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Torsion Barriers of End-Groups in Cumulenes

II. Results of Calculations and Discussion

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Computational results are presented for the torsion barriers of end-groups in cumulenes, C_nH_4 up to $n = 20$, obtained by the restricted Hartree-Fock method in a semiempirical approximation of closed and open shell theories. In this approximation we found that the barrier height is equal to 0.2 eV for infinite cumulene with equal CC bond lengths. The origin of this asymptotical barrier is connected with the fact that the field described by the Hückel Hamiltonian with equal CC bond lengths is closer to the SCF Hamiltonian for odd chains than for even ones. The reason why the closed shell theory is inapplicable for cumulene barrier calculations is given, and it is shown that an appearance of alternation of barriers in the extended Hückel theory is wrong.

Die Berechnung der Rotationsbarriere von Endgruppen in Cumulenen mittels eines semiempirischen SCF-Verfahrens für abgeschlossene und offene Schalen zeigt, daß diese Schwelle für große Ketten gegen 0.2 eV geht. Der Grund für dieses asymptotische Verhalten liegt darin, daß der Hamiltonoperator der Hückeltheorie bei gleichen C—C-Abstand dem der SCF-Theorie für ungerade Ketten ähnlicher ist als für geradzahlige. Es wird gezeigt, warum die Theorie für abgeschlossene Schalen versagt und daß die alternierenden Rotationsbarrieren, die in der erweiterten Hückeltheorie auftreten, falsch sind.

Les barrières de rotation des groupes terminaux dans les cumulènes de formule générale C_nH_4, n variant jusqu'à 20, sont evaluées par la méthode autocohérente semi-empirique pour les systèmes à couches complètes ainsi que ceux à couches incomplètes. On a constaté le décroissement monotone de ces barrières et la convergence vers une valeur finie d'environ 0.2 eV pour les n infiniment grands. L'origine de cette limite finie est liée au fait que le champ, décrit avec un hamiltonien du type Hückel avec des liaisons égales, est plus proche au champ autocohérent dans le cas des chains à nombre impair que dans les chains à nombre pair. La non validité de la théorie des couches complètes pour le calcul des barrières de rotation est évidente, ainsi que l'invraisemblance de l'alternance des barrières, calculées par la méthode étendu de Hückel.

A previous communication [1] contained a general theoretical consideration of the electronic structure of stable and unstable cumulene conformations. It was particularly shown that within the zero differential overlap approximation and for equivalent π-AO of inner and outer C atoms of cumulene the energy of the stable conformation (closed shell states $^1A_1$, respectively ^1A_g) and of the unstable conformation (open shell states $^1B_1$, respectively ^1A_u) can be separated into E_x, E_y

which correspond to orthogonal chains of AO π_x and π_y, and the energy of electronic interaction between both chains E_{int}:

$$E = E_x + E_y + E_{\text{int}} + E^{\text{core}} . \tag{1}$$

E_{int} does not depend on the MO coefficients. Thus, the energy of cumulene in the states previously mentioned can be found by a solution of the appropriate equations for separate chains. This fact essentially facilitates the computations of the barriers in cumulenes.

It was also shown that in the approximation of fully localized alternating double bonds in separate chains the barrier height is independent of the length of the cumulene molecule and is equal to that in ethylene. On the other hand the calculation on the basis of Hückel orbitals yields zero in the case of infinite cumulene. These two cases should be considered as extreme ones which do not exist in reality. Therefore, it should be interesting to study the same problem on the basis of SCF orbitals, and this is the subject of the present communication.

If one calculates the barrier heights in the SCF approximation by Eqs. (4) and (5) from [1], then E_x and E_y should be calculated for the ground state of the linear chains which contain an even or odd number of atoms. In the former case the shell is closed but in the latter it is open and the ground state is a doublet. In both cases calculations were performed by the restricted Hartree-Fock method with semiempirical approximations. The closed shell theory was used for even membered chains and the open shell theory for odd chains. In the following the details of computations, the most important results and their discussion are given together with data about barriers calculated by simple [2, 3] and extended [4, 5] Hückel methods.

