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# Torsion Barriers of End-Groups in Cumulenes

## I. General Consideration

Yuri A. Kruglyak
Quantum Chemistry Group, Division of Theory of Chemical Structure and Reactivity, L.V. Pisarzhevsky Institute of Physical Chemistry, Academy of Sciences of the Ukraine, Kiev, U.S.S.R.

G. G. Dyadyusha
Division of Colour and Structure of Organic Molecules, Institute of Organic Chemistry, Academy of Sciences of the Ukraine, Kiev, U.S.S.R.

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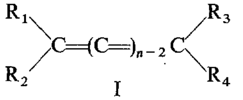
The theory of $\pi$-electronic structure is presented for molecules of organic cumulenes $C_nH_4$ which have two perpendicular subsystems of $\pi$-AO. Elementary considerations from simple MO theory show stability of planar $D_{2h}$ conformations for cumulenes with an even number of carbon atoms and of turned $D_{2d}$ conformations — with odd number of carbon atoms. The lowest electronic configuration of a cumulene molecule in its unstable conformation has a multiplet structure with states ${}^3A_2$, ${}^1B_1$, ${}^1A_1$, and ${}^1B_2$ for even cumulenes with symmetry $D_{2d}$ and states ${}^3A_u$, ${}^1A_u$, ${}^1A_g$, and ${}^1A'_g$ for odd cumulenes with symmetry $D_{2h}$. When electronic interaction is taken into account, the lowest states are ${}^3A_2$, ${}^1B_1$, resp. ${}^3A_u$, ${}^1A_u$. In approximations of zero differential overlap and equivalence of inner and outer $\pi$-AO energy of cumulene molecule in the states with closed shell ${}^1A_1$, ${}^1A_g$ and with open shell ${}^1B_1$, ${}^1A_u$ is possible to divide on energies of subsystems and their electronic interaction energy. The later does not depend on MO coefficients. Useful formulae are given for calculation of torsion barriers of end-groups in cumulenes. In this paper barriers are considered in two extreme approximations — with localized and Hückel orbitals. With the first ones barriers do not depend on chain length and are equal to ethylene barrier. When Hückel orbitals are used, barriers are inversely proportional to chain length and approach zero with increasing $n$. The true state of electrons in chains is some-where between these two extreme cases.

Die $\pi$-Elektronenstruktur für Cumulene des Typs $C_nH_4$ mit zwei aufeinander senkrecht stehenden $\pi$-Elektronensystemen wird berechnet. Die einfache MO-Theorie ergibt, daß gradzahlige C-Ketten im energieärmsten Zustand planare Struktur ($D_{2h}$) und ungradzahlige eine Struktur mit verdrehten H-Atomen besitzen. Die Multiplettstruktur in den um 90° verdrehten Konformationen sind bei der gradzahligen Kette (jetzt $D_{2d}$) ${}^3A_2$, ${}^1B_1$, ${}^1A_1$ und ${}^1B_2$ und bei der ungradzahligen ($D_{2h}$) ${}^3A_u$, ${}^1A_u$, ${}^1A_g$ und ${}^1A'_g$, wobei die ersten beiden Terme jeweils tiefer als die letzten beiden liegen. Macht man die Voraussetzung, daß zero differential overlap gilt und die Randzustände äquivalent den inneren Zuständen sind, läßt sich die Energie bei Singulett-Zuständen in diejenige der Untersysteme und eine Wechselwirkungsenergie zerlegen, wobei letztere nicht mehr von den MO-Koeffizienten abhängt. Formeln zur Berechnung der Rotationsbarrieren werden für zwei Grenzfälle angegeben: lokalisierte und Hückelorbitale. Bei ersterer hängt die Schwelle nicht von der Kettenlänge ab und ist gleich der beim Äthylen, bei letzterer ist sie umgekehrt proportional zur Zahl der C-Atome.

