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A STUDY OF CONDENSED CYCLOBUTADIENES BY A VARIABLE-BETA HÜCKEL SCHEME

A. Y. MEYER

Department of Organic Chemistry, Hebrew University, Jerusalem

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Abstract—The "self-consistent beta" modification of the Hückel method is applied to several condensed cyclobutadienes, and the results compared with those of other approaches and of the Hückel scheme itself. Structural indices corresponding to bond-orders, free valences, transition and delocalization energies, and frontier-orbital coefficients are evaluated and used in a discussion of the stability and chemical properties of these compounds.

INTRODUCTION

RECENTLY, a hydrocarbon $C_{28}H_{18}$ has been obtained in this laboratory by dehydration of 9-(1-hydroxy-2,3-diphenyl-2-cyclopropen-1-yl)fluorene;[20] this hydrocarbon has been assigned tentatively the structure XII (Table 1) of 1,2-diphenylphenanthro[1]cyclobutadiene. It seemed of interest to study the probability of such a structure in the framework of a systematic theoretical investigation of benzocyclobutadienes in general. Indeed, some work in this field has been done experimentally[1] and theoretically,[2] in order to determine why certain cyclobutadienes are capable of existence and others apparently not. Three main types of argument, based on Hückel calculations, have been used.

1. *Through the bond orders, or bond lengths.* The pure cyclobutadienoid structure **1** appears to be strained and less stable than the arrangements **2** or **3**, which, e.g. explains[2] the failure to obtain phenanthro[1]cyclobutadiene (XI).

2. *Through the index of delocalization energy.* This is defined in the Hückel method[3] by

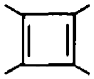
$$DE = 2\left(\sum_{i=1}^{n/2} \varepsilon_i - n\right) \quad \text{(beta units);} \tag{1}$$

n-number of π-centres, ε_i — the characteristic numbers obtained upon diagonalization of the secular matrix. The higher its DE value in a series of similar molecules, the more stable the compound in question is considered to be. This index was invoked to explain[4] the difference in stability between benzo[b]biphenylene (II) and benzo[a]biphenylene (III).

3. *Through the low value of the difference ΔE between the $(n/2)$ and $(n/2 + 1)$ characteristic numbers.*[5] Thus it was explained[2,6] that 1,2-diphenylphenanthro[1]cyclobutadiene (XII) would not be capable of existence.[7]

None of these approaches appears to be generally applicable. The DE values depend primarily on the dimension of the Hückel matrix and are, furthermore, reduced when account is taken of the dependence of the resonance integrals β_{rs} upon bond length. This treatment also increases the ΔE values. Thus low ΔE for

XII, to which we have referred, becomes similar in magnitude to that of dibenzo-[a.i]biphenylene (V) and 1,2-diphenylnaphtho[b]cyclobutadiene (IV), which do



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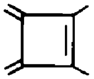

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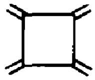


3

exist. The alleged greater stability of "quinonoid" structures such as **2** or **3** would not explain why biphenylene (I) is stable (exocyclic bond orders of 0·683), and its "quinonoid" isomer, naphtho[b]cyclobutadiene (X) is not (bond orders 0·768); equally, V is capable of existence, though it is definitely cyclobutadienoid (bond orders: a, 0·572; b, 0·619; c, 0·222; d, 0·644).

Abandoning the exclusive use of the Hückel method, Coulson *et al.*[4,8] have applied its so-called "SC-β modification" (see below) to a number of compounds, and Fernàndez-Alonso and Domingo[9] have used a free-electron approach. Dewar and Gleicher[10] used their PFP and SPO variants of the SCF method and concluded that stable compounds of the series were "aromatic" or "only slightly antiaromatic", unstable ones "antiaromatic", and furthermore that they were the more stable, the more "single" the bond lengths in the 4-membered ring were calculated to be.