Methods and Details of Computation

Closed shell states of separate chains with an even number of atoms were computed by the traditional Pariser-Parr-Pople method [6, 7], neglecting penetration integrals. The odd separate chains are in a doublet ground state with one open shell. MO equations for open shell states were found by Lennard-Jones [8], and their solutions in LCAO approximation were suggested by McWeeny [9] and Roothaan [10]. Vectors $\boldsymbol{C}_i$ are solutions of an eigenvalue problem for a certain Hermitian operator $\boldsymbol{\Omega}$:

$$\boldsymbol{\Omega}\boldsymbol{C}_i = \varepsilon_i \boldsymbol{C}_i .$$

It may be shown that Roothaan's operator is the particular case of a general operator discussed in [11]. In our calculations we used one particular form of that general operator which is more useful for programming and seems to give faster computation speed. SCF solutions of Roothaan's operator and of that used by us are different. Nevertheless orbital sets for each shell are unitary equivalent. Thus, density matrices and average values of other physical quantities are the same for both operators. In our computations operator $\boldsymbol{\Omega}$ was the following[1]:

$$\boldsymbol{\Omega} = \boldsymbol{H}^{\text{core}} + 2\boldsymbol{J}^c - \boldsymbol{K}^c + f(2\boldsymbol{J}^o - \boldsymbol{K}^o) - \boldsymbol{P}^o \boldsymbol{A}(s\boldsymbol{P}^c + \boldsymbol{P}^u) - (s\boldsymbol{P}^c + \boldsymbol{P}^u)\boldsymbol{A}\boldsymbol{P}^o .$$

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[1] Detailed discussion of the operator $\boldsymbol{\Omega}$ may be found in [5, 12–16]. As in the first communication [1], upper indices c, o, and u designate closed, open, and unoccupied shells respectively.

Operators $\boldsymbol{J}^c$, $\boldsymbol{K}^c$, $\boldsymbol{J}^o$, and $\boldsymbol{K}^o$ have their usual meaning and are formed from the density matrices[2]:

$$\boldsymbol{P}^c=\sum_{i=1}^{q}\boldsymbol{C}_i\tilde{\boldsymbol{C}}_i,\qquad \boldsymbol{P}^o=\sum_{i=q+1}^{p}\boldsymbol{C}_i\tilde{\boldsymbol{C}}_i.$$

Matrix $\boldsymbol{P}^u$ is defined formally in the same way:

$$\boldsymbol{P}^u=\sum_{i=p+1}^{n}\boldsymbol{C}_i\tilde{\boldsymbol{C}}_i,\qquad \boldsymbol{P}^u=\boldsymbol{I}-\boldsymbol{P}^o-\boldsymbol{P}^c.$$

For the ground doublet ($p-q=1$) and lowest triplet ($p-q=2$) states of systems without additional degeneration caused by space symmetry

$$A=f\boldsymbol{K}^o,\qquad f=1/2,\qquad s=f/(f-1)=-1.$$

The total energy of π-electrons in the open shell state is

$$E^o=\sum_{i=1}^{q}\varepsilon_i+f\sum_{i=q+1}^{p}\varepsilon_i+\mathrm{Sp}(\boldsymbol{H}^{\mathrm{core}}(\boldsymbol{P}^c+f\boldsymbol{P}^o))-f\,\mathrm{Sp}(A\boldsymbol{P}^o),\tag{2}$$

while for closed shell states with $2m$ electrons

$$E^c=\sum_{i=1}^{m}\varepsilon_i+\mathrm{Sp}(\boldsymbol{H}^{\mathrm{core}}\boldsymbol{P}^c).\tag{3}$$