Les états singulets les plus bas des cumulènes organiques $C_nH_4$ en conformation plane $D_{2h}$ ou tournée $D_{2d}$ sonst étudiés en tenant compte de l'interaction électronique. Seule l'interaction de configuration entre états dégénérés est considérée. Dans l'approximation du recouvrement différentiel nul et de l'équivalence de toutes les orbitals $p$ du carbone les énergies de ces états (${}^1A_1$ ou ${}^1A_u$ pour $n$ pair et ${}^1B_1$ ou ${}^1A_g$ pour $n$ impair) sont séparables en somme des énergies de deux systèmes $\pi$ isolés et de leur énergie d'interaction qui ne dépend pas des orbitales moléculaires occupées. On est ainsi conduit à des expressions commodes pour l'évaluation des barières de rotation interne dans les cumulènes. En utilisant des orbitales moléculaires localisées on obtient des barrières constantes, égales à la barrières de l'éthylène, pour tous les cumulènes. Avec des orbitales de Hückel les barrières sont inversement proportionnelles à la longueur de la chaîne et tendent à s'annuler lorsque cette longueur augmente indéfiniment. La réalité est sans doute entre ces deux çase extrêmes.

Cumulene molecules have the general formula I and contain a linear chain of $n$ carbon atoms. The inner $n-2$ atoms are characterized by diagonal hybridization $sp$ and are in valence state didi$\pi_x\pi_y$. Hybridization of end-C-atoms should be close to trigonal $sp^2$, and these atoms can be in valence states $tr\,tr\,tr\pi_x$ or $tr\,tr\,tr\pi_y$. Even cumulenes (EC) are known to be planar[1] (symmetry $D_{2h}$ in case of equal $R_i$). In odd cumulenes (OC) the two end-groups are perpendicular to one another (symmetry $D_{2d}$ in case of equal $R_i$). Both facts are in accordance with VB-theory.



$R_1R_2C{=}(C{=})_{n-2}CR_3R_4$

I

The ease of cis-trans isomerization for the EC's or of stereoisomerization for the OC's is determined first of all by the barrier height of internal rotation of the $CH_2$ group in unsubstituted cumulenes, for substituents of different end-groups are moved away from each other in space and the influence of their interaction on the activation energy of the isomerization reaction should be small, particularly for large $n$.

Rotation of one of the $CH_2$ groups by 180° returns the cumulene molecule to its initial state. It is a natural suggestion that the barrier height is determined by the energy of such a molecular conformation in which one of the $CH_2$ groups is turned by 90° in comparision with the most stable conformation. In the following under "barrier height" we shall always imply the difference between energies of the lowest *singlet* states of the molecular conformations with symmetry $D_{2h}$ and $D_{2d}$. The reason for the choice of both singlet states will be made clear later.

The barriers $V$ in cumulenes were considered theoretically in the papers [3—7]. Dunitz and Orgel [4], Fischer [3], Shustorovich [5], and Popov [6] used a simple Hückel method which leads to the conclusion that with an increase of the number of C atoms the barrier tends to zero:

$$\lim_{n\to\infty} V_n = 0\,. \tag{1}$$

Popov [6] has shown analytically that within the frame of the Hückel method the result $V_\infty \neq 0$ is obtained if alternation of Coulomb integrals is introduced. Hoffmann [7] studied cumulenes by the extended Hückel method [8]. He also gave asymptotics (1), but the change of $V$ with $n$ was found to be alternating: $V_2 > |V_3| < V_4 > |V_5| < V_6 > \cdots$. In the Hückel approximation we have a smooth dependence of $V_n$ upon $n$. Borden [9] calculated the ground and excited states of allene $C_3H_4$ by the Pariser-Parr-Pople (PPP) method [10, 11] and the configuration interaction method.

In the present and following communications we develop quite generally (at least enough for our purposes) the theory of the electronic structure of organic cumulenes. We discuss in detail its application for calculation of barrier and give the results for $2 \leqq n \leqq 20$ performed by the restricted Hartree-Fock method in a

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[1] Properties of cumulenes are discussed in reviews [1—3].

semi-empirical approximation of the closed and open shell theory. Equations of the later theory used by us are given in the next paper[2].

$\sigma$-Bonds of cumulene chains have cylindrical symmetry and their energy does not depend upon the angle of rotation of the end-groups. Therefore if direct interaction of the substituents is neglected the barrier height is determined by the energy change of the $\pi$-electrons with the change of the molecular conformation.

