE(PE), is used (4)

\[ \text{TRE (PE)} = \frac{\text{TRE}}{N} \]  

(2)

where \( N \) is the total number of \( \pi \) electrons in the system.
Theoretical predictions that these all coumarins should exhibit aromatic properties are sustained by the ample experimental evidence (6). In addition, coumarin and isocoumarin are predicted to be much more stable than the corresponding quinonoid isomer.

REFERENCES


Abstractor: N. Trinajstić
ON THE TOPOLOGICAL RESONANCE ENERGY OF PORPHINS AND RELATED STRUCTURES

P. Ilić and N. Trinajstić

‘Ruder Bošković’ Institute, P.O.Box 1016, 41001 Zagreb, Croatia, Yugoslavia

Porphinoid, both existing and hypothetic systems, are represented by graphs at the nearest-neighbour level of approximation. By covering a graph by a dimer (1), one gets the characteristic polynomial in the form (2,3)

\[ P(G;z) = \sum_{i=0}^{\text{max}} \sum_{j(i)} (-1)^{i+1} 2^l \ D(G-R_{i,j(i)}, d) z^{N-2d-n_{i,j(i)}} \]  

(1)

d the number of dimers; dimer is defined as such: \( \circ \rightarrow \)

D the number of arguments of \( d \) dimers on a graph G,

N the number of vertices of a graph G,

R ring that are to be excised from a graph G,

m the maximal d number in a subgraph G–R,

n the number of vertices in a subgraph G–R,

i, j(i) index for counting of disjoint elements; \( i = 1, 2, ..., r, \)

\( i = 2d + n_{i}, j(i) \)

r the number of principal rings in a G.
Linearily related structures have interesting combinatorial properties; since they are obtained by covering a graph $G$ with monovalent, dimer subgraphs, we imputed them a name 'acyclic'. Thus, the acyclic polynomial of a complete graph, $G$, reads,

$$ P_{ac}(G; \chi) = \sum_d (-1)^d D(G; d) \chi^{d-\chi} \quad (2) $$

This polynomial was given a meaning of reference polynomial. Associating to the zeros of both polynomials, i.e. characteristic and acyclic, respectively, the common quantity $\beta$, ($\approx 2.3 \times 10^5$ J/mol) (4), one can speak about the energy of a conjugated molecule and its reference structure. A simple linear relation,

$$ \Delta = a_1 x_1 + a_2 x_2 + \ldots + a_k x_k - b_1 y_1 - b_2 y_2 - \ldots - b_m y_m = $$

$$ = (a_1 x_1 - b_1 y_1) + (a_2 x_2 - b_2 y_2) + \ldots + (a_k x_k - b_m y_m) \quad (3) $$

where,

$x_k, y_m$ are the zeros of the characteristic and the acyclic polynomial, respectively, and

$a_k, b_m$ are the corresponding 'orbital' occupancy numbers, quantifies the $\pi$-electron energy difference between conjugated cyclic system and its reference structure. This difference was named the topological resonance energy, TRE, and has been shown (2-4), to correlate with the general properties of conjugated hydrocarbons. In this work has been found that aromatic stabilization of porphins is mainly due to the high topological resonance energy value of pyrrole-type rings, while aromatic stabilization of phthalocyanins is due mainly to high resonance stabilization of i-indole-type rings.

REFERENCES


Abstractor: *N. Trinajstić*
CHARGE DISTRIBUTION FROM MOLECULAR TOPOLOGY AND $\pi$ ORBITAL ELECTRONEGATIVITY

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The automatic and computer-aided prediction of reactivity by means of a few basic atomic parameters is achieved. Considering that only the topology of a molecule is required for the computation it is evident that PEOE (partial equalization of orbital electronegativity) and SD-POE (sigma dependent POE) models proposed by the authors together establish a valid alternative to the presently available, time consuming quantum mechanical procedures.