When carrying out barrier calculations by SCF methods one-center integrals $\gamma_{\mu\mu}$ were estimated by Pariser's recipe [17]:

$$\gamma_{\mu\mu}=I_\mu-A_\mu,$$

where I_μ and A_μ are the first ionization potential, respectively, the electron affinity of atom μ in the appropriate valence state. Numerical values of I_μ and A_μ were taken from the work of Hinze and Jaffé [18]:

$$I_{\mathrm{C}}(sp^2)=11.16\,eV,\qquad A_{\mathrm{C}}(sp^2)=0.03\,eV,\qquad I_{\mathrm{C}}(sp)=11.19\,eV,\qquad A_{\mathrm{C}}(sp)=0.10\,eV.$$

Two-center integrals $\gamma_{\mu\nu}$ were computed by the formulae due to Mataga-Nishimoto [19, 20]

$$\gamma_{\mu\nu}=\left(\frac{2}{\gamma_{\mu\mu}+\gamma_{\nu\nu}}+0.06944\,R_{\mu\nu}\right)^{-1}$$

or Ohno [21]

$$\gamma_{\mu\nu}=\left[\frac{4}{(\gamma_{\mu\mu}+\gamma_{\nu\nu})^2}+0.004822\,R_{\mu\nu}^2\right]^{-1/2}:$$

An exponential R-dependence was used for integrals $\beta_{\mu\nu}$ from [22]:

$$\beta_{\mu\nu}=-2518\exp(-5.007\,R_{\mu\nu}).$$

(In these formulae $\gamma_{\mu\nu}$ and $\beta_{\mu\nu}$ are measured in eV, and distances $R_{\mu\nu}$ in Å).

The computations were performed for equally spaced chains with $R_{\mathrm{CC}}=1.31$ Å. A rotational structure analysis of a highly resolved Raman spectra of gaseous allene, allene-d_4, and allene-1,1-d_2 led to $R_{\mathrm{CC}}=1.308_8\pm0.001$ Å [23]. An analogous investigation of the simple butatriene C_4H_4 under the assumption that $R_{\mathrm{C_1C_2}}=R_{\mathrm{C_3C_4}}=1.309$ Å led to $R_{\mathrm{C_2C_3}}=1.284\pm0.006$ Å [24]. Structure analysis of

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[2] The electrons on the p MO have spin α and those on the remaining q MO spin β ($p>q, p+q=n$).

$C_6(C_6H_5)_4$ with assumed equality of all CC bond lengths led to $R_{CC} = 1.31 \pm 0.03$ Å [25].

The results of our computation have shown that the assumption of equating all bond lengths is fairly well supported for the inner bonds of sufficiently long cumulenes by the bond orders which have been calculated with the above mentioned approximations. Considerable deviations are found only for the two end-bonds. In the SCF approximation they are decreased to some extent compared with the results of the simple Hückel method, but they still remain sizable. Large differences in bond orders are found in short cumulenes. Inclusion of a possible unequality of the bond lengths may lead, of course, to certain small changes of the numerical results. It is remarkable that especially in the SCF approximation the bond orders in stable and unstable conformations of sufficiently long cumulenes are practically equal. Thus, the assumed equality of all bond lengths leads presumably for both conformations to the same correction for end-effects which will not change the barrier heights. Excluding the D_{2d} conformation of even cumulenes (EC), one may note the lack of a tendency to bond alternation in the middle of the chain which was postulated by Shustorovich as the reason for existence of a non-zero barrier for an infinitely long cumulene molecule [26, 27].

Computations of closed shell states were performed by the program PPP-1 and of open shell states by PPP-2 [28], the detailed description of which are given in our book [5]. These programs performed on a Soviet computer M-20 were able to calculate separate cumulene chains containing up to 20 atoms.

Hückel barriers mentioned in [1] were also calculated by the programs PPP-1 and PPP-2. The diagonal elements of the input matrices were all equal to $-I_\mu = -11.19$ eV and the nondiagonal elements for closed neighbours $\beta_{\mu,\mu+1} = -3.569$ eV. Eigenvalues and eigenvectors of these matrices were used for the computation of chain energies by formulae (2) and (3) depending on whether the number of atoms in the chain is odd or even.