Cumulenes $C_nH_4$ have $2n-2$ $\pi$-electrons. In accordance with the simple MO theory $2n-2$ cumulene levels can contain either $n-1$ bonding levels and equally many antibonding levels or $n-2$ bonding and equally many antibonding levels plus 2 nonbonding levels. In the former $2n-2$ $\pi$-electrons occupy all $n-1$ bonding levels; in the latter — all $n-2$ bonding levels and the 2 remaining electrons occupy the two-fold degenerate nonbonding level. The first distribution is energetically more favorable than the second one. This is achieved for even $n$ for planar conformations and for odd $n$ for twisted conformation. This may be considered as a simple explanation of the known experimental fact [13—16] that the stable conformation of the EC's is planar, but that of the OC's is twisted with perpendicular arrangement of planes of the end-groups. This very interesting propertyof the cumulenes was first explaned by van't Hoff [17] using the tetrahedral model of the carbon atom.

Let us choose the coordinate system in a way so that in the conformation $D_{2h}$ $\pi$-AO's of the subsystems with $n$ AO's are directed along $x$-axis and with $n-2$ AO's — along $y$-axis. The $z$-axis passes through the C atoms. Conformation $D_{2d}$ is formed by a rotation of one of the end-AO's by 90°. In this case the number of AO's which are directed along the $x$- and $y$-axis equals $n-1$ in both cases.

In the conformation $D_{2h}$ $\pi_x$-states have symmetry $b_{2g}$ and $b_{3u}$, and $\pi_y$-states — $b_{2u}$ and $b_{3g}$. In the conformation $D_{2d}$ all $\pi$-MO transform according to the irreducible representation $e$. Therefore in this conformation the frontier MO (pair of nonbonding orbitals) is degenerated by symmetry. Accidental degeneration of the frontier MO's in the conformation $D_{2h}$ remains in the PPP method also, for in this case zero differential overlap approximation is used. It is removed by alternation of bond lengths.

The lowest electronic configuration of the cumulene molecule in its unstable conformation has a multiplet structure with states $^3A_2$, $^1B_1$, $^1A_1$, and $^1B_2$ for EC and $^3A_u$, $^1A_u$, $^1A_g$, and $^1A'_g$ for OC. We shall see later that when electronic interaction is accounted for the lowest states are $^3A_2$, $^1B_1$, resp. $^3A_u$, $^1A_u$. The states $^1A_1$, $^1B_2$, resp. $^1A_g$, $^1A'_g$ correspond to electron transfer between the perpendicular $x$- and $y$-subsystems of $\pi$-AO. The molecule in its stable conformation, which is $^1A_g$ for EC and $^1A_1$ for OC, has a closed shell. The degeneration of the frontier $\pi$-MO's is removed for inorganic cumulenes with alternating atoms of different electronegativity. To a smaller degree the same is true if the difference in the hybridization between the parameters of inner and outer C atoms is taken into account. But even in this case the lowest singlet state may be $^1A_u$ if the orbital energy splitting does not exceed the splitting of even and odd states.

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[2] It contains also all basic numerical results as well as discussions of the following: asymptotic behaviour of the barrier, origin of non-zero barrier height found by us for infinite cumulene chain with all $C=C$ bond lengths assumed equal, contradictions between simple and extended Hückel methods in the prediction of barrier behaviour with increasing chain length. Some results of the present investigations are also briefly discussed in [12].

In the following we shall neglect the difference in hybridization between outer and inner C atoms. This approximation is sufficiently good because the integrals for $sp^2$ and $sp$ states are almost equal [18].

Let us the $x$- and $y$-MO's in the conformation $D_{2h}$ write down as a linear combination of the $\pi$-AO's $x_\nu$ and $y_\nu$[3]:

$$\varphi_i = \sum_\nu C_{\nu i} x_\nu , \qquad \varphi'_i = \sum_\nu C'_{\nu i} y_\nu .$$

The summation is extended over all AO's of the chain. In the same manner it is possible to set up the components of the degenerate pairs of the MO's in the conformation $D_{2d}$.

Let $a_i^+$ be the creation operator for an electron $i$ of orbital state $\varphi_i$ and spin state $\alpha$, and $\bar{a}_i^+$ be the same for spin state $\beta$. Degenerate orbital pairs of open shell will be denoted by the symbols $k$ and $k'$, and orbitals of closed shell by $j$ and $j'$. Then wave functions of states with closed shell $\Psi^c$ may be written as

$$\Psi^c({}^1A_1, {}^1A_g) \equiv \Psi^c ,$$

$$\Psi^c = \prod_j \bar{a}_j^+ a_j^+ \prod_{j'} \bar{a}_{j'}^+ a_{j'}^+ |0\rangle ,$$

where $|0\rangle$ is the vacuum state.