To prove the reliability of the $\sigma$ charges calculated by the PEOE model, the authors compared them with experimental quantities known to be intrinsically related to atomic charges. This test is of great importance for defining the quality of predicted $\sigma$ charges which are necessary to enter the $\pi$-level calculation. Atomic potential models have been quite successful in correlating core electron binding energy shifts as obtained through ESCA measurements. Authors therefore correlated the carbon charges of a large and representative number of organic molecules with their C-1s-ESCA shifts as shown in Fig 1.

The result is excellent as evident from the correlation coefficient of 0.987. In comparison, for the same compounds, the $ab\ initio$ charges calculated on a STO-3G basis set show a much poorer agreement.
Furthermore, this approach gives a new insight into the interaction between $\sigma$ and $\pi$ electrons which seems worthy of further investigation. In addition, the authors have revived the concept of orbital electronegativity (1-3), especially in the case of the $\pi$ electrons for which no calculation based on POE ($\pi$ orbital electronegativity) has, up to now, ever been performed.

REFERENCES


Abstractor: N. Trinajstić
A REMARKABLY STABLE AND SIMPLE MONOCYCLIC THIEPIN. SYNTHESIS AND PROPERTIES OF 2,7-DI-tert-BUTYL-4-ETHOXYCARBONYL-5-METHYLTIIIEPIN

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A simple monocyclic 8π electron thiiepin, 2,7-di-tert-butyl-4-ethoxycarbonyl-5-methylthiepin (2) stabilized by two bulky tert-butyl groups at 2- and 7-positions, was synthesized from 2,6-di-tert-butyl-4-methylthiopyrylium tetrafluoroborate (1). This is shown below:

\[
\begin{align*}
&\text{CH}_3 & \text{LiCN}_2\text{COOC}_2\text{H}_5 \\
&\text{S} & \rightarrow -120^\circ\text{C} \\
&\text{H}_3\text{C} & \text{COOC}_2\text{H}_5 \\
&\text{S} & \rightarrow \text{Pd(II)} \\
&\text{H}_3\text{C} & \text{COOC}_2\text{H}_5 \\
\end{align*}
\]

Aromaticity of 8π electron monocyclic thiiepin,

Heterocyclic compounds, preparation of thiiepin derivative,
The compound 1 is prepared in the following way:

\[
\text{t-BuCOCl} \xrightarrow{\text{SnCl}_4} \text{t-BuOH} \xrightarrow{\text{Li/NH}_3} \text{Me}_3\text{SiCl/Zn} \xrightarrow{\text{Ph}_3\text{C}^+\text{BF}_4^-} \xrightarrow{\text{CH}_3\text{L}_1} \]

In spite of its monocyclic thiepin structure, the compound 2 showed remarkable thermal stability and half-life of 7.1 h at 130 °C. Judging from the \(^1\text{H-NMR}\) spectrum, the thiepin 2 is considered to be an atropic molecule.

Abstractor: N. Trinajstić
It is well known that pentafulvenes are very sensitive towards traces of acid, but the structure of the polymers has never been determined so far (1,2). The authors found that the cationic polymerisation of 6,8-disubstituted pentafulvenes yields highly unsaturated, reactive macromolecules (1) of high molecular weight. The mechanistic pathways leading to the polymers are discussed, and the spectroscopic evidence for structure (1) is presented.

\[
\begin{align*}
\text{(1)} & \quad \text{Diels-Alder reaction in thermal oligomerization of pentafulvene,} \\
\text{(2)} & \quad \text{Fulvene polymerization of,} \\
\text{(3)} & \quad \text{Polymerization cationic, of fulvene derivatives,}
\end{align*}
\]

\[
\begin{align*}
R, R' & = \text{Alkyl, Aryl} \\
R, R' & = \text{H, CH}_3
\end{align*}
\]
In contrast to indications of the literature (3) the main process in thermal oligomerisation of simple pentafulvenes is a Diels-Alder-reaction, giving products of the type (2). Anionic polymerization of pentafulvenes may be initiated by traces of sodium cyclopentadienide and phenylsodium, respectively. The reaction product consists of a mixture of oligomers of the series (fulvene)$_n$. This surprising result is explained by structure elucidation of the fulvene dimers, which gives formula (3). The mechanistic aspects of the reaction are discussed.