The programs were not specially prepared for the computation of a whole cumulene molecule with simultaneous self consistency over both chains. It seemed useful to check numerically the validity of the expansion (4) found in reference [1] in which it was derived theoretically and used for barrier calculations. For this purpose we devised what we call a "polycentric model of the atom" *(vide infra)* which gave us the possibility of performing computations of a whole cumulene molecule by the usual SCF programs for planar conjugated systems. Results obtained by the use of this model coincide with high precision to the results based on formula (4) from [1] which are discussed below.

We shall describe the application of this model to cumulene. Each C atom is reflected on the plane by two points. Then the stable and unstable conformation, e.g. butatriene, would look as in Fig, 1. The numerical value of the splitting parameter ϱ may be estimated by the following simple procedure. The theoretical value of the integral $\gamma^t_{\mu\mu}$ calculated with Slater type orbitals $2p_z$ is $\gamma^t_{\mu\mu} = 501\,\xi/1280$. Let us choose the orbital exponent ξ equal to 1.57 which minimizes the ground state energy of the atom $C(s^2p^2, {}^3P)$ [29]. A semi-empirical value for $\gamma^s_{\mu\mu}$ is known. Then the coefficient $k = \gamma^t_{\mu\mu}/\gamma^s_{\mu\mu}$ is equal to 1.50 for $C(sp^2)$ and 1.51 for $C(sp)$. If taken from Hurley [30], $\gamma^t_{\mu\nu'}$ for $\mu = 2$ and $\nu' = 5$ (Fig. 1) is equal to 14.92 eV. Then γ^s_{25} is 9.89 eV. Using the equation for $\gamma_{\mu\nu}$ $(\mu \neq \nu)$ of Mataga-Nishimoto (MN) respectively of Ohno one finds

$$\varrho_{\mathrm{MN}} = 0.16\ \text{Å}\,,$$
$$\varrho_{\mathrm{Ohno}} = 0.66\ \text{Å}\,.$$

Integrals $\beta_{\mu\nu'} = 0$, by symmetry.

Treating cumulene C_nH_4 as a $2n-2$ center problem with the ϱ's as parameters the correct calculation of all integrals $\gamma_{\mu\nu}$ and $\gamma_{\mu\nu'}$ is possible with sufficient accuracy for semi-emperical integral values. This can be justified by verifying the reliability of the computations of the two-center integrals γ_{15} (Fig. 1) in the given model. One finds from the tables of Preuss [31] that for $R_{12} = 1.31$ Å and $\xi = 1.57$ the integral $\gamma_{12}^t = 9.43$ eV. With ϱ as above one gets $\gamma_{12}^t/\gamma_{15}^t = 1.03$ which is quite satisfactory for semi-empirical calculations.

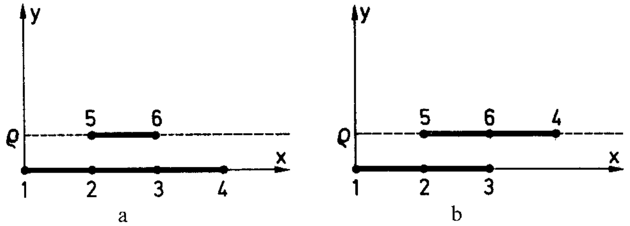

Fig. 1a and b. Two-center model of a carbon atom in the application to butatriene C_4H_4. a Stable planar conformation of symmetry D_{2h}, b unstable twisted conformation of symmetry D_{2d}; thick lines correspond to the separate chains of the cumulene bonds system; the value of the splitting parameter ϱ see in text

The extended Hückel method [4, 5] was applied to cumulenes with $n = 2, 3, 4$ in both of their conformations. All parameters were taken from Hoffmann's paper [4]. Angles between CH bonds were assumed equal to 120°. The following bond lengths were used: in C_2H_4 $R_{\mathrm{CC}} = 1.34$ Å, $R_{\mathrm{CH}} = 1.10$; in C_3H_4 $R_{\mathrm{CC}} = 1.309$, $R_{\mathrm{CH}} = 1.07$; in C_4H_4 $R_{C_1C_2} = R_{C_3C_4} = 1.309$, $R_{C_2C_3} = 1.284$, $R_{\mathrm{CH}} = 1.07$.