Wave functions of states with open shell $\Psi^o$ will be written as follows:

$$\Psi^o({}^3A_2, {}^3A_u) = \frac{1}{\sqrt{2}} (\bar{a}_{k'}^+ a_k^+ + a_{k'}^+ \bar{a}_k^+) \Psi^c ,$$

$$\Psi^o({}^1B_1, {}^1A_u) = \frac{1}{\sqrt{2}} (\bar{a}_{k'}^+ a_k^+ - a_{k'}^+ \bar{a}_k^+) \Psi^c ,$$

$$\Psi^o({}^1B_2, {}^1A_g) = \frac{1}{\sqrt{2}} (\bar{a}_k^+ a_k^+ - \bar{a}_{k'}^+ a_{k'}^+) \Psi^c ,$$

$$\Psi^o({}^1A_1, {}^1A'_g) = \frac{1}{\sqrt{2}} (\bar{a}_k^+ a_k^+ + \bar{a}_{k'}^+ a_{k'}^+) \Psi^c .$$

For these states the $z$-component of the total spin $M_S$ is 0. Two other components of the triplet state ${}^3A_2$ or ${}^3A_u$ with $M_S = \pm 1$ are described by the functions

$$a_{k'}^+ a_k^+ \Psi^c \quad \text{and} \quad \bar{a}_{k'}^+ \bar{a}_k^+ \Psi^c .$$

Let us introduce the usual notations:

$$H_k = \int \bar{\varphi}_k^* H^{\text{core}} \bar{\varphi}_k \, d\tau ,$$

$$J_{ij} = \int \varphi_i^* \bar{\varphi}_j^* \frac{1}{r_{12}} \varphi_i \bar{\varphi}_j \, d\tau_1 \, d\tau_2 ,$$

$$K_{ij} = \int \bar{\varphi}_i^* \varphi_j^* \frac{1}{r_{12}} \varphi_i \bar{\varphi}_j \, d\tau_1 \, d\tau_2 .$$

Then the energy of states with closed shell will be:

$$E^c({}^1A_1, {}^1A_g) = 2 \sum_j H_j + 2 \sum_{j'} H_{j'} + \sum_{j_1 j_2} (2J_{j_1 j_2} - K_{j_1 j_2}) + \sum_{j_1 j'_2} (4J_{j_1 j'_2} - 2K_{j_1 j'_2}) + \sum_{j'_1 j'_2} (2J_{j'_1 j'_2} - K_{j'_1 j'_2}) + E^{\text{core}} ,$$

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[3] The chain of AO's $y_\nu$ will be denoted by primed symbols.

where $E^{\text{core}}$ is the core total energy. If we denote

$$E_1 = E^c + H_k + H_{k'} + \sum_j (2J_{jk} - K_{jk} + 2J_{jk'} - K_{jk'}) + \sum_{j'} (2J_{j'k} - K_{j'k} + 2J_{j'k'} - K_{j'k'}),$$

where $E^c$ means an expression which has the same structure as $E^c({}^1A_1, {}^1A_g)$ above, the sums being taken over the closed shells only, the energy of the states with open shell are:

$$\begin{aligned} E^o({}^3A_2, {}^3A_u) &= E_1 + J_{kk'} - K_{kk'}, \\ E^o({}^1B_1, {}^1A_u) &= E_1 + J_{kk'} + K_{kk'}, \\ E^o({}^1B_2, {}^1A_g) &= E_1 + \frac{1}{2}(J_{kk} + J_{k'k'}) - K_{kk'}, \\ E^o({}^1A_1, {}^1A_g') &= E_1 + \frac{1}{2}(J_{kk} + J_{k'k'}) + K_{kk'}. \end{aligned}$$

Usually

$$J_{ij} < \frac{1}{2}(J_{ii} + J_{jj})$$

holds. This means that among the lower singlet states the lowest are ${}^1B_1$ and ${}^1A_u$.