REFERENCES

Abstractor: N. Trinajstić

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Previously, the authors have reported (1) the synthesis of furanoid [15] annulenones (A and D) and their protonated species (B and C). With the benefits of FT nmr spectroscopy, some of experiments have now been reinvestigated.

The annulenone A may undergo dynamic conformational changes to provide an interesting cycle, which can be driven by protonation-deprotonation sequence. Annulenyl ion B formed by protonation step 1 triggers the movement of the inside OH group to the outside positions of the ring as depicted in step 2. The resulting isomeric annulenyl ion C is then deprotonated to provide a less stable annulenone D. The geometrical properties of annulenone D would result in its isomerization to regenerate annulenone A in step 4.

This cycle is of interest in connection with a real biological cycle, proton pump cycle of bacteriorhodopsin (2).

![Diagram of the annulenone and annulenyl ion cycle](image-url)
REFERENCES


Abstractors: A. Graovac and N. Trinajstić
Thermal rearrangements, though commonplace among unsaturated aliphatic hydrocarbons (1), have only rarely been observed in completely aromatic systems (2). The thermal isomerization of azulene (1) to naphthalene (2) undoubtedly qualifies as the oldest and best known example of such a skeletal reorganization and has stood as a mechanistic puzzle for many decades (2). In particular, the question has arisen (3) as to whether or not this rearrangement occurs via sequential, concerted, pericyclic reactions analogous to those which so often prevail in nonaromatic systems. Scheme 1 depicts one of possible mechanism (3).

Scheme 1
The simplicity and symmetry-allowed nature of this mechanism make it most appealing. But the $^{13}$C-nmr spectrum of naphthalene product has shown that the $^{13}$C-label originating in the angular position of azulene are found after isomerization over $\gamma$, $\alpha$, and $\beta$ positions of naphthalene in a ratio 3:2:1, respectively. Therefore, no single pathway, including the bicyclobutane mechanism, proposed until now could account for the results of this experiment. Scheme 2, however, illustrates the authors' proposal for the thermal rearrangement of azulene to naphthalene.

![Scheme 2](image)

**REFERENCES**


Abstractor: N. Trinajstić
BONDING IN FUNCTIONALIZED AZIRIDINES: NITROGEN-15 AND CARBON-13 STUDIES


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Two isomeric pairs of cis- and trans-1-cyclohexyl-2-phenyl-3-benzoylaziridines have been synthesized: (a) with a nitrogen-15 labelled nitrogen, and (b) with carbon-13 labelled ring carbons. The carbon-13 to X (where X = nitrogen-15, carbon-13 or hydrogen-1) spin-spin coupling constants were measured and interpreted in terms of stereoelectronic effects. X-ray crystallographic data of cis- and trans-1-cyclohexyl-2-phenyl-3-(p-tolyl)aziridines appear in good agreement with their NMR data and theoretical calculations based on INDO method (1).

Bonding is discussed for the three-ring itself (NMR studies) and for its substituents (X-ray studies). It is concluded that stereocchemical interaction of the Van der Waals type is an important determinant of aziridine bond length. Three-ring to carbonyl hyperconjugation is correlated with stereoelectronic interactions in the trans isomer.

REFERENCE


Abstractor: N. Trinajstić
The Diels-Alder cycloaddition of dimethyl-1,2-cyclobutenedicarboxylate to a 1,3-diene results in the formation of an adduct which can subsequently be decarboxylated and dehydrogenated to provide a cyclobutene-fused benzenoid system (1,2). The use of appropriate dienes has led to the preparation of a series of para- and meta- bis-annelated benzenes including 1, 2, and higher homologs. Variations in the $^1H$ and $^{13}C$ nmr and in the UV spectra are found to be a function of the size of the annelated rings as well as their relative orientation.