The interatomic distances calculated by these three new methods (Table 2) are usually similar to each other, as are their deviations from the experimental values.[11] As the SC-β method is the simplest, an attempt is made here to use it more extensively *in conjunction* with the Hückel method, a procedure which promises to have a number of advantages, as has been shown recently[12] in the study of aromatic substitution.

DISCUSSION

In the SC-β, or "beta" approach, as recently explored by Boyd and Singer,[13] one starts with the usual Hückel positions, ascribing a constant value β° to all neighbouring resonance integrals β_{rs}, the zero value to all others. Diagonalization leads to bond orders p_{rs} which serve to calculate new β_{rs} values,

$$\beta_{rs} = \beta^\circ \exp(0{\cdot}55\, p_{rs} - 0{\cdot}3666) \qquad (2)$$

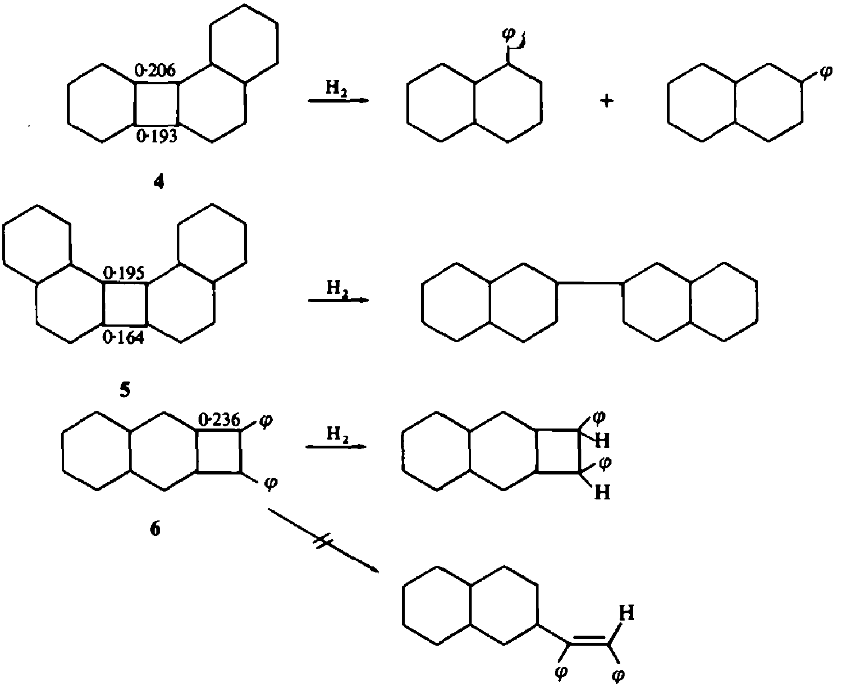
and the process is iterated to self-consistent β_{rs}; finally, bond lengths r_{rs} are estimated from the relation

$$r_{rs} = 1{\cdot}524 - 0{\cdot}194\, p_{rs}$$

In our calculations, the maximum deviation between successive β-values was fixed at 10^{-3}; three to five iterations were needed to achieve this tolerance.

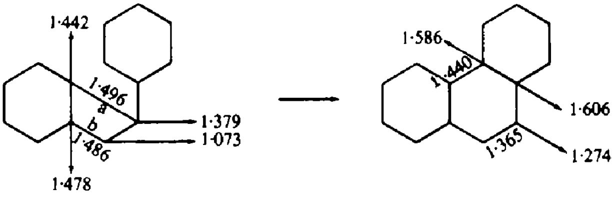
Table 1 lists the compounds studied and indicates the type of the various bonds and also frontier-orbital coefficients, when these exceed 0·250. Results are summarized in Table 3, where subscript H stands for Hückel, B for "beta" values.