Reducing the MO's to AO's the integrals over the AO's

$$(\varkappa\lambda \mid \mu\nu') = \int x_\varkappa^*(1)\, x_\mu^*(2) \frac{1}{r_{12}} x_\lambda(1)\, y_\nu(2)\, d\tau_1\, d\tau_2$$

will have to be calculated. Zero differential overlap

$$(\varkappa\lambda \mid \mu\nu) = \delta_{\varkappa\lambda}\delta_{\mu\nu}(\varkappa\varkappa \mid \mu\mu) = \delta_{\varkappa\lambda}\delta_{\mu\nu}\gamma_{\varkappa\mu}$$

will be used in this context.

Core integrals $H_{\mu\nu}$ with $\mu \neq \nu$ will be accounted for only in case of neighbouring atoms and renamed $\beta_{\mu\nu}$ ($\beta_{\mu\mu} \equiv 0$). Integrals between AO's $\pi_x$ and $\pi_y$ $H_{\mu\nu'}$ are zero for symmetry reasons. Integrals $H_{\mu\mu}$ will be calculated in the Goeppert-Mayer and Sklar approximation [19], neglecting penetration integrals

$$\begin{aligned} H_{\mu\mu} &= -I_\mu - \sum_\nu \gamma_{\mu\nu} - \sum_{\nu'} \gamma_{\mu\nu'} + \gamma_{\mu\mu}, \\ H_{\mu'\mu'} &= -I_\mu - \sum_\nu \gamma_{\mu'\nu} - \sum_{\nu'} \gamma_{\mu'\nu'} + \gamma_{\mu\mu}. \end{aligned}$$

Here $I_\mu$ is ionization potential of $\pi$-electron in the corresponding valence state and in the outer field of neighbouring neutral atoms. It is obvious that $I_{\mu'} = I_\mu$ as well as $\gamma_{\mu'\mu'} = \gamma_{\mu\mu}$. The summation runs over all AO $\pi_x$ resp. $\pi_y$.

Let us introduce the following notations for density matrix elements in AO representation:

$$P_{\mu\nu}^c = \sum_j C_{\mu j} C_{\nu j}, \quad P_{\mu\nu}^o = C_{\mu k} C_{\nu k}, \quad P_{\mu\nu}^T = 2P_{\mu\nu}^c + P_{\mu\nu}^o,$$

and analogous expressions for the primed symbols. For the states with closed shell $P_{\mu\nu}^o$ is equal to zero.

Using these notations and under the assumption of the approximations mentioned above we obtain

$$\begin{aligned} \sum_j J_{jk} &= \sum_{\mu\nu} P_{\mu\mu}^c P_{\nu\nu}^o \gamma_{\mu\nu}, \\ \sum_j K_{jk} &= \sum_{\mu\nu} P_{\mu\nu}^c P_{\mu\nu}^o \gamma_{\mu\nu}, \\ J_{kk'} &= \sum_{\mu'\nu} P_{\nu\nu}^o P_{\mu\mu}^{o'} \gamma_{\mu'\nu}. \end{aligned}$$

In the zero differential overlap approximation all exchange integrals of the type $K_{ij'}$ are zero. When the necessary substitutions are done we get the following expressions for the energy of states with closed shell:

$$\begin{aligned} E^c({}^1A_1, {}^1A_g) = {} & \sum_{\nu} (\gamma_{\nu\nu} - I_{\nu})\, P^T_{\nu\nu} + \sum_{\nu'} (\gamma_{\nu'\nu'} - I_{\nu'})\, P^{T'}_{\nu\nu} \\ & + \sum_{\mu\nu} \left\{ \left[ \frac{1}{2} P^T_{\nu\nu} P^T_{\mu\mu} - P^T_{\nu\nu} - \frac{1}{4} (P^T_{\mu\nu})^2 \right] \gamma_{\mu\nu} + P^T_{\mu\nu} \beta_{\mu\nu} \right\} \\ & + \sum_{\mu'\nu'} \left\{ \left[ \frac{1}{2} P^{T'}_{\nu\nu} P^{T'}_{\mu\mu} - P^{T'}_{\nu\nu} - \frac{1}{4} (P^{T'}_{\mu\nu})^2 \right] \gamma_{\mu'\nu'} + P^{T'}_{\mu\nu} \beta_{\mu'\nu'} \right\} \\ & + \sum_{\mu\nu'} (P^{T'}_{\nu\nu} P^T_{\mu\mu} - P^{T'}_{\nu\nu} - P^T_{\mu\mu})\, \gamma_{\mu\nu'} \,. \end{aligned}$$

Further simplifications will follow if we take into account that for alternant hydrocarbons it holds that $P^T_{\nu\nu} = P^{T'}_{\nu\nu} = 1$ [20]. This is also true for the SCF method in the PPP approximation, which is assumed, if the ionization potentials and integrals are put equal for all atoms C [11, 24] including the end atoms:

$$I_{\nu} \equiv I_{\nu'} \equiv I \,, \qquad \gamma_{\nu\nu} \equiv \gamma_{\nu'\nu'} \equiv \gamma \,.$$

This assumption seems to be not far from the truth for organic cumulenes.

