amples are the one-ring flip for **10** and the two-ring flip for **16**.

An interesting related question is whether a shift to a threshold mechanism with a lower number of flipping rings would be observed by modifying system **2** not by changing X, but by diminishing the size of one of the rotors; e.g., the modification Mes → Ph in **5** will reduce the energy of the transition state for the nonflip process of the phenyl ring. Preliminary results showed, however, that such a change can lead to a different type of rotational mechanism. In a 2,2-dimesityl-1-(3′,5′-disubstituted-aryl)ethenol the result is a noncorrelated rotation of the less bulky α-aryl ring.[33]

Comparison of the Threshold Mechanisms of 16 and Trimesitylmethane. It is interesting to compare the rotational barriers for trimesitylmethane (**17**)[34] and its vinyl analogue **16**. The threshold mechanism for both compounds is the two-ring flip but the barrier for **17** (21.9 kcal mol^{-1} at 167 °C)[34] is 5.1 kcal mol^{-1} higher. We attribute the lower barrier of **16** to the different geometries. In the vinyl propeller the three rings are attached to a multiatomic frame and this should reduce the steric interaction between the flipping α and β rings in the [α,β]-two-ring flip compared with that in **17**, where both rings are connected to a single carbon. Another difference is that due to the C_3 point group symmetry of **17** the three two-ring flips involving each of the three mesityl rings are degenerate, while for **16** the three mechanisms are nondegenerate since the three mesityl rings are chemically distinct. Therefore, there is no need to multiply the rate constant derived from the coalescence of the signals of **16** by three, as in the case of **17**.[34]

Experimental Section

The 2D spectra were recorded on a Bruker WP 200 SY pulsed FT spectrometer equipped with an aspect 2000 computer. For the 2D exchange experiments and for the ^{13}C, ^{1}H correlation 64 FID's and 128 FID's (each consisting of 16 scans of 512 data points) were accumulated, respectively. In the case of the 2D exchange experiment the FID was zero filled to 256 W in the F_1 dimension. Typical aquisition parameters were the following: SW_2 170 Hz, SW_1 ±85 Hz (for the 2D exchange) and SW_3 113 Hz, SW_1 ±120 Hz (for the ^{13}C, ^{1}H correlation) a sine bell window function was used.

Trimesitylethylene (16). To a solution of 1,1,2-trimesitylethanol (**15**)[13] (100 mg, 0.25 mmol) in toluene (10 mL) was added p-toluenesulfonic acid (5 mg), and the mixture was refluxed overnight. The solvent was evaporated, and the residue was dissolved in ether. The ethereal solution was washed with aqueous solution of 5% K_2CO_3 (20 mL) and dried ($MgSO_4$), and the solvent was evaporated, giving a residue which after recrystallization from ethanol gave trimesitylethylene (**16**) (70 mg, 73%): mp 136 °C; ^{13}C NMR ($CDCl_3$, room temperature) δ (sp^2 region) 128.50, 129.17, 129.25, 129.60, 129.98, 134.19, 135.22, 135.54, 135.80, 136.06, 136.19, 136.33, 136.83, 136.92, 137.06, 137.14, 137.49, 138.69, 140.71. For the Me region see Table I.[35] Anal. Calcd for $C_{29}H_{34}$: C, 91.04; H, 8.96. Found: C, 91.20; H, 8.82.

Acknowledgment. This work was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to which we are indebted. We are grateful to a referee for very helpful comments.

Registry No. **15**, 94203-60-8; **16**, 94800-90-5.

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[33] Nadler, E. B., unpublished results.

[34] Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *96*, 2165.

[35] For a discussion of the reciprocal Me/H transfer in the cation radical of **16** in the gas phase see: Biali, S. E.; Depke, G.; Rappoport, Z.; Schwarz, H. *J. Am. Chem. Soc.* **1984**, *106*, 496.

Localized Molecular Orbitals of Acyclic Polyenes as a Basis for a New Approach to Resonance Energies

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Received September 20, 1985

π-Localized molecular orbitals have been obtained for a large set of acyclic conjugated polyenes in the HMO approximation. On the basis of these results, a convenient classification of π-bond types of conjugated hydrocarbons is proposed. This bond type classification is subsequently used to obtain a set of π-bond energy reference parameters for the calculation of resonance energies of conjugated hydrocarbons. The parameters resulting from the present method have a direct physical significance, contrary to those obtained by using previously reported methods.

One important concern of theoretical organic chemistry has always been the quantification and interpretation of aromaticity in cyclic conjugated systems, leading to several definitions of the resonance energy (RE) of a molecule.[1] These can be grouped in the following general expression:

$$\mathrm{RE} = E_\pi(\text{conjugated molecule}) - E_\pi(\text{reference structure})$$

The simplest choice for the reference structure of a conjugated system with $n_{\mathrm{C=C}}$ double bonds consists in taking $n_{\mathrm{C=C}}$ isolated carbon–carbon double bonds. Making this choice and using the Hückel method to calculate the π-energies, we obtain the classical Hückel resonance energy[2] (HRE):

$$\mathrm{HRE} = E_\pi(\text{conjugated molecule}) - n_{\mathrm{C=C}}(2\alpha + 2\beta)$$

In what follows we will take β as the energy unit and $\alpha = 0$ as the energy origin, so that

$$\mathrm{HRE} = E_\pi(\text{conjugated molecule}) - 2n_{\mathrm{C=C}}$$

[†] Department of Physical Chemistry.

[1] Salem, L. *The MO Theory of Conjugated Systems*; Benjamin: New York, 1966; Chapter 3.

[2] Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; Wiley: New York, 1961; Chapter 10.

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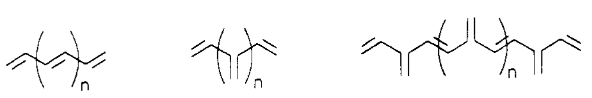

1 2 3

Figure 1. Some structural types of acyclic conjugated polyenes.

This definition has been applied with success to some benzenoid hydrocarbons but leads to frequent disagreements with experience for non-benzenoid systems. For instance, similar values are obtained for the HRE per electron of benzene (0.33) and pentalene (0.31), the latter being a very unstable molecule that does not show the characteristic properties of aromatic systems. Moreover, these results are not improved by using calculation techniques more sophisticated than the Hückel method.

A much better agreement between REs and experimental facts was obtained by Dewar and de Llano[3] by using an acyclic polyene-like reference structure in the framework of Pariser–Parr–Pople (PPP) theory. In this approach, the bonds of acyclic polyenes are classified in a certain number (k) of types and the Dewar resonance energy (DRE) is defined as

$$\mathrm{DRE} = E_\pi(\text{conjugated molecule}) - \sum_i^k n_i E_i \qquad (1)$$

where n_i is the number of bonds of each type and E_i is a parameter that represents some mean energy of the corresponding bond type. Although the success of DREs in correlating with observed stabilities and chemical behavior of cyclic conjugated systems might be attributed to the use of a SCF method to calculate π-energies, as it was originally claimed,[3a] the crucial point has been shown[4-6] to be the definition of an acyclic polyene-like reference structure.