Bond orders. Comparison of Hückel and "beta" results shows that the elements of the characteristic vectors depend to a large extent upon the parametrization, whereas bond-orders are less sensitive to it, and agree with each other within ±0·03. This is in line with other calculations[14] and with a statistical study[15] of a similar problem, except that we do not find any exceptional properties associated with the first vector. The "beta" method emphasizes single- and double-bond character, so that when p_{H} is small ($<0{\cdot}45$), p_{B} is smaller, and when p_{H} is high ($>0{\cdot}7$), p_{B} is even higher. This decrease in the value of π-bond orders at the two "single" bonds in cyclobutadienes may be associated with the fact that they are sometimes cleaved upon catalytic reduction. Thus, from 1,2-benzo[a]biphenylene **4** (Hückel bond-orders of 0·262 and 0·246, but smaller, almost equal "beta" values) a mixture of 1- and 2-phenylnaphthalenes is obtained,[16] and in dibenzol[a.i]biphenylene **5** a preferential cleavage of *one* of the bonds occurs, in accord with the noticeable difference of indices.



1,2-Diphenylnaphtho[b]cyclobutadiene **6**, of higher bond-order, on the other hand, is not hydrogenated at the analogous position.[17] We have, therefore, indicated in Table 3 the sums $\sum r_{\mathrm{B}}$ of the lengths of the bonds in the 4-membered ring. This index is higher for stable than for unstable compounds; it replaces the demand for quinonoid structure, and applies also to the non-quinonoid molecules III and IV. The index would further suggest that XII is capable of existence.

Free valence. Instead of the notion of "free valence", we consider, for each atom r, the sum $\sum p_{rs}$ of the orders of bonds in which it participates. The sum $\sum\limits_{1-4} \sum p_{rs}$ of the values of $\sum p_{rs}$ for the four cyclobutadienic atoms, denoted in Table 3 as R_{H} (Hückel) and R_{B} ("beta"), appears to be of significance: small values (R_{B}: 4·8–5·4; R_{H}: 4·9–5·5) define unstable, high ones (R_{B}: 5·7–6·0; R_{H}: 5·8–6·1) stable structures. Compounds VI and XII fall between these two categories. This result replaces the generalization that small free-valence values are a prerequisite of stability; it may also explain the observation[18] that 1-phenylcyclobutadiene 7 rearranges spontaneously to phenanthrene **8**:



7 **8**

(the figures indicate calculated bond-lengths and $\sum p_{rs}$ values). In 7, bond a is longer than b, and the geometry of the compound favours an isomerization which increases the *R* value.

Characteristic numbers. Upon passing from the Hückel to the "beta" computations, the first *n*/2 characteristic numbers (and, symmetrically, the others) change in such a way that the first diminish, and the last one or two increase; sometimes there is in the middle a region of no change. It may be mentioned that, regarding the change in characteristic numbers, benzo[a]biphenylene (III) resembles the phenanthroid structures (XI, XII) more than the benzo- or naphtho-compounds.

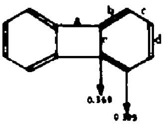
One consequence of this change in characteristic numbers is that the transition energy ΔE is always higher in the "beta" (ΔE_B) than in the simple Hückel scheme (ΔE_H); instability arguments based on triplet ground-states lose thus somewhat of their force. From the tabulation of ΔE_H, ΔE_B and their difference, $\Delta\Delta E$, it is seen that $\Delta\Delta E$ values corresponding to stable compounds are lower than the values for unstable ones. Hückel ΔE values are relatively insensitive to refinements for compounds capable of existence.

Delocalization energies. The delocalization energies DE_H, DE_B and their difference ΔDE are evaluated in both methods from Eq. (1), which is not compatible with Eq. (2). *DE* increases with the number *n* and is not a useful index of stability, except in some groups of isomers (I, IX, X; II, III). But as the DE_H and DE_B are different. the tabulated examples show that ΔDE is usually small (−0·13 to 0·24) for unstable structures, higher (>0·30) for stable ones.

Frontier orbital. Another difference between stable and unstable derivatives expresses itself in the coefficients of the frontier orbital,[19] that is, the components of the *n*/2 characteristic vector. No regularity is found for coefficients belonging to atoms other than those of the cyclobutadiene moiety, but these are sometimes almost equal in the Hückel and "beta" treatments. If the differences are added for the four cyclobutadienic atoms (the sum is denoted *S* in Table 3), the compounds fall again into two groups: stable structures have small *S* (0·0–0·04), unstable ones higher values (0·11–0·17). VII is an exception.