If the alternant properties of cumulenes are taken into acount then the energy of the states with closed shell can be divided up as follows:

$$E^c({}^1A_1, {}^1A_g) = E^c_x + E^c_y + E_{\text{int}} + E^{\text{core}} \,,$$

where

$$E^c_x = \sum_{\nu} (\gamma_{\nu\nu} - I_{\nu}) + \sum_{\mu\nu} \left[ P^T_{\mu\nu} \beta_{\mu\nu} - \frac{1}{2} \gamma_{\mu\nu} - \left( \frac{1}{2} P^T_{\mu\nu} \right)^2 \gamma_{\mu\nu} \right], \tag{2a}$$

$$E^c_y = \sum_{\nu'} (\gamma_{\nu'\nu'} - I_{\nu'}) + \sum_{\mu'\nu'} \left[ P^{T'}_{\mu\nu} \beta_{\mu'\nu'} - \frac{1}{2} \gamma_{\mu'\nu'} - \left( \frac{1}{2} P^{T'}_{\mu\nu} \right)^2 \gamma_{\mu'\nu'} \right], \tag{2b}$$

$$E_{\text{int}} = - \sum_{\mu\nu'} \gamma_{\mu\nu'} \,.$$

The energy $E^c_x$ represents the $\pi$-electron energy of a hypothetical compound with the same space structure as the corresponding cumulene with closed shell but having only one system of AO of type $\pi_x$. The same is true for the energy $E^c_y$. $E_{\text{int}}$ represents the energy of the static electron interaction of the two chains and does not depend upon the MO coefficients.

Analogous transformations for the states with open shell ${}^1B_1$ and ${}^1A_u$ lead to the following result:

$$E^o({}^1B_1, {}^1A_u) = E^o_x + E^o_y + E_{\text{int}} + E^{\text{core}} \,,$$

where

$$E^o_x = \sum_{\nu} (\gamma_{\nu\nu} - I_{\nu}) + \sum_{\mu\nu} \left[ P^T_{\mu\nu} \beta_{\mu\nu} - \frac{1}{2} \gamma_{\mu\nu} - \left( \frac{1}{2} P^T_{\mu\nu} \right)^2 \gamma_{\mu\nu} - \left( \frac{1}{2} P^o_{\mu\nu} \right)^2 \gamma_{\mu\nu} \right], \tag{3a}$$

$$E^o_y = \sum_{\nu'} (\gamma_{\nu'\nu'} - I_{\nu'}) + \sum_{\mu'\nu'} \left[ P^{T'}_{\mu\nu} \beta_{\mu'\nu'} - \frac{1}{2} \gamma_{\mu'\nu'} - \left( \frac{1}{2} P^{T'}_{\mu\nu} \right)^2 \gamma_{\mu'\nu'} - \left( \frac{1}{2} P^{o'}_{\mu\nu} \right)^2 \gamma_{\mu'\nu'} \right]. \tag{3b}$$

As we see, division into two chains is possible also in this case, but now each chain is in a doublet state and has an open shell structure as in organic free radicals. The theory of the states with open shell will be given in the next paper.

However, for the open shell states ${}^1A_1$, ${}^1B_2$, ${}^1A_g$, and ${}^1A'_g$ division of the $\pi$-electron system in two subsystems is not possible inspite of the fact that rule $P^T_{\nu\nu} = P^{T'}_{\nu\nu}$ is satisfied.

The energy $E_{\text{int}}$ is not the same for different cumulene conformations. A simple calculation yields

$$E_{\text{int}}(D_{2d}) - E_{\text{int}}(D_{2h}) = -\gamma_{\alpha\omega'}$$

where $\alpha$ and $\omega$ are the indices of the end-atoms.