The possibility of evaluation of the parameters E_i in eq 1 relies on the fact that acyclic conjugated polyenes can be successfully included in an energy additivity scheme. Due to the lack of experimental heats of formation for a wide range of acyclic conjugated systems, the energy additivity of these compounds can only be tested by theoretical calculations. The results obtained by Dewar using the PPP method[3,7] have been corroborated by a number of ab initio calculations (STO-3G with partial[8] and complete[9] geometry optimization, 3-21G and 6-31G* with complete optimization[10]). These have been restricted to linear conjugated polyenes up to decapentaene, because of obvious computational limitations, so that an extensive theoretical investigation of energy additivity in a wide range of acyclic polyenes is only possible within the framework of π-SCF or even HMO methods.

The existence of approximately linear relationships between the total π-energy (E_π) and the number of carbon–carbon bonds ($\nu = N - 1$, where N is the number of carbon atoms in the molecule) for acyclic conjugated polyenes is easily shown in the framework of the HMO method. For a linear conjugated polyene of N carbon atoms (L_N) (structure 1 of Figure 1), E_π can be expressed in a closed form[11]

$$E_\pi(L_N) = 2 \csc (\pi/2(N + 1)) - 2$$

and for sufficiently large N,

$$E_\pi(L_N) = (4/\pi)N + 4/\pi - 2 = (4/\pi)\nu + 8/\pi - 2 \qquad (2)$$

Gutman and co-workers[12] have shown that the energy of *any* acyclic conjugated polyene of N atoms (P_N) is related to that of the corresponding linear polyene in an approximate way by eq 3

$$E_\pi(P_N) = E_\pi(L_N) - 0.09T \qquad (3)$$

where T is the number of branching sites in the polyene. In other words, every branch in P_N introduces a negative contribution to E_π of approximately 0.1 (in β units). On the other hand, T can be expressed as a linear function of ν for any given structural type of acyclic polyene: $T = 0$ for linear polyenes, $T = (1/2)(\nu - 3)$ for comb polyenes (structure 2), $T = (1/4)(\nu - 1)$ for polyenes of general structure 3, (see Figure 1) and so on.

Combining eq 2 and 3 and the above observation, we can conclude that for a series of acyclic conjugated polyenes of a given structure, one can write a linear relationship between the number of carbon–carbon bonds and the total π-energy,

$$E_\pi(P_N) = a_p\nu + b_p \qquad (4)$$

where the actual values of the coefficients a_p and b_p in eq 4 depend on the degree and type of branching characterizing the series.

This has the important consequence that the number (k) of bond types in eq 1 cannot be just two (i.e., "single" and "double") if an acyclic polyene-like reference structure valid for cyclic conjugated systems other than simple annulenes is desired, and further bond-type differentiation is necessary to allow for the presence of branching in the reference structure. According to this, Hess and Schaad[4] classified the bonds of acyclic conjugated polyenes into eight different types, five types of carbon–carbon double bonds and three types of carbon–carbon single bonds, depending upon the number of attached hydrogens; the presence of branching is thus implicitly accounted for in their bond-type classification. In this eight-bond parameter scheme, eq 1 takes the explicit form:

$$\begin{aligned}\mathrm{DRE(Hess\text{–}Schaad)} &= E_\pi(\text{conjugated molecule}) - \\ &n_{\mathrm{C-C}}E_{\mathrm{C-C}} + n_{\mathrm{HC-C}}E_{\mathrm{HC-C}} + n_{\mathrm{HC-CH}}E_{\mathrm{HC-CH}} + \\ &n_{\mathrm{C=C}}E_{\mathrm{C=C}} + n_{\mathrm{HC=C}}E_{\mathrm{HC=C}} + n_{\mathrm{H_2C=C}}E_{\mathrm{H_2C=C}} + \\ &n_{\mathrm{HC=CH}}E_{\mathrm{HC=CH}} + n_{\mathrm{H_2C=CH}}E_{\mathrm{H_2C=CH}}\end{aligned}$$

with the following values for the parameters:

$$E_{\mathrm{C\text{-}C}} = 0.4358 \quad E_{\mathrm{HC\text{-}C}} = 0.4362 \quad E_{\mathrm{HC\text{-}CH}} = 0.4660$$
$$E_{\mathrm{C=C}} = 2.1716 \quad E_{\mathrm{HC=C}} = 2.1083 \quad E_{\mathrm{H_2C=C}} = 2.0000$$
$$E_{\mathrm{HC=CH}} = 2.0699 \quad E_{\mathrm{H_2C=CH}} = 2.0000$$

The bond-energy values were obtained by means of a least-squares fit so that the calculated HMO π-energy of a set of 40 acyclic polyenes of several structural types could be reproduced as accurately as possible as a sum of these bond-energy terms. Resonance energies of a wide range of conjugated systems have been calculated with this method;[4,13] the parametrization has been extended in order

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[3] (a) Dewar, M. J. S.; de Llano, C. *J. Am. Chem. Soc.* **1969**, *91*, 789. (b) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; Chapter 5. (c) Dewar, M. J. S.; Harget, A. J.; Trinajstić, N. *J. Am. Chem. Soc.* **1969**, *91*, 6321.

[4] Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 305.

[5] Milun, M.; Sobotka, Z.; Trinajstić, N. *J. Org. Chem.* **1972**, *37*, 139.

[6] Gutman, I.; Milun, M.; Trinajstić, N. *Chem. Phys. Lett.* **1973**, *23*, 284.

[7] Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685, 692.

[8] (a) Haddon, R. C.; Starnes, J. *Adv. Chem. Ser.* **1978**, No. 169, 333. (b) Haddon, R. C. *Pure Appl. Chem.* **1982**, *84*, 1129.

[9] Ichikawa, H.; Ebisawa, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1161.

[10] Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *103*, 7500.

[11] Gutman, I.; Milun, M.; Trinajstić, N. *Croat. Chem. Acta* **1972**, *44*, 207.

[12] Gutman, I.; Ruscić, B.; Trinajstić, N.; Wilcox, C. F., Jr. *J. Chem. Phys.* **1975**, *62*, 3399.

to account for heteroatoms[13] and σ-contributions[14] and the method is now included in textbooks of theoretical chemistry.[15]

