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MOLECULAR GEOMETRY, BOND ENERGY AND REACTIVITY OF CONJUGATED HYDROCARBONS
IV FULVENES

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Abstract—The LCAO-MO-SCF-PPP ($\pi + \sigma$) method developed previously[1a–c] is found to depend fundamentally on the valence state sp^2 carbon ionization potential, and this dependence is discussed. The method is then applied to the fulvenes, dibenzofulvenes, and heptafulvenes, and the calculated bond lengths are analysed systematically in terms of substituent effect, π-electron density distribution, dipolar character and molecular stability. The reactivities of the fulvenes are related to the polarity of the exocyclic double bond. Six reactions of the fulvenes are discussed. Reaction sites are predicted using the SCF π-electron densities of reactants and the calculated energies of possible products. Good agreements are obtained. An Analysis of Component Stabilization is developed to estimate the contribution of composite structural units to the total stabilization as measured by the Empirical Resonance Energy. The Heats of Hydrogenation are calculated in three cross-conjugated fulvenes. Annelation in these 5- and 7-membered ring compounds is found to result in the loss of fulvenic character.

INTRODUCTION

THE electron-withdrawing power of the cyclopentadienyl ring and the electron-donating power of the tropylium ring enable the fulvenes to exhibit properties that are uncommon to conjugated hydrocarbons, such as the benzenoids and the linear polyenes.[1a] The strong alternation of bond lengths, the polarity, and the high stabilities of the composite 5- and 7-membered ring units with "4n + 2" π-electron occupations, are primarily responsible for the special characters in the fulvenes.

The present theoretical consideration applies the LCAO-MO-SCF-PPP ($\pi + \sigma$) method[1] to calculate the total bond energies, bond lengths and π-electron densities of the fulvenes in their ground state. Conventional HMO[2a] and SCF[2b] π-electron theories have been carried out exclusively for calculating π-electronic excitation energies; these procedures do not give the ground state total energy. The present method differs in that both the π and σ electronic energies are treated explicitly, using a consistent set of semi-empirical parameters, and predicts accurate *total* energies. The σ-electronic energy plays a more significant role than the π-electronic energy in molecular stability. The emphasis is on the ground state properties of the fulvenic systems, and *not* on their excited states, as in conventional theories.[2a, b]

Previous investigations using π-electron methods[2a, b] or all valence electron method[2c] treated only one or two fulvenes by any particular theory. A large set of fulvenes is examined by the present procedure, in order to facilitate comparisons and correlations of their characteristic properties and aromaticities, in a consistent and systematic manner.

THEORY

(a) The present calculations are based on a modified version of the Pariser–Parr–Pople (ZDO) π-SCF-MO-LCAO method for conjugated systems, which has been fully described previously.[1a,c] Thus, only a brief outline on the essential features of the theory, as applied to conjugated hydrocarbons, is given.

The matrix elements of the π-Hamiltonian are evaluated semi-empirically.[1a] These include W_{p_t}, the valence state ionization potential, γ_{ii} and γ_{ij}, the one-centre and two-centre repulsion integrals and β_{ij}, the resonance integral. W_{p_t} and γ_{ii} are estimated from the trigonally hybridized carbon valence state energies, since γ_{ii} is approximately equal to the difference between the valence state ionization potential and the valence state electron affinity. γ_{ij} is represented by Ohno's semi-empirical form

$$\gamma_{ij} = \frac{14{\cdot}398}{\sqrt{[R_{ij}^2 + (14{\cdot}398/\gamma_{ii})^2]}} \text{ (eV)}$$

where R_{ij} is the interatomic separation in Å between the A.O.'s ϕ_i and ϕ_j. This form is adopted because it reproduces the theoretical repulsion energies, calculated using Slater-type A.O., with Paoloni's semi-empirical orbital exponents.[1a] With the above choice of parameters (W_{p_t}, γ_{ii}, γ_{ij}), then β_{ij} and $E_{\sigma b}$, the CC sigma bond energy, can be evaluated as functions of distance, R_{ij}, using the experimental total bond energies and the equilibrium bond lengths of ethylene and benzene. Bond lengths are calculated by a direct minimization of the total CC $\pi + \sigma$ energy with respect to each bond length in the molecule. An iterative procedure is carried out to self-consistency.[1] Consequently, the calculated molecular properties are associated with a minimum energy planar structure, and are not subject to an arbitrarily preassumed initial geometry, as used in π-electron theories.[2a,b]

(b) *((One" parameter molecular orbital method*

The above choice of parameters dictates the fundamental dependence of the theory on only one parameter, W_{p_t}; all other parameters are changed, if a different value of W_{p_t} is used.

In the present work, as in previous investigations,[1] Hinze and Jaffe's valence state energies are used,[1] where W_{p_t} is equal to 11·16 eV. However, transition energies[3] and open-shell molecular properties[4] are improved by using a lower W_{p_t} value, because an "atom-in-molecule" would have a lower energy than a free valence state atom. A wide range of W_{p_t} values from 11·16 eV to 9·4 eV have been used, in order to study the effect of changing W_{p_t} on the calculated heats of atomization (25°) of neutral closed shell conjugated hydrocarbons, and their geometries. The heats of atomization and geometry were insensitive to changes in W_{p_t}. However, open-shell properties, such as the vertical and adiabatic ionization potential and unpaired spin densities are improved by lowering W_{p_t} below 11·16 eV. These calculations will be reported elsewhere.[1d]

A W_{p_t} of 11·16 eV is used in this work, since only the close-shell ground state properties of the minimum energy planar structures are considered.

The Stabilization Energy per CC bond (SECC), defined as the calculated Empirical Resonance Energy (ERE)[1a] divided by the number of CC bonds in the molecule, gives an average measure of molecular stability.