Let us note one incorrectness of the Goeppert-Mayer and Sklar approximation [19] when one calculates the interaction energy of positive core charges $E_D$. In fact, if we try to find $E_D$ in this approximation by the method of Dewar and Gleicher [22]:

$$E_D = \sum_{\mu<\nu}{}' \gamma_{\mu\nu}$$

where the summation is taken over all AO's of the two chains, one gets different interaction energies for different conformations:

$$E_D(D_{2d}) - E_D(D_{2h}) = \gamma_{\alpha\omega'} - \gamma_{\alpha\omega}\,.$$

However on physical grounds the interaction energies of positive charges in different core conformations of cumulenes can not be different. These differences are small, of course, and decrease rapidly with increasing chain length.

If one accepts the differences mentioned then the barrier heights $V$ may be found from the relation:

$$V = E_x(D_{2d}) + E_y(D_{2d}) - E_x(D_{2h}) - E_y(D_{2h}) - \gamma_{\alpha\omega}\,. \tag{4}$$

The last term will then result from compensations of changes of $E_{\text{int}}$ and $E^{\text{core}}$.

If, on the other hand, one takes the same core energies $E^{\text{core}}$ for both conformations then

$$V = E_x(D_{2d}) + E_y(D_{2d}) - E_x(D_{2h}) - E_y(D_{2h}) - \gamma_{\alpha\omega'}\,. \tag{5}$$

Values of $V$ by (4) and (5) are almost identical especially for large $n$.

As we see from Eq. (4) and (5) the barrier height is determined first of all by energies of the $\pi$-electrons subsystems which may be calculated from formulae (2a, b) and (3a, b). The results of computations of the barriers based on SCF theory will be given in the next communication.

In concluding this paper we restrict ourselves by the estimation of barriers in the case of two limiting assumptions about the density matrices. Let consider for the first the assumption of isolated bonds when the MO's of a chain with $m$ atoms have following coefficients:

$$C_{2\mu-1,j} = \sqrt{\frac{\delta_{\mu j} + \delta_{\mu,m+1-j}}{2}}\,,$$

$$C_{2\mu,j} = \frac{1}{\sqrt{2}}\,(\delta_{\mu j} - \delta_{\mu,m+1-j})\,.$$

The orbitals with the lowest $j$ are filled first. In this approximation all elements of density matrices $P^T$ and $P^o$ are equal zero except

$$P^T_{\mu\mu} \equiv 1\,, \qquad P^T_{\mu,2\mu-1} \equiv 1$$

and for odd $m$

$$P^o_{\frac{m+1}{2},\frac{m+1}{2}} \equiv 1$$

holds.

Let put the exchange integral $\beta = -3.569$ eV. This value follows from exponential dependence of $\beta$ upon $R$ [23] for $R = 1.31$ Å [13, 14, 24]. Two-center integrals $\gamma_{\mu\nu}$ are calculated by the formulae due to Mataga-Nishimoto [25, 26] or Ohno [27]. One-center integrals $\gamma_{\mu\mu}$ are estimated by Pariser's suggestion [28] from the ionization potential and the electron affinity of the C atom in the valence state $sp$ from Hinze and Jaffé [18]. Detailed information about parameters used will be given in the next paper.

Let all $\beta_{\mu,\mu+1}$ and $\gamma_{\mu,\mu+1}$ being equal. One gets

$$\sum_{\mu=1}^{m-1} P^T_{\mu,\mu+1} = \text{entier}\,(m/2)\,, \qquad \sum_{\mu=1}^{m} (P^o_{\mu\mu})^2 = 1\,,$$
$$\sum_{\mu=1}^{m-1} (P^T_{\mu,\mu+1})^2 = \text{entier}\,(m/2)\,,$$

where entier $(E)$ is the greatest integer which is smaller than $E$[4].

Finally, we find that with the approximations discussed the barrier heights which are determined by formula (4) are the same for all cumulenes and are equal to

$$V^{\text{loc}} = -2\beta_{\mu,\mu+1} + \frac{1}{2}\gamma_{\mu,\mu+1} - \frac{1}{2}\gamma_{\mu\mu}\,.$$

With the values of the parameters as mentioned above $V^{\text{loc}} = 4.353$ eV resp. $V^{\text{loc}} = 5.497$ eV depending on which $\gamma_{\mu\nu}$ integrals are used — Mataga-Nishimoto or Ohno.