It is important to observe, however, that the classification of bond types in acyclic polyenes made by Hess and Schaad is somewhat arbitrary and the bond-energy parameters are devoid of physical significance, as will be shown presently. Due to the existence of two inherent redundancy relations between the numbers of the eigh bond types in any given molecule,[4]

$$n_{HC-C} + 2n_{HC-CH} - n_{HC=C} - 2n_{HC=CH} - n_{H_2C=CH} = 0$$

$$2n_{C-C} + 2n_{HC-C} + 2n_{HC-CH} - 4n_{C=C} - 3n_{HC=C} - 2n_{HC=CH} - 2n_{H_2C=C} - n_{H_2C=CH} = 0$$

it follows that the number of bond energy parameters can be reduced to six. One could, for instance, express $n_{H_2C=CH}$ and $n_{H_2C=C}$ as a function of the remaining bond type numbers and substitute them in the expression of the total π-energy of the acyclic polyene,

$$E_\pi(P_N) = n_{C-C}E_{C-C} + n_{HC-C}E_{HC-C} + n_{HC-CH}E_{HC-CH} + n_{C=C}E_{C=C} + n_{HC=C}E_{HC=C} + n_{HC=CH}E_{HC=CH} + n_{H_2C=C}E_{H_2C=C} + n_{H_2C=CH}E_{H_2C=CH}$$

to obtain the rearranged expression

$$E_\pi(P_N) = n_{C-C}(E_{C-C} + E_{H_2C=C}) + n_{HC-C}(E_{HC-C} + E_{H_2C=CH} + (1/2)E_{H_2C=C}) + n_{HC-CH}(E_{HC-CH} + 2E_{H_2C=CH}) + n_{C=C}(E_{C=C} - 2E_{H_2C=C}) + n_{HC=C}(E_{HC=C} - E_{H_2C=CH} - E_{H_2C=C}) + n_{HC=CH}(E_{HC=CH} - 2E_{H_2C=CH}) = n_{C-C}E_{I} + n_{HC-C}E_{II} + n_{HC-CH}E_{III} + n_{C=C}E_{IV} + n_{HC=C}E_{V} + n_{HC=CH}E_{VI}$$

In this way we have six new parameters ($E_I \cdots E_{VI}$) which, after being evaluated by a least-squares fit to the HMO energies, will give the bond energies $E_{C-C} \cdots E_{H_2C=CH}$. Nevertheless, since in this last step one has a linear system of six equations with eight unknowns, it is necessary to fix arbitrarily the value of two of them in order to determine the remaining six. Hess and Schaad[4] adopted the convention of taking $E_{H_2C=C} = E_{H_2C=CH} = 2.0000$, but any other value would have led to a different (and physically indistinguishable) set of bond energies.

As a consequence of this, no physical significance can be attached to the bond energies used by Hess and Schaad for the acyclic polyene reference structure. For instance, one could expect a close relationship between the parametrized bond energies and the corresponding bond orders, since the total HMO energy is given by

$$E_\pi(P_N) = \sum_{r-s} 2p_{rs} \tag{5}$$

However, Hess and Schaad's parametrization assigns a smaller bond energy for a terminal double bond ($E_{H_2C=CH} = 2.0000$) than for a disubstituted one ($E_{HC=CH} = 2.0699$), while the corresponding bond orders always show the opposite behavior.

In fact, if for a given classification of bond types, the corresponding bond orders were transferable from molecule to molecule, eq 5 would provide an exact parametrization of bond energies. However bond orders are not transferable, even within a series of polyenes of similar structure. For instance, the bond orders of a linear conjugated polyene can be expressed in the form[16]

$$p_{r,r+1} = (1/(N+1)) \times (\csc(\pi/2(N+1)) \pm \csc((2r+1)\pi/2(N+1)))$$

where the signs + and − correspond to odd and even values, respectively, of r (i.e., to "double" and "single" bonds). Assuming that N is sufficientlfy large compared to r, we obtain the approximate expression

$$p_{r,r+1} = (2/\pi)(1 \pm 1/(2r+1)) \tag{6}$$

In addition to showing the alternance of the bond orders of "double" and "single" bonds, this equation shows that the bond order for a given bond type depends on its distance to the end of the chain, being maximal for a terminal double bond. As it can be expected that a physically meaningful parametrization of bond energies bears some relationship with bond orders, the dependence of $p_{r,r+1}$ on r indicates that such a parametrization would require differentiating a large number of bond types (at least when single and double bonds are considered independently). However, the sum of the inverses of the bond orders of two adjacent bonds, as given by eq 6, is a constant.[23]

$$(p_{r,r+1})^{-1} + (p_{r+1,r+2})^{-1} = \pi \tag{7}$$

This suggests that a magnitude related to pairs of consecutive bonds could serve as a basis for an energy parametrization with a small number of bond types.

Localized π-molecular orbitals always extend somewhat over neighbor bonds, so that they should be related not only to the order of the bond upon which they are localized but also to those of the adjacent bonds, which according to eq 7 could explain the transferability of those orbitals. Hence, the corresponding orbital energies could serve as the basis for the physically meaningful parametrization of bond energies we are looking for. Moreover, the tails of a localized molecular orbital (LMO) over the next neighbor bonds could provide the information necessary to distinguish the different surroundings that will characterize each bond type.

Proceeding along these lines, we have undertaken a systematic study of π-LMOs of a wide range of acyclic conjugated polyenes. The results obtained could be interesting not only to obtain a natural classification of bond types in acyclic conjugated polyenes and a subsequent physically meaningful parametrization of reference bond energies but also to analyze the electronic delocalization in those systems. Moreover, we shall see that the use of a parametrization based on π-LMOs does not require the arbitrary assignment of any bond-energy value, a condition which is essential in order that those parameters can have some physical significance.

Procedure

In the present work a π-orbital localization procedure has been applied to the same set of 40 acyclic polyenes originally used by Hess and Schaad for the bond-energy parametrization.[4] In order that our results were compa-

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[13] (a) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1971**, *93*, 2413. (b) *J. Org. Chem.* **1971**, *36*, 3418. (c) Hess, B. A., Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Tetrahedron* **1972**, *28*, 3657, 5299. (d) Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 3907. (e) Hess, B. A.; Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Tetrahedron* **1975**, *31*, 295. (f) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1976**, *41*, 3508. (g) Schaad, L. J.; Hess, B. A., Jr. *Isr. J. Chem.* **1980**, *20*, 281. (h) Hess, B. A., Jr.; Schaad, L. J.; Agranat, I. *J. Am. Chem. Soc.* **1978**, *100*, 5268. (i) Agranat, I.; Hess, B. A., Jr.; Schaad, L. J. *Pure Appl. Chem.* **1980**, *52*, 1399. (j) Hess, B. A., Jr.; Schaad, L. J. *Pure Appl. Chem.* **1980**, *52*, 1471. (k) Bates, R. B.; Hess, B. A., Jr.; Ogle, C. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1981**, *103*, 5052.

[14] Schaad, L. J.; Hess, B. A., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3068.

[15] Cf: (a) Lowe, J. P. *Quantum Chemistry*; Academic Press: New York, 1978. (b) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981.

[16] Cf: Aono, S.; Ohmae, T.; Nishikawa, K. *Bull. Chem. Soc. Jpn.* 1981, *54*, 1645.

rable with theirs, the localization has been effected on canonical molecular orbitals obtained at the Hückel level, so that we have used a localization method recently developed by us[17] which relies only on molecular topology and which has been shown to give results in good accordance with those obtained by using more sophisticated methods. Next follows a brief outline of the procedure.