The computations were performed by the program RMH [5, 32, 33]. The computation of the barrier heights by the simple Hückel method was done by programs of the type Hückel [3, 34, 35][3].

Computational Results and Discussion

First we shall discuss the barriers calculated by the extended Hückel method. Hoffmann [3] found an alternation of the barrier heights with n (Table 1). This result is not obtained either in the simple Hückel method or in the π-electron approximation of SCF method. The values of the MO energies and the symmetry of the corresponding levels are given in Table 1, and Hoffmann's barriers are estimated from Fig. 2 of his work [38] in Table 2.

In the extended Hückel method the ground state of *EC* (symmetry D_{2h}) has the correct symmetry ^1A_g. It is also seen from Table 1 that the frontier MO of the

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[3] All computations were performed on a computer M-20 [36, 37] of the Institute of Cybernetics of the Academy of Sciences of the Ukraine (Kiev).

Table 1. *Energies of the lowest* MO *for both conformations of* C_2H_4, C_3H_4, *and* C_4H_4 *computed by the extended Hückel method, in eV. (Highest filled* MO *is marked out by boldface, and highest half-filled by italics)*

C_2H_4		C_3H_4		C_4H_4	
D_{2h}	D_{2d}	D_{2h}	D_{2d}	D_{2h}	D_{2d}
$53.123\ b_{1u}$		$14.239\ b_{2u}$	$62.469\ b_2$	$-6.584\ b_{3g}$	$18.355\ a_1$
$21.228\ a_g$		$12.120\ b_{3g}$	$50.571\ a_1$	$-9.362\ b_{3u}$	$15.788\ b_2$
$15.560\ b_{3g}$		$-5.927\ b_{3u}$	$20.357\ b_2$	$\mathbf{-12.193}\ b_{2u}$	$13.267\ e$
$10.469\ b_{1u}$	$52.277\ b_2$	$-9.293\ b_{2u}$	$14.344\ a_1$	$-12.519\ b_{2g}$	$-5.375\ e$
$6.431\ b_{2u}$	$22.713\ a_1$	$\mathbf{-11.204}\ b_{2g}$	$13.227\ e$	$-14.183\ a_g$	$\mathit{-10.636\ e}$
$-8.242\ b_{2g}$	$10.962\ e$	$-13.898\ b_{3u}$	$-7.340\ e$	$-14.208\ b_{3u}$	$-13.647\ e$
$\mathbf{-13.216}\ b_{3u}$	$9.635\ b_2$	$-14.262\ b_{1u}$	$\mathbf{-12.752}\ e$	$-15.434\ b_{3g}$	$-14.183\ a_1$
$-13.777\ b_{3g}$	$\mathit{-10.405\ e}$	$-15.090\ b_{3g}$	$-14.264\ b_2$	$-15.735\ b_{2u}$	$-15.612\ e$
$-14.449\ a_g$	$-14.423\ a_1$	$-15.881\ b_{2u}$	$-15.600\ e$	$-16.578\ b_{1u}$	$-16.578\ b_2$
$-16.215\ b_{2u}$	$-15.535\ e$	$-17.948\ a_g$	$-17.946\ a_1$	$-21.267\ a_g$	$-21.267\ a_1$
$-20.605\ b_{1u}$	$-20.619\ b_2$	$-23.874\ b_{1u}$	$-23.874\ b_2$	$-25.601\ b_{1u}$	$-25.601\ b_2$
$-26.980\ a_g$	$-26.981\ a_1$	$-28.050\ a_g$	$-28.050\ a_1$	$-28.606\ a_g$	$-28.606\ a_1$