Table 1 indicates the absolute values of frontier orbital coefficients ("beta" method) when they exceed 0·25. These can be used in predicting chemical properties. Thus, the proneness of biphenylene (I) to electrophilic substitution at position 2, and the reactivity at positions 1 and 2 of 1,2-diphenylnaphtho[b]cyclobutadiene (IV) and at positions 6a and 10b of benzo[a]biphenylene (III) are accounted for.

TABLE 1. COMPOUNDS STUDIED



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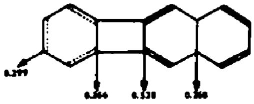

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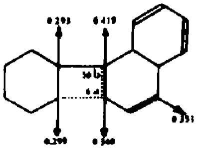

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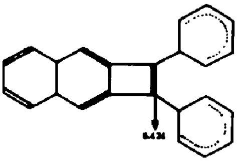

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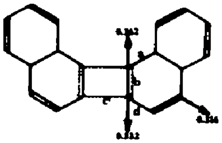

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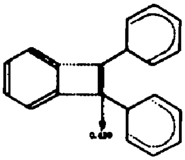

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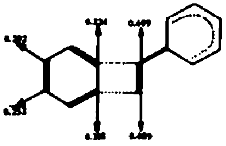

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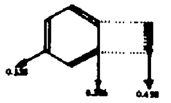

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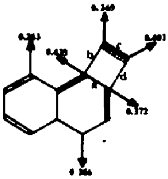

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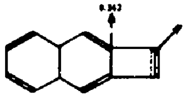

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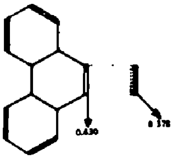
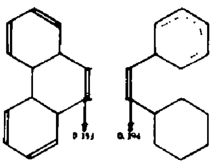


XI



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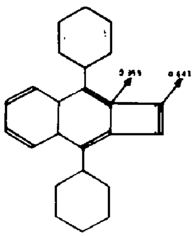


XIII

"Beta" bond orders: $p < 0{\cdot}2$ $\cdot\cdot\cdot$ (single); $0{\cdot}2 < p < 0{\cdot}65$ —— ; $0{\cdot}65 < p < 0{\cdot}69$ (aromatic); $0{\cdot}69 < p < 0{\cdot}9$ ═══ ; $p > 0{\cdot}9$ (double). "Beta" frontier orbital coefficients (→).

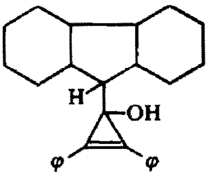
Benzocyclobutadiene (VIII), with high coefficients at the 1 and 6a positions, dimerizes by both the linear and angular mechanism, whilst 3,8-diphenylnaphtho[b]cyclobutadiene (XIII) manifests linear reactivity only,[1] probably for steric reasons.

TABLE 2. COMPARISON OF BOND ORDERS AND LENGTHS IN DIFFERENT METHODS

Structure	Bond	p_H	p_B	r_B	r_{PPP}	r_{FE}	r_{exp}
I	a	0·263	0·212	1·483	1·478	1·474	1·52
	b	0·683	0·703	1·387	1·389	1·399	1·38
	c	0·620	0·610	1·405	1·407	1·383	1·42
	d	0·690	0·707	1·386	1·379	1·379	1·36
	e	0·564	0·572	1·413	1·411	1·432	1·38
IX	a	0·615	0·657	1·396	1·394	1·422	—
	b	0·193	0·122	1·500	1·491	1·460	—
	c	0·913	0·961	1·337	1·346	1·322	—
	d	0·169	0·106	1·503	1·493	1·464	—

Specific examples

1,2-Diphenylphenanthro[1]*cyclobutadiene* (XII). According to one report,[7] this molecule polymerizes when generated, a behaviour rationalized[2] on the basis of its low ΔE_H value; according to another,[20] as mentioned already, dehydration of 9-(1-hydroxy-2,3-diphenyl-2-cyclopenten-1-yl) fluorene **9**, gives XII. Its UV spectrum is described as similar to that[17] of 1,2-diphenylnaphtho[b]cyclobutadiene (IV), except for features such as a slight bathochromic shift of the lowest transition band.