Let $(\chi_r)_{r=1...N}$ be the set of $2p_\pi$ atomic orbitals (AO) centered on the N carbon atoms of a conjugated polyene and let ϕ_i be a MO built as a real linear combination of these AOs:

$$\phi_i = \sum_r^N \chi_r C_{ri} = \mathbf{X}\mathbf{C}_i \qquad i = 1, ..., N$$

In the Hückel formalism, the M occupied canonical MOs (CMOs) are the M eigenvectors of the adjacency matrix **T** with lowest eigenvalues:

$$\mathbf{TC} = \mathbf{CE} \tag{8}$$

where **C** is an $N \times M$ matrix whose columns are the $\mathbf{C}_i$ vectors and **E** is a diagonal $M \times M$ matrix whose diagonal elements are the CMOs energies. An orthogonal transformation **O** of the occupied CMOs gives a new set of MOs $\mathbf{C}' = \mathbf{CO}$ which, in general, are no longer eigenvectors of **T**:

$$\mathbf{TC}' = \mathbf{C}'\mathbf{E}' \tag{9}$$

where $\mathbf{E}' = \mathbf{O}^t\mathbf{EO}$, this matrix being in general no longer diagonal but still symmetric. One can always find an orthogonal transformation **O** for which the resulting set of MOs $\mathbf{C}'$ exhibit a maximum degree of localization. These MOs are known as localized molecular orbitals and the diagonal elements of $\mathbf{E}'$ can be associated to the energies of the LMOs.

According to the commonly used intrinsic localization criteria, the LMOs are obtained by maximizing a localization sum

$$S = \sum_i^M (\phi_i\phi_i|\phi_i\phi_i) \tag{10}$$

where, in general

$$(\phi_i\phi_j|\phi_k\phi_l) = \int \phi_i(1)\phi_j(1)f(r_{12})\phi_k(2)\phi_l(2)\, dv_1dv_2$$

and the form of the function $f(r_{12})$ depends on the criterion being used.[18-20]

Introducing the LCAO expression in the localization sum (10) and using the ZDO approximation, one obtains

$$S = \mathrm{Tr}(\mathbf{Q}^t\mathbf{LQ})$$

where we have defined a $N \times M$ matrix **Q**

$$\mathbf{Q}_{ri} = (\mathbf{C}_i\mathbf{C}^t_i)_{rr} = (\mathbf{C}_{ri})^2$$

and a N × N matrix **L**

$$\mathbf{L}_{rt} = (\chi_r\chi_r|\chi_t\chi_t) \tag{11}$$

which will be referred to as the "localization matrix". It has been shown[17] that in order to obtain LMOs consistent with the HMO method one can take the localization matrix in the form

$$\mathbf{L} = 1 + k\mathbf{T}$$

where k is a parameter whose value has, in general, little influence on the shape of the resulting LMOs.[21] For the sake of simplicity we will take $k = 0$, which amounts to taking for the localization matrix elements the integrals (11) in the von Niessen localization criterion[20] and applying the ZDO approximation. In this case, the localization sum (10) becomes

$$S = \mathrm{Tr}(\mathbf{Q}^t\mathbf{Q})$$

The maximization of S is then effected through an iterative sequence of 2 × 2 rotations.[18]

Table I. Classification of Double Bonds in Acyclic Conjugated Polyenes according to the Energies of the Corresponding π-Localized Molecular Orbitals

bond type	abridged notation[a]	mean energy[b,c]	standard deviation[b]
$H_2C{=}CH{-}HC{=}$	1l	1.1270	0.0033
$H_2C{=}CH{-}C{=}$	1c	1.1181	0.0064
${=}CH{-}HC{=}CH{-}HC{=}$	2ll	1.2637	0.0071
${=}CH{-}HC{=}CH{-}C{=}$	2lc	1.2459	0.0077
${=}C{-}HC{=}CH{-}C{=}$	2cc	1.2329	0.0033
$H_2C{=}C{-}$	2′	1.2219	0.0070
${-}HC{=}C{-}$	3	1.3570	0.0068
${-}C{=}C{-}$	4	1.4737	0.0082

[a] The first index shows the number of carbon atoms adjacent to the double bond and the remaining indices show the conjugation type of those adjacent carbons: linear (l) or cross-conjugated (c). The prime indicates that both substituents are in the same carbon. [b] In β units. [c] For each bond type, the average is made over the energies of the localized orbitals corresponding to all of the bonds of that type occurring in the set of 40 acyclic polyenes considered by Hess and Schaad.[4]

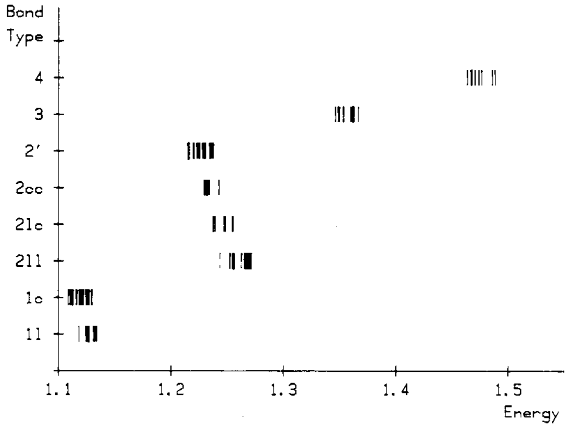

Figure 2. Energies (in β units) of the π-LMOs of the 40 acyclic conjugated polyenes considered in ref 4, classified according to the bond types shown in Table I. See footnote a in Table I for the notation.

Results

1. LMOs of Acyclic Conjugated Polyenes. The results obtained in the π-localization of the set of acyclic polyenes used by Schaad and Hess to parametrize their reference structures[4] are summarized in Table I and Figure 2.

An inspection to the energies of the resulting π-LMOs reveals that they are grouped in a natural way in four different types. The first two bond types can be further classified into two and four types, respectively. The mean energies and standard deviations are shown in Table I. The latter are of the order of 0.6% of the mean energy value, which corroborates the good degree of transferability of these orbitals. As a reference, they can be compared

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(17) Paniagua, J. C.; Moyano, A.; Tel, L. M. *Theoret. Chim. Acta (Berlin)* **1983**, *62*, 265.

(18) (a) Edmiston, C.; Ruedenberg, K. *Rev. Mod. Phys.* **1963**, *35*, 457; (b) *J. Chem. Phys.* **1965**, *43*, S97.

(19) (a) Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 296. (b) Foster, J. M.; Boys, S. F. *Ibid.* **1960**, *32*, 300. (c) Boys, S. F. In *Quantum Theory of Atoms, Molecules and the Solid State*; Löwdin, P. O., Ed.; Academic Press: New York, 1966.

(20) von Niessen, W. *J. Chem. Phys.* **1972**, *56*, 4290.

(21) Moyano, A.; Paniagua, J. C.; Tel, L. M. *Theoret. Chim. Acta (Berlin)* **1983**, *62*, 277.

with the results obtained for benzenoid hydrocarbons,[21] whose standard deviations have considerably greater values.