Table 2. *Barrier heights* ($|V_n|$) *of the cumulenes* C_nH_4 *computed by different methods, in eV*

	Method of computation due to						
n	Hoffmann		Hückel			Hartree-Fock	
	1[a]	2[b]	3[c]	4[d,e]	5[d,f]	6[e,g]	7[f,g]
3	1.25	**2.12**	2.550	2.324	3.311	2.324	3.311
4	**1.77**	0.95	1.775	1.702	2.377	1.737	2.457
5	0.77	**1.36**	1.419	1.356	1.936	1.396	2.036
6	**1.20**	0.63	1.158	1.126	1.603	1.173	1.718
7	0.57	**1.03**	0.995	0.968	1.401	1.026	1.535
8	**0.90**	0.49	0.862	0.846	1.212	0.914	1.381
9	0.44	**0.80**	0.768	0.753	1.076	0.833	1.281
10	**0.72**	0.40	0.687	0.678	0.976	0.766	1.192
11			0.626	0.618	0.902	0.715	1.131
12			0.572	0.566	0.817	0.671	1.075
13			0.529	0.523	0.748	0.637	1.035
14			0.490	0.486	0.694	0.606	0.997
15			0.458	0.454	0.649	0.582	0.970
16			0.428	0.426	0.608	0.560	0.943
17			0.404	0.401	0.573	0.542	0.924
18			0.380	0.379	0.541	0.526	0.905
19			0.361	0.359	0.514	0.512	0.891
20			0.342	0.341	0.488	0.499	0.877

[a] Calculated from the ground state energies of both conformations D_{2h} and D_{2d}.

[b] Calculated from the ground state energy of the conformation D_{2d} and from the first excited state energy of the conformation D_{2h}.

[c] Energies of both conformations are calculated by the usual additive formula of the simple Hückel method; the β integral used ($\beta = -2.177$ eV) is calibrated by means of ethylene barrier $V_2 = 4.353$ eV.

[d] Energies of the even separate chains calculated by formula (3), those of the odd chains by formula (2).

[e] γ integrals used are due to Mataga-Nishimoto.

[f] γ integrals used are due to Ohno.

[g] Energies of the odd separate chains are calculated by the open shell theory.

unstable conformation D_{2d} is doubly degenerate and half-filled. Its AO representation $(\pi_x \pi_y)^2$ leads to the correct configuration $(\pi_x^1 \pi_y^1)$. One finds an analogous situation in the simple Hückel method where there are two non-bonding MO's in the odd separate chains. This ensures the correct barrier values of EC in the extended Hückel method to be obtained.

The extended Hückel method leads to a zero barrier value for an infinite cumulene chain. The correlation equation for $n = 4, 6, 8, 10$ is

$$V_n = 0.07(\pm 0.05) + 6.6(\pm 0.3)\frac{1}{n}$$

with a regression coefficient $r = 0.998 \pm 0.002$.

The situation is entirely different for odd cumulenes (OC). The ground state of the stable conformation D_{2d} has the correct symmetry ${}^1A_1$ but the symmetry of the unstable conformation is ${}^1A_g$ instead of ${}^1A_u$, in the π-electron approximation. The electronic shell is closed. The AO representation of the upper filled level b_{2_g} is $(\pi_x)^2$ which is a state with an electron transfer from the short to the long chain.

In contrast with this the SCF method in the π-electron approximation gives an open shell for the ground state of a planar OC with separate delocalization of the two unpaired electrons at the different chains. This is the reason for the alternation effect in the extended Hückel method.

Correct values of the barriers for OC are achieved if instead of the closed shell of the unstable conformation D_{2h}, an open shell obtained by excitation of an electron from the highest filled orbital b_{2g} to the lowest empty one b_{2u} is introduced:

$$(b_{2g})^2 (b_{2u})^0 \rightarrow (b_{2g})^1 (b_{2u})^1 \, [(\pi_x)^1 (\pi_y)^1] \, .$$

The corresponding values for the barriers are collected in column 2 of Table 2. Therefore, the extended Hückel method is useless for the calculation of excited and ionized cumulene states. Our calculations show that in the frame of the extended Hückel method two electrons on the highest occupied MO (b_{2u} of planar C_4H_4) are mainly localized in the short chain with AO's π_y. On the contrary, in the Hartree-Fock method these electrons are localized in the long chain with AO's π_x. This is important for the calculation of the electronic spectra, ionization potentials and electron affinity of cumulenes.