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The calculations indicate that XII fits neither into the group of stable, nor in that of unstable structures, and constitutes an intermediate case. It may thus be capable of existence, though—unfortunately—the theory does not give an unequivocal answer. The same applies to 1,2-diphenylbenzocyclobutadiene (VI).

As the slight bathocromic shift of XII with respect to IV is accounted for by our ΔE_B values, we have evaluated other transition energies using the scheme of Crawford,[21] except that results are expressed in β-units (the γ-integral is undefined in the "beta" method). Taking into account the characteristic numbers from $(n/2 - 3)$ to $(n/2 + 4)$, these energies are found to cluster in the following bands: for XII, 0·51, 1·03, 1·27, 1·55, 1·78, 2·02; for IV, 0·76, 1·1, 1·3–1·45, 1·63–1·73, 1·9, 1·96–2·0. This similarity justifies the comparison of XII with IV, because the "beta" calculations yield a different pattern for compounds whose spectrum does not resemble that of IV. For benzo[a]biphenylene[22] (III) we get, for example, 1·0, 1·28, 1·44, 1·58–1·67, 1·8, 2·0–2·1, 2·26.

Diphenylnaphtho[b]*cyclobutadienes* (IV, XIII). In conclusion, let us compare the calculated values for the stable 1,2-diphenylnaphtho[b]cyclobutadiene (IV) with those obtained for the 3,8-isomer (XIII), of only transient existence.[23] By all conventional indices these two structures should be about equally stable: both are quinonoid and have almost equal ΔE and DE. However, the data of Table 3 clearly place IV with compounds capable of existence (high $\sum r_B$ and R, low $\Delta\Delta E$ and S) and XIII—with the structures that will not be stable (low $\sum r_B$ and R, high $\Delta\Delta E$ and S).

TABLE 3 (see text)

Structure	r_B	R_H	ΔE_H	DE_H	S
		R_B	ΔE_B	DE_B	
			$\Delta\Delta E$	ΔDE	
I, known	5·792	6·040	0·890	4·505	0·004
		5·948	1·132	4·206	
			0·242	0·299	
II, known	5·778	6·066	1·004	6·225	0·024
		5·972	1·185	5·731	
			0·181	0·494	
III, known	5·779	5·961	0·641	6·166	0·040
		5·866	0·894	5·651	
			0·253	0·515	
IV, known	5·779	5·876	0·492	9·118	0·030
		5·732	0·762	8·411	
			0·290	0·707	
V, known	5·774	5·796	0·456	7·819	0·018
		5·710	0·728	7·083	
			0·272	0·736	
VI, unknown	5·762	5·818	0·381	7·323	0·040
		5·668	0·718	6·866	
			0·337	0·457	
VII, unknown	5·752	5·503	0·448	4·844	0·033
		5·372	0·880	4·683	
			0·432	0·161	
VIII, unknown	5·668	5·208	0·525	2·381	0·110
		5·104	1·060	2·518	
			0·535	−0·137	
IX, unknown	5·736	5·079	0·295	3·996	0·168
		4·963	0·805	3·935	
			0·510	0·061	
X, unknown	5·751	5·286	0·678	4·199	0·110
		5·178	1·105	4·058	
			0·427	0·141	
XI, unknown	5·729	4·952	0·167	5·692	0·176
		4·818	0·723	5·454	
			0·556	0·238	
XII, conflicting evidence	5·746	5·624	0·128	10·673	0·014
		5·428	0·511	9·786	
			0·383	0·887	
XIII, unknown	5·656	5·188	0·610	9·026	0·110
		5·120	1·016	8·412	
			0·406	0·614	

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