These results stress the fact, pointed out by Dewar a number of years ago[3b] but even today not generally recognized,[15b] that acyclic conjugated polyenes should be considered as localized molecules in exactly the same way that paraffins, for instance, are considered to be. This misunderstanding arises from the fact that while saturated hydrocarbons are commonly visualized in the light of the localized-bond model, conjugated π-systems are usually described by means of their canonical MOs. Since these orbitals must adapt to the symmetry of the effective monoelectronic hamiltonian, they are always delocalized and, in order to establish the electron delocalization in a molecule, one should analyze the delocalization degree of the localized MOs, since these are free of such symmetry implications.

Let us now consider the topological factors which govern the energies of π-LMOs of acyclic polyenes. The most important factor is the degree of substitution of the double bond upon which the orbital is centered, in accordance to the surmises of Schaad and Hess.[4] As can be seen in Figure 1, orbitals centered on monosubstituted double bonds have energies in the range of 1.10–1.13; orbitals centered on disubstituted (either terminal or central) double bonds have energies in the range of 1.21–1.27; orbitals centered on trisubstituted double bonds have energies ranging from 1.35 to 1.37; and orbitals centered on tetrasubstituted double bonds have energies between 1.46 and 1.48. On the other hand, in orbitals centered upon monosubstituted or central disubstituted double bonds, branching in carbons adjacent to the central double bond has a small negative effect of about 0.01 per branching.

At first sight these results seem to be at variance with the fact, already stated in the introduction, that every branching site in an acyclic polyene introduces a negative contribution to E_π of about 0.1[12] (see eq 3), since we have found in the above analysis of LMO energies that the branching caused by an increase of substitution implies in some instances an increase in orbital energy of about 0.1 per orbital, i.e., an energy stabilization per branch of about 0.2 β unit. A closer examination reveals that this is not true. In effect, let us assume that the energy of a LMO of an acyclic polyene can be decomposed in the following contributions: (i) the energy of an isolated, ethylene-like π-bond, exactly 1 β unit, (ii) the stabilization energy due to increased conjugation (c), which is proportional to the number of adjacent carbon atoms, and (iii) the destabilization energy associated with branching (b), proportional to the number of branching sites in the double bond.

For the sake of simplicity, we have not considered the aforementioned additional small negative contribution to orbital energy associated to branching in adjacent carbon atoms, so that some of the bond types (namely, 1lc, 2lc, and 2cc according to the notation used in Table I) are omitted in the following discussion. Making these assumptions the localized bond energies should approximately obey the following set of equations (see footnote a in Table I for the notation):

$$\begin{aligned} e_{1l} &= 1 + c \\ e_{2ll} &= 1 + 2c \\ e_{2'} &= 1 + 2c - b \qquad (12) \\ e_3 &= 1 + 3c - b \\ e_4 &= 1 + 4c - 2b \end{aligned}$$

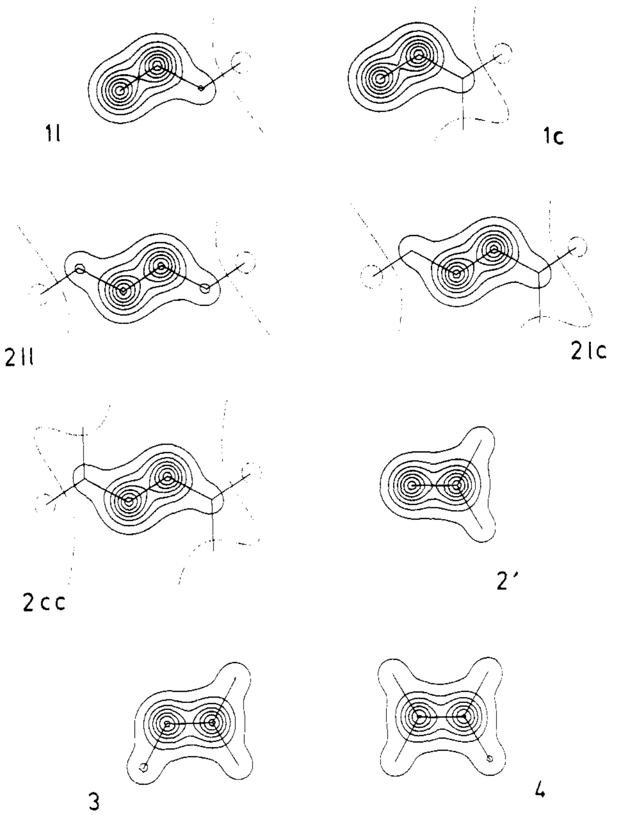

Figure 3. Contour plots of π-LMOs representative of the bond types shown in Table I. The bond chosen to represent each bond type, together with the energy of the corresponding π-LMO, is shown in Figure 4. The difference between the orbital values of two consecutive lines is 0.04 au. Dotted lines correspond to zero and negative values. The bond distances for single and double carbon–carbon bonds are 1.48 Å and 1.35 Å, respectively.[3a] See footnote a in Table I for the notation.

From the results of Table I, one easily obtains that c and b have the approximate values of 0.13 and 0.04 respectively, so that we can predict the decrease in the total π-energy per branching site as about $2b = 0.08$, in good accordance with the previously obtained value of 0.09.[12] Moreover, an equation of the same form of eq 3 can be deduced by using the above expressions for localized bond energies (see Appendix). The decrease of E_π with branching is not evident on direct inspection of the orbital energy values (Table I) due to the fact that both conjugation and branching change when passing from one bond type to another, except for the case of bond types 2ll and 2′, which only differ in one branching site.

In Figure 3 we have represented a LMO characteristic of each of the eight types. This has been chosen with the requirement that its orbital energy should approach the mean value for the corresponding bond type (see Figure 4). For each orbital, contours of constant value on a plane parallel to the molecular plane passing through the point of maximum $2p_\pi$ AO value have been plotted. Basis orbitals have been taken as $2p_\pi$ STOs with the carbon exponential coefficient given by the Slater rules. In each case we have represented only the atoms necessary to identify the bond type, while truncating the orbital coefficients upon the remaining atoms.

One can see that the localized orbitals have always significant positive contributions from the centers adjacent to the double bond, so that both the delocalization degree and the orbital energy (in β units) increase with increasing substitution of the double bond upon which the orbital is centered. However, the delocalization degree is in every case significantly smaller than that of aromatic hydro-

Table II. Coefficients of the π-Localized Molecular Orbitals of Naphthalene and of the Localized Molecular Orbitals of Types 2lc and 4 of an Acyclic Conjugated Polyene[a]

	naphthalene π-LMOs	
AO no.[b]	"peripheric" LMO	"central" LMO
1	0.6555	0.2013
2	0.6532	−0.1487
3	0.2168	−0.1487
4	−0.1694	0.2013
5	−0.0070	0.2013
6	0.0544	−0.1487
7	−0.0350	−0.1487
8	−0.0327	0.2013
9	0.2082	0.6122
10	−0.1389	0.6122

	acyclic polyene π-LMOs	
AO no.[b]	2lc-type LMO	4-type LMO
1	0.0123	−0.1372
2	−0.0133	0.1630
3	−0.0119	0.6324
4	0.1728	0.6349
5	0.6661	0.1755
6	0.6654	−0.1255
7	0.1728	−0.0496
8	−0.1544	0.0695
9	−0.0237	0.1630
10	−0.1404	−0.1372
11	−0.0512	0.1603
12	−0.0001	−0.1353
13	0.0132	−0.0064
14	0.0805	−0.0311
15		−0.0496
16		0.0695

[a] The acyclic polyene chosen in each case is the same we have used to represent 2lc and 4 type orbitals in Figure 3 and is plotted in Figure 5 in a conformation that approaches the structure of naphthalene. [b] See Figure 5 for the AO numbering.

carbon LMOs with similar topological features, as can be seen by comparing the contour plots of the π-LMOs of naphthalene (Figure 5a) with those of 2lc and 4 type orbitals in an acyclic polyene. These have been plotted in Figure 5b together with the complete molecular skeleton in a conformation that parallels the geometry of the aromatic system. A quantitative comparison can be made by looking at the coefficients of both sets of orbitals shown in Table II.