Let us discuss the barrier heights calculated with SCF orbitals. It was shown analytically in [1] that the states ${}^1A_1$, ${}^1B_2$ for EC of symmetry D_{2d} and ${}^1A_g$, ${}^1A'_g$ for OC of symmetry D_{2h} which correspond to electron transfer between the chains are less stable than the states ${}^3A_2$, ${}^1B_1$, respectively ${}^3A_u$, ${}^1A_u$. To check this conclusion numerically we computed the charged doublet states D^+, D^- for even separated chains and singlet states S^+, S^- for odd separated chains. The results confirmed the prediction.

Final results for the barriers calculated by Eq. (4) from [1] are presented in Table 2, and the n-dependence of the barriers is shown in Fig. 2. The barriers computed with electronic interaction γ calculated accordingly to Ohno are 1.4–1.8 times greater than those with γ's due to Mataga-Nishimoto. The latter correspond to a weaker interaction of the electrons on small distances. A greater electronic interaction should lead to larger barriers although the mutual influence of end-groups has practically not changed.

There is a striking coincidence between the barriers computed in the modified way by the extended Hückel method (boldface in columns 1 and 2 of Table 2) and in the π-electron approximation with γ integrals after Mataga-Nishimoto (columns 4 and 6 of Table 2), particularly those by open shell techniques. Moreover, our values for the barriers for allene are in good agreement with the values $V_3 \cong -2.9\,\text{eV}$ computed by Borden [39] by PPP method with $\beta = -2.9\,\text{eV}$ and γ integrals according to Parr's model of charged spheres. Unfortunately reliable experimental data for cumulene barriers are still not known[4]. In this connection good quantitative agreement between experimental values of the barrier heights and of those calculated by the simple Hückel method [26, 27] seems premature. In fact, from Hückel values of the barrier heights in the units of the integral β [40][5] and from so called experimental values one finds $\beta \approx -1$ eV which is close to its thermochemical value [2]. At the same time it follows from the nature of the cumulene barriers that for β one should expect its spectroscopic value of 2.5–3 eV [2] which corresponds to a more correct account of the electron interaction in the Hückel method.

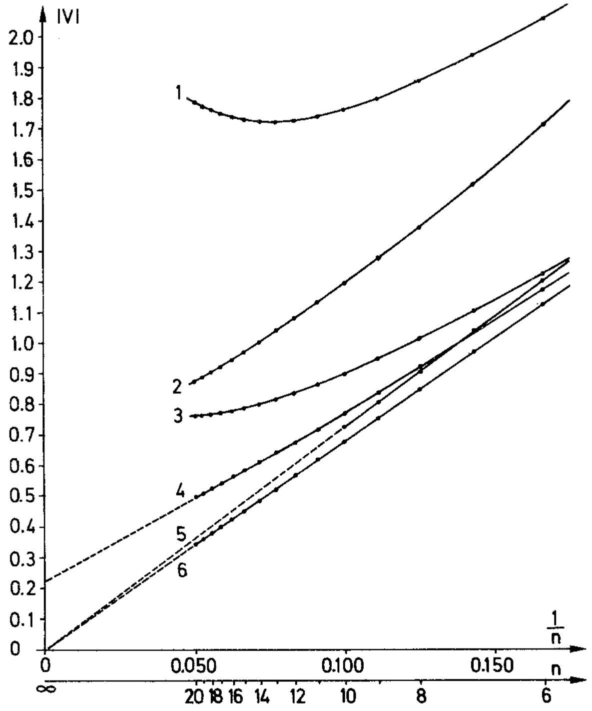

Fig. 2. n^{-1}-Dependence of the cumulenes barrier heights $|V_n|$ computed by different methods. *1–4* SCF method with γ integrals due to Ohno (1, 2) and due to Mataga-Nishimoto (3, 4) in closed (1, 3) and open shell (2,4) approximations, *5* extended Hückel method, *6* simple Hückel method

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[4] See comments of Hoffmann in footnote 37 of his paper [38].