RESULTS AND DISCUSSION

The results are discussed in three sections; the *fulvenes* in section A, the *dibenzofulvenes* in section B, and the *heptafulvenes* in section C.

A. *Fulvenes*

The geometries of the fulvenes are shown in Fig. 1; their bond energies and SECC values are in Table 1.

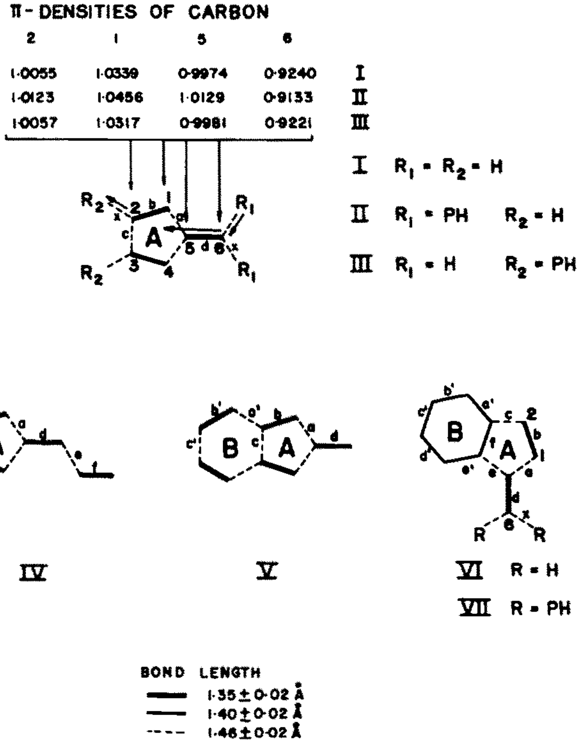

FIG. 1 Bond length diagrams of the fulvenes and π-densities illustrating the polarities of I, II, III.

TABLE 1. BOND ENERGIES* AND SECC OF THE FULVENES (IN eV)

	Molecule		$E^{CC}_{\pi b}$	$E^{CC}_{\sigma b}$	SECC
I	Fulvene	C_6H_6	8·198	21·573	0·2044
II	6,6-Diphenylfulvene	$C_{18}H_{14}$	26·055	73·574	0·3086
III	2,3-Diphenylfulvene	$C_{18}H_{14}$	26·074	73·502	0·3059
IV	6-Vinylfulvene	C_8H_8	10·913	28·783	0·2046
V	2,3-Benzofulvene	$C_{10}H_8$	13·877	40·122	0·2284
VI	1,2-Benzofulvene	$C_{10}H_8$	14·412	40·293	0·2927
VII	6,6-Diphenyl-2,3-benzofulvene	$C_{22}H_{16}$	32·303	92·262	0·3267
VII^{2-}	Dianion		33·454	92·862	0·4644

* $E^{CC}_{\pi b}$ and $E^{CC}_{\sigma b}$ are the total carbon–carbon π and σ bond energies.

The heat of atomization ΔH^a (25°) of a neutral conjugated hydrocarbon is the sum of $E^{CC}_{\pi b} + E^{CC}_{\sigma b} + N_{CH}E^{CH}_{\sigma b}$.[1a,c] N_{CH} is the number of CH bonds with bond energy $E^{CH}_{\sigma b}$ of 4·43 eV (102·13 kcal/mole).[1a]

I. *Effect of substituents on fulvene*

The SECC of fulvene I, 0·2044 eV, is much smaller than those of the benzenoids[1a] (0·34 eV), and slightly greater than the SECC typical of the linear polyenes[1a] (0·18 eV) and may characterize a cyclic polyolefin. The dipolar character of fulvene, resulting from the shift of π-electrons from the exocyclic carbon towards the cyclopentadienyl ring is well-known.[5] This dipolar contribution is more pronounced in the excited state, and is responsible for a decrease of the excitation energy. Hence, the fulvenoids absorb at longer wave lengths than the benzenoids.[6]

Experimentally it is found that the conjugation of electron-releasing substituents with increasing donating power at the exocyclic carbon of fulvene gradually shift the pronounced diene properties of the fulvenoid system towards the full cyclic conjugated benzenoidal character, as the R_1 group of I, Fig. 1 is replaced in the sequence H, alkyl, aryl, OH, $N(CH_3)_2$.[6] However, the introduction of a powerful electronegative substituent (for example, CN) obliterates the fulvenic character. The dipole moment is now directed towards the "negative" exocyclic carbon. Any good electron-releasing group or heteroatom with a lone pair of π-electrons at the exocyclic carbon will increase the dipolar contribution, and give greater molecular stability.

The theoretical calculations show that the SECC of 6,6-diphenyl fulvene II is increased substantially from its parent I; 2,3-diphenyl fulvene III has a smaller SECC, since the phenyl groups are not directly operating on the electron deficient C-6. Figure 1 shows that a phenyl group at C-6 in II is electron-releasing (total net π-charge $+0{\cdot}0217$ on Ph^-), resulting in cross-conjugation stabilization, in contrast to the electron-withdrawing property of the phenyl group (total net π-charge $-0{\cdot}0025$) joined directly to the ring at C_2 and C_3 in III. The difference in spectral shifts[7] between II and III is a consequence of this opposite behaviour of the phenyl groups.

Experimentally, polarographic analysis of a series of substituted 6,6-diphenyl fulvenes has been carried out;[8] the ease of reduction is increased by electron-withdrawing substituents in the phenyl ring, and decreased by electron-releasing groups, in agreement with the above theory.

The vinyl group in IV does not stabilize the parent fulvene I, as shown by their SECC values. This is in agreement with the experimental properties of this molecule.[9]

In the benzologues of fulvene, the annelation of benzene rings to the cyclopentadienyl ring increases the stability of