2. A New Bond-Energy Parametrization for Polyene-like Reference Structures. The mean localized-orbital energy values of Table I could be directly used in the evaluation of total π-energies of reference structures. However, in order to obtain resonance energies directly comparable to those of Schaad and Hess,[4] it is more convenient to apply to the eight bond types resulting from the localization the same treatment used by those authors, i.e., to evaluate the bond-energy parameters by making a least-squares fit to the total π-energies of the acyclic polyenes. The parameters thus obtained are summarized in Table III.

It can be seen that these values are in good agreement with the localized orbital energies; they follow the same general trends we have discussed in the previous section except for an inversion in the two first values (cf. Table I).

Contrary to that of Schaad and Hess,[4] this is a true eight-bond parametrization: although also in this case a dependency relation between the numbers of bonds of each type exists, namely

$$n_{ll} + n_{1c} - n_3 - 2n_4 = 2 \qquad (13)$$

the presence of the constant term in this equation ensures that the number of energy parameters is not reducible. Let us, for instance, express n_{ll} as a function of the remaining bond type numbers in eq 13:

$$n_{ll} = 2 + n_3 + 2n_4 - n_{1c}$$

substituting in the expression of the total energy of the acyclic polyene:

$$E_\pi = n_{ll}E_{ll} + n_{1c}E_{1c} + n_{2ll}E_{2ll} + n_{2lc}E_{2lc} + n_{2cc}E_{2cc} + n_{2'}E_{2'} + n_3E_3 + n_4E_4$$

we obtain

$$E_\pi = n_{1c}(E_{1c} - E_{ll}) + n_{2ll}E_{2ll} + n_{2lc}E_{2lc} + n_{2cc}E_{2cc} + n_{2'}E_{2'} + n_3(E_3 + E_{ll}) + n_4(E_4 + 2E_{ll}) + 2E_{ll} = n_{1c}E_{\mathrm{I}} + n_2E_{\mathrm{II}} + n_{2lc}E_{\mathrm{III}} + n_{2cc}E_{\mathrm{IV}} + n_{2'}E_{\mathrm{V}} + n_3E_{\mathrm{VI}} + n_4E_{\mathrm{VII}} + E_{\mathrm{VIII}}$$

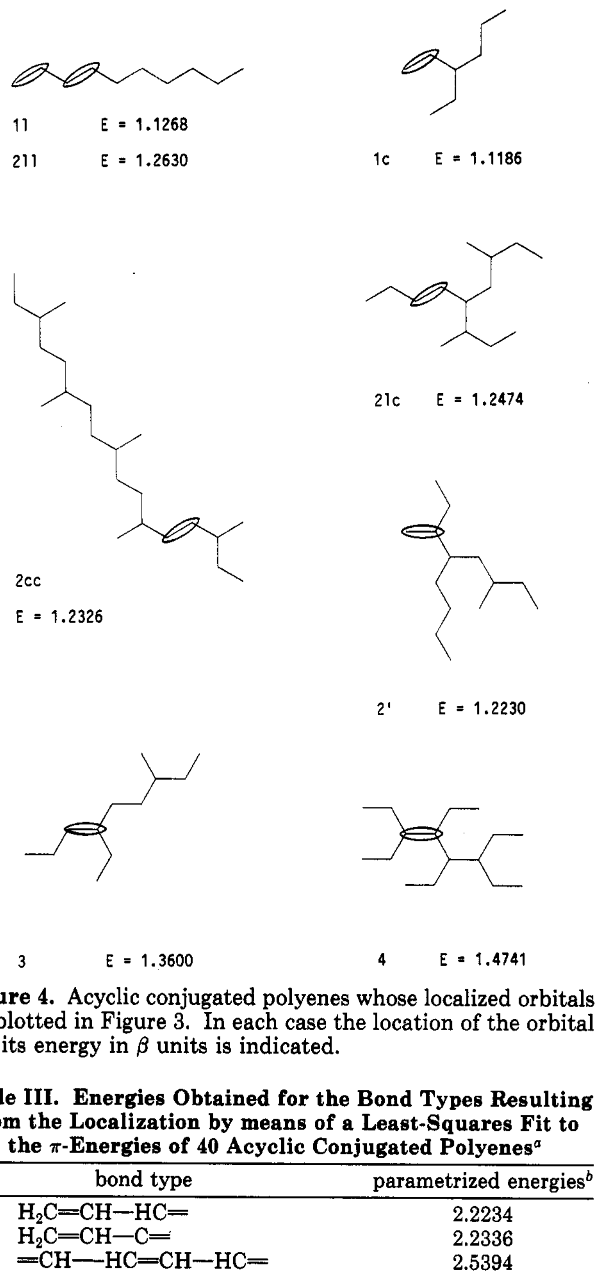

Figure 4. Acyclic conjugated polyenes whose localized orbitals are plotted in Figure 3. In each case the location of the orbital and its energy in β units is indicated.

Table III. Energies Obtained for the Bond Types Resulting from the Localization by means of a Least-Squares Fit to the π-Energies of 40 Acyclic Conjugated Polyenes[a]

bond type	parametrized energies[b]
$H_2C{=}CH{-}HC{=}$	2.2234
$H_2C{=}CH{-}C{=}$	2.2336
${=}CH{-}HC{=}CH{-}HC{=}$	2.5394
${=}CH{-}HC{=}CH{-}C{=}$	2.5244
${=}C{-}HC{=}CH{-}C{=}$	2.4998
$H_2C{=}C{-}$	2.4320
${-}HC{=}C{-}$	2.7524
${-}C{=}C{-}$	2.9970

[a] Orbital energies in Table I must be multiplied by a factor of 2 in order to get bond energy terms comparable to the values of the present table, since the corresponding localized orbitals are doubly filled. [b] In β units.