[5] An account for end-effect in the Hückel approximation done by Shustorovich [26] has no influence on our discussion.

When passing from a closed to open shell theory one finds a significant decrease of the barrier heights which are increased with the increasing of the chain length (Fig. 2). On one hand this is explained due to additional possibilities for reminimization of the doublet state energy computed by closed shell theory. On the other hand, and this is more important, the computation of the odd separate chains by the closed shell method leads to an irregular distribution of the electron density on atoms with non-zero atomic charges and with alternation of their signs. The open shell theory always leads to a uniform distribution of the electron density on the atoms. This fact is the main reason for a false effect of the increasing of the barriers with an increasing of n (curve 1 in Fig. 2). This effect appears at shorter chain lengths when the electronic interaction is larger (compare curves 1 and 3 in Fig. 2). In this connection we note that the closed shell theory with γ integrals due to Mataga-Nishimoto leads to lower separate chain energies when compared with the Hückel results. For the odd chains one has the reverse picture when γ integrals due to Ohno are used. In other words the odd chains are better described by Hückel orbitals than by closed shell SCF orbitals. This observation suggests that we should be more careful with the use of the closed shell SCF orbitals for the open shell systems, e.g. radicals.

Fig. 2 definitely shows that the asymptotic value of the barrier height calculated by the open shell theory (curves 2 and 4) differs from zero by the value which can not be assigned to an error in the correlation equation. In fact, when the electron interaction is accounted for accordingly to Mataga-Nishimoto (curve 4) one has the following correlation equation for $n = 8, 9, \ldots, 20$:

$$|V_n| = 0.216(\pm 0.005) + 5.528(\pm 0.057)\frac{1}{n}$$

with $r = 0.994 \pm 0.0003$. It is also obvious that inclusion of longer chains into the correlation should only increase, a bit, the value V_∞.

A non-zero barrier height $V_\infty \approx 0.2$ eV requires a careful consideration, especially, as the cumulenes considered have all CC bond lengths as well as the corresponding resonance integrals equal.

For any value n the barrier height is a difference between the energies of two odd separate chains and of two even ones, and the energy of the later are lower. The barrier height asymptotically approaches zero if one uses a single-configuration approximation with Hückel orbitals as the basis. The use of the SCF orbitals as the basis in the same approximation leads to higher values of the barrier heights as well as to the non-zero barrier height for an infinitely long chain. The reason is that the field described by the Hückel Hamiltonian with all equal bond lengths is closer to the SCF Hamiltonian for odd chains rather than for even ones. One may reach this conclusion in the following way. Let us calculate for all n the value

$$\delta P = \frac{1}{n-1}\sum \left|P^{T,\mathrm{SCF}}_{\mu,\mu+1} - P^{T,\mathrm{Hückel}}_{\mu,\mu+1}\right|,$$

where the summation is carried over all $(n-1)$ bonds forming the chain, and $P^T_{\mu\nu}$ is the bond order of the bond $\mu\nu$. The value δP characterizes an average difference between the bond orders in the cumulene chains computed on SCF orbitals and on Hückel ones. Our calculations show that the value δP alternates depending on whether n is even or odd, and δP is always lower for an odd n. In other words the use of SCF orbitals leads to a considerably larger lowering of the energy for the even chains than for the odd ones. In the Hückel approximation one has a larger error for the even chains, from which the stable conformation is made, than for the odd chains. This error does not disappear with an increase in the cumulene chain length and leads to the non-zero barrier height for an infinitely long chain.

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