This approximation, naturally, is merely a quantitative expression of the primitive calculation of the effective $\pi$-bonds number in a given cumulene conformation mentioned at the beginning. The number of atoms on which the electrons are localized in the unstable conformation is not important at all. It is evident that the energy necessary for breaking one effective $\pi$-bond is equal to the barrier height in ethylene the MO coefficients of which are completely determined by symmetry conditions. In fact, when values of $E_{x(y)}$ calculated from the ethylene density matrix are putted to formula (4) one gets the above given numerical values of $V^{\text{loc}}$.

On the other hand it is of interest to consider the case of Hückel orbitals for a chain with all bond lengths equal. These orbitals are expressed analytically as:

$$C_{\mu j} = \sqrt{\frac{2}{m+1}}\,\sin\frac{\mu j\pi}{m+1}\,.$$

Let us take into account the integrals $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ only for neighbouring atoms and use following relations:

$$\sum_{\mu=1}^{m-1} P^T_{\mu,\mu+1} \equiv Q_m = \begin{cases} \operatorname{cosec}\dfrac{\pi}{2m+2} - 1 & m \text{ even} \\[2ex] \operatorname{ctg}\dfrac{\pi}{2m+2} - 1 & m \text{ odd} \end{cases}$$

$$\sum_{\mu=1}^{m-1} (P^T_{\mu,\mu+1})^2 = \frac{Q_m^2}{m+1} + \begin{cases} m/(m+1) & m \text{ even} \\ (m-1)/m & m \text{ odd} \end{cases}$$

$$\sum_{\mu=1}^{m} (P^o_{\mu\mu})^2 = \frac{2}{m+1} \qquad m \text{ odd}$$

$$\sum_{\mu=1}^{m-1} (P^o_{\mu,\mu+1})^2 = 0\,.$$

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[4] Function entier $(E)$ is taken from syntax of algorithmic language Algol 60 [29].

It is possible then to show analytically that barriers calculated by formula (4) tend asymptotically to zero with increasing $n$ in accord with simple [3—6] and extended [7] Hückel methods. Their numerical values and even their signs depend upon the choice of parameters. With a reasonable choice the barrier heights are negative for OC and positive for EC. With the parameters indicated above we calculated the barriers of the cumulenes for $2 \leqq n \leqq 20$ on Hückel orbitals, taking account of all integrals $\gamma_{\mu\nu}$. Computations were performed on a Soviet computer M-20 of the Institute of Cybernetics (Academy of Sciences of the Ukraine, Kiev) by a series of programmes MN, PPP-1, and PPP-2 described in detail and presented in Algol 60 in our book [30]. The self-consistency in programms PPP-1 and PPP-2 were blocked during these computations. Results which will be given together with other numerical material in the next communication show that the absolute values of barriers regularly decrease with increasing $n$ and correlate linearly with $n^{-1}$. For $6 \leqq n \leqq 20$ the following equations and correlation coefficients $r$ are obtained:

$$\gamma_{\mu\nu} \text{ by Mataga-Nishimoto}$$

$$|V_n| = 0.0057\,(\pm 0.0004) + 6.725\,(\pm 0.004)\,\frac{1}{n}\,, \quad r = 0.999998 \pm 0.000001$$

$$\gamma_{\mu\nu} \text{ by Ohno}$$

$$|V_n| = 0.0066\,(\pm 0.0055) + 9.663\,(\pm 0.059)\,\frac{1}{n}\,, \quad r = 0.9998 \pm 0.0001\,.$$

The brackets in these equations contain the derivations. Linear correlation equations show that the barrier computed from non-SCF Hückel orbitals tend to zero when $n \to \infty$.

Because the true state of electrons in chains is somewhere between these two extreme cases [11] one may except that the barrier heights do decrease with increasing cumulene chain but not so rapidly as $n^{-1}$ and possibly tend to a nonzero limit for an infinite chain. The next communication will be devoted to dependence upon length of barriers computed from SCF orbitals.

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Yuri A. Kruglyak
Quantum Chemistry Group
Institute of Physical Chemistry
Academy of Sciences of the Ukraine
Bol'shaya Kitacvskaya Street 97
Kiev-28, U.D.S.S.R.