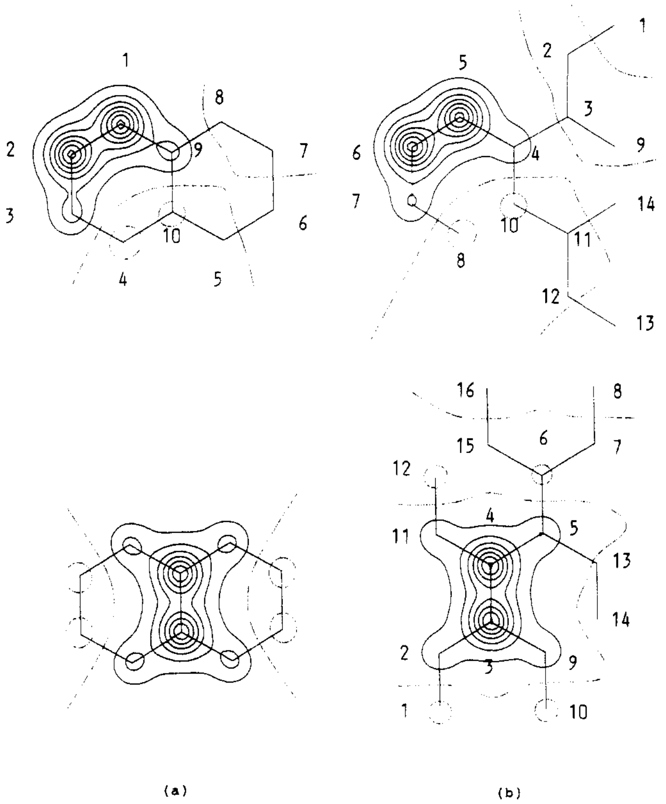

Figure 5. Contour plots for the two different types of π-LMOs of naphthalene (a) and for 2lc and 4 type LMOs of acyclic polyenes (b). The difference between the orbital values of two consecutive lines is 0.04 au. Dotted lines correspond to zero or negative values. The carbon–carbon bond distance in (a) is 1.40 Å. In (b) the bond distances for single and double carbon–carbon bonds are 1.48 Å and 1.35 Å, respectively.[3a]

This is again an eight-parameter equation so that no arbitrary value has to be given to any of the reference bond energies, which is an essential condition for them to possess physical significance.

The resonance energies obtained with the parameters of Table II for the set of conjugated hydrocarbons used by Schaad and Hess,[4] together with the values obtained by those authors, are shown in Table IV.

The REs and REs per electron (REPEs) obtained in both cases are quite similar and the aromaticity/antiaromaticity trends coincide in all of the studied compounds. Only a few points deserve a special comment: (i) our parametrization predicts a limiting REPE value of 0.051 for linear polyacenes (**24–27**); (ii) the difference in sign obtained for radialenes (**40–44**) is irrelevant, since for all of them our absolute REPE values are smaller than 0.002 and, therefore, they are to be considered nonaromatic; (iii) in our method phenanthrene (**28**), benzophenanthrene (**31**), and triphenylene (**32**) are predicted to have REPEs much closer to that of benzene (**23**), in accordance with the fact that these compounds possess a Kekulé structure in which all the rings are benzene-like; and (iv) finally, our RE for biphenyl (**63**) is closer to that of two isolated benzene molecules.

Conclusions

The results obtained in the π-MO localization of a large set of acyclic conjugated polyenes give a fundamental explanation to the observed good bond additivity (i.e., localizability) of these compounds. In addition to that, we have obtained a natural classification of bond types which is mainly determined by topological factors such as conjugation and branching.

Table IV. Resonance Energies (REs) and Resonance Energies per Electron (REPEs) of Conjugated Hydrocarbons, Determined with the Parameters of Table III

conjugated hydrocarbon	no.[a]	RE[b]	REPE[b]	REPE[b,c]
benzene	**23**	0.38	0.064	0.065
naphthalene	**24**	0.59	0.059	0.055
anthracene	**25**	0.71	0.051	0.047
naphthacene	**26**	0.83	0.051	0.042
pentacene	**27**	0.93	0.051	0.038
phenanthrene	**28**	0.85	0.061	0.055
chrysene	**29**	1.07	0.059	0.053
benzanthracene	**30**	1.00	0.055	0.050
benzophenanthrene	**31**	1.10	0.061	0.053
triphenylene	**32**	1.13	0.063	0.056
pyrene	**33**	0.95	0.053	0.051
perylene	**34**	1.15	0.057	0.048
acenaphthylene	**35**	0.57	0.047	0.039
pyracylene	**36**	0.42	0.030	0.019
cyclohept[*fg*]-acenaphthylene	**37**	0.70	0.044	0.034
[4]annulene	**38** ($n = 1$)	−1.08	−0.270	−0.268
[8]annulene	($n = 3$)	−0.50	−0.062	−0.060
[10]annulene	($n = 4$)	0.24	0.024	0.026
[12]annulene	($n = 5$)	−0.31	−0.026	−0.024
[14]annulene	($n = 6$)	0.20	0.015	0.016
[16]annulene	($n = 7$)	−0.20	−0.013	−0.011
[18]annulene	($n = 8$)	0.19	0.010	0.012
[20]annulene	($n = 9$)	−0.14	−0.007	−0.006
[22]annulene	($n = 10$)	0.18	0.008	0.010
bicyclo[2.2.0]hexatriene	**39**	−0.34	−0.056	−0.067
[3]radialene	**40**	0.01	0.002	−0.002
[4]radialene	**41**	0.01	0.001	−0.010
[5]radialene	**42**	0.02	0.002	−0.002
[6]radialene	**43**	0.02	0.001	−0.001
[7]radialene	**44**	0.03	0.002	−0.002
fulvene	**45**	−0.01	−0.002	−0.002
heptafulvene	**46**	−0.03	−0.004	−0.002
trimethylenecyclo-pentene	**47**	0.00	0.000	−0.002
benzocyclobutadiene	**48**	−0.16	−0.021	−0.027
2,3-naphthocyclo-butadiene	**49**	0.15	0.012	0.007
1,2-naphthocyclo-butadiene	**50**	−0.04	−0.004	−0.012
biphenylene	**51**	0.42	0.035	0.027
stilbene	**52**	0.55	0.040	0.051
trifulvalene	**53**	−0.54	−0.090	−0.100
tripentafulvalene	**54**	0.39	0.049	0.043
fulvalene	**55**	−0.29	−0.029	−0.033
sesquifulvalene	**56**	0.30	0.025	0.022
heptafulvalene	**57**	−0.17	−0.012	−0.014
pentalene	**58**	−0.09	−0.012	−0.018
azulene	**59**	0.27	0.027	0.023
heptalene	**60**	−0.01	−0.001	−0.004
octalene	**61**	0.13	0.009	0.007
s-indacene	**62**	0.17	0.014	0.009
biphenyl	**63**	0.75	0.063	0.060
3,4-dimethylenecyclo-butene	**64**	−0.15	−0.026	−0.028

[a] The structure number as well as the Kekulé structure used to set up the reference structure are both the same as ref 4. [b] In β units. [c] Values obtained by Hess and Schaad.[4]

On the other hand, this bond-type classification allows the setting up of a bond-energy scheme for acyclic conjugated polyenes useful for the evaluation of HMO π-resonance energies, which gives results of the same quality of previously published similar[3,4,22] methods. The bond-energy terms resulting from the parametrization are however

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(22) (a) Aihara, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 2750. (b) Gutman, I.; Milun, M.; Trinajstić, N. *J. Am. Chem. Soc.* **1977**, *99*, 1692.