A similar approach has been employed in a preparation of the very elusive tricyclobutabenzene (5) which may represent the missing link between 1,5,9-cyclododecatrione and 6-radialene. Tricyclobutabenzene is a stable crystalline material whose physical properties are quite consistent with higher homologs. An X-ray structure of the perfluoro analog of 5 shows no evidence for any bond alternation.
A double-barreled application of the Diels-Alder approach has led to the synthesis of naphtho[b,e]dicyclobutene (6). The physical properties (3) of this molecule will also be compared to higher homologs.

REFERENCES


Abstractor: N. Trinajstić
The macrocyclic systems studied were annulenes and corannulenes.

There is considerable interest in the chemical and physical properties of annulenes (1), i.e. completely conjugated monocarbocyclic polyenes, the ring size being indicated by a number in brackets. It is well known that \([4n + 2]\)- and \([4n]\)-annulenes can be classified as aromatic and antiaromatic concerning their ground state stabilities (2) and magnetic properties as proton chemical shifts (1,3) or diamagnetic exaltations (4). Corannulenes (5) consist of two perimeters which are connected by radial bonds. Considering benzenoid alternant corannulenes the inner and the outer annulene are always of the same type and differ by 12 carbon atoms. Up to now only three members of this class of compounds have been synthesized, i.e. pyrene, coronene and kekulene (6).

The triplet zero-field splitting parameters \(D\) of \([4n]\)- and \([4n + 2]\)-annulenes are calculated within a pi-model (7). The zero-field splitting (ZFS) parameter \(D\) is a measure of the magnetic dipole-dipole interaction of the two unpaired electrons of the triplet state.

Annulenes
zero-field splitting parameters calculation of,

Bond length alternation in annulenes compared with ground state properties,
The dependence of parameter $D$ on $n$ and the degree of bond lengths alternation is compared with that of ground state properties like magnetic ring currents. Furthermore it is shown that corannulenes which consist of two concentric perimeters with connecting radial bonds cannot be regarded as macrocyclic annulenoid systems in the triplet state.

REFERENCES


Abstractor: N. Trinajstić
The electronic structures of nonbenzenoid aromatic hydrocarbons containing a four-membered ring have been of interest since Lin and Krantz provided the first physical evidence for the structure of cyclobutadiene (1).

The position dependence of the SCF screened potential in several nonbenzenoid aromatic hydrocarbons containing a four-membered ring (Scheme 1) has been investigated using the SCF screened potential MO Cl method (2,3).

Aromatic hydrocarbons, properties
nonbenzenoid systems, MO calculations,
Molecular orbital
SCF screened potential in nonbenzenoid systems, position dependence of,
The starting bond distortions, belonging to the $A_1$, $B_{1g}$, and $B_{3u}$ representations, all converge into the unique self-consistent set of bond lengths belonging to the molecular symmetry group $D_{2h}$, while the distortions belonging to $B_{2u}$ converge into another set of bond lengths belonging to $C_{2v}$.

From the dependence of the SCF screened potential for a number that indicates the kind of screened potential, it can be seen that there is only one kind of screened potential at each of the numbers in the $D_{2h}$ structure and at the even numbers in the $C_{2v}$ structure. However, under the influence of the bond-length alternation, there are two kinds of screened potentials, screening and anti-screening, at the odd numbers in the $C_{2v}$ structure. Such characteristics of the screened potentials in the $C_{2v}$ structure show a tendency similar to those of the polyene ($C_{10}H_{12}$).

From the above results, it may be concluded that molecules I, II, and III have polyolefinic character.

REFERENCES


Abstractor: N. Trinajstić

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- Da li C-H veze doprinose energiji stabilizacije benzena?
- Zašto su svojstva poliklikličkih ugljikovodika aditivna po krugovima konjugacije
- Traženje benzenoidnih polimera sa nultim energetskim rascjepom pomoći teorije grafoa
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- Neobične stabilne i jednostavne monocikličke tiepine. Priprava i svojstva 2,7-di-t-bušilt-4-etoksikarborril-5-metil tiepine
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