(23) In fact, this expression is only mathematically exact for odd values of r. This is, however, irrelevant, since any given carbon atom can have an odd or even r value, depending on the end of the polyene being chosen to begin the numbering.

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superior in some respects to those, commonly used,[15] of Schaad and Hess,[4] given that a physical significance can be ascribed to them: they can be regarded as being approximately twice the orbital energy values of the π-localized molecular orbitals centered upon the corresponding double bonds. In accordance to that, their values are completely determined by the least-squares fit and do not contain any arbitrarily assigned parameter.

An even more promising application of these new parameters relies on the fact that, due to their close relationship to LMOs, they allow the decomposition of the RE of a conjugated molecule into local contributions, i.e., they can be used to evaluate "local" or "bond" aromaticities. The results of our studies on this subject will be reported in a forthcoming paper. It must be also kept in mind that the treatment presented in this article can be effected at any level of approximation higher than that of the presently used HMO method, although we have refrained from doing so because the resonance energy values are only semiquantitative and do not justify the huge amount of computational time required for a more precise evaluation.

Acknowledgment. Computational facilities given to us by the Centre de Càlcul de la Universitat de Barcelona are gratefully acknowledged.

Appendix: Derivation of a Two-Parameter Expression for the Total π-Energy of an Acyclic Conjugated Polyene

If the small energy effect associated to branching in adjacent carbon atoms is neglected, the eight bond types of Table I reduce to five; if we simplify accordingly the notation by dropping the subscripts in the bond-type notation, we obtain the following expression for the total π-energy of an acyclic conjugated polyene P_N, in terms of the π-LMO energies e_i:

$$E_\pi(P_N)/2 = n_1e_1 + n_2e_2 + n_{2'}e_{2'} + n_3e_3 + n_4e_4$$

Introducing the set of eq 12 in the π-LMO energies we obtain

$$E_\pi(P_N)/2 = n_1(1 + c) + n_2(1 + 2c) + n_{2'}(1 + 2c - b) + n_3(1 + 3c - b) + n_4(1 + 4c - 2b) = (n_1 + n_2 + n_{2'} + n_3 + n_4) + c(n_1 + 2n_2 + 2n_{2'} + 3n_3 + 4n_4) - b(n_{2'} + n_3 + n_4)$$

Expressing the total number of carbon atoms (N), the total number of branching sites (T) and the total number of end-chain carbons (S) of the polyene in terms of the n_i's,

$$N = 2(n_1 + n_2 + n_{2'} + n_3 + n_4)$$

$$T = n_{2'} + n_3 + 2n_4$$

$$S = n_1 + n_{2'}$$

and using the trivial relationship

$$S = T + 2$$

one obtains the desired two-parameter expression:

$$E_\pi(P_N) = N + c(2N - 4) - 2bT \qquad (14)$$

For the particular case of a linear conjugated polyene of N atoms (L_N), $T = 0$ and the total π-energy reduces to

$$E_\pi(L_N) = N + c(2N - 4) = N(1 + 2c) - 4c$$

so that expression (14) can be written in the same form as eq 3

$$E_\pi(P_N) = E_\pi(L_N) - 2bT$$

A direct least-squares fit of this equation to the π-energies of the set of acyclic polyenes considered in this paper gives a b value of 0.05 β unit. This is somewhat greater than that (0.04 β unit) derived from the π-LMOs energies (Table I) and eq 12 due to the effect of branching on carbons adjacent to the double bonds (see text).

Registry No. **23**, 71-43-2; **24**, 91-20-3; **25**, 120-12-7; **26**, 92-24-0; **27**, 135-48-8; **28**, 85-01-8; **29**, 218-01-9; **30**, 56-55-3; **31**, 65777-08-4; **32**, 217-59-4; **33**, 129-00-0; **34**, 198-55-0; **35**, 208-96-8; **36**, 187-78-0; **37**, 194-32-1; **38** (n = 1), 1120-53-2; **38** (n = 3), 629-20-9; **38** (n = 4), 3227-76-7; **38** (n = 5), 3227-77-8; **38** (n = 6), 2873-14-5; **38** (n = 7), 3332-38-5; **38** (n = 8), 2040-73-5; **38** (n = 9), 3227-78-9; **38** (n = 10), 3227-79-0; **39**, 1552-98-3; **40**, 3227-90-5; **41**, 3227-91-6; **42**, 3227-92-7; **43**, 3227-93-8; **44**, 3332-43-2; **45**, 497-20-1; **46**, 539-79-7; **47**, 53477-08-0; **48**, 4026-23-7; **49**, 277-98-5; **50**, 249-99-0; **51**, 259-79-0; **52**, 588-59-0; **53**, 1608-08-8; **54**, 6249-23-6; **55**, 91-12-3; **56**, 1961-84-8; **57**, 531-45-3; **58**, 250-25-9; **59**, 275-51-4; **60**, 257-24-9; **61**, 257-55-6; **62**, 267-21-0; **63**, 92-52-4; **64**, 5291-90-7.

Oxygenation of *tert*-Butylphenols with an Unsaturated Side Chain

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Received December 30, 1985

Base- and Co(Salpr)-promoted oxygenations of title compounds have been investigated with a view to obtaining further details concerning controlling factors in regioselective O_2 incorporation into phenols. In the oxygenation of 4-alkenyl-2,6-di-*tert*-butyl- and 2-alkenyl-4,6-di-*tert*-butylphenols (**1** and **12**), the reactivity of the substrates and regioselectivity in the O_2 incorporation may be interpreted in terms of electronic and steric effects of the alkenyl group as well as association effect of the countercation K^+ on the transition-state **26** involving a charge transfer from the substrate anion to O_2. With 4-alkynyl-2,6-di-*tert*-butylphenols (**21**), dioxygen was incorporated exclusively into the ortho position only when the phenolate anion was associated with K^+. On the contrary, in the oxygenation of **1** and **12** with Co(Salpr), O_2 was incorporated exclusively into the alkenyl side chain, regardless of the nature of the substituent, whereas with **21**, O_2 incorporation was distributed to both the ortho and the alkynyl side chain. The substituent-dependent regioselectivity in the oxygenation of phenols with Co(Salpr) is because the reactive phenolate–Co^{III} species undergo homolysis to form phenoxy radical–Co^{II} species reversibly, whose oxygenations compete with each other. When the oxygenation of the anionic species predominates, O_2 is incorporated into the ortho position, whereas with the radical species the para and side chain oxidations predominate.

4-Substituted 2,6-di-*tert*-butylphenols are normally oxygenated by promotion of Co(Salpr), a five-coordinate cobalt(II) Schiff base complex, resulting in regioselective dioxygen incorporation into the phenol substrates. The regioselectivity depends on the nature of substituent in the 4-position of the phenols. With 4-alkyl-2,6-di-*tert*-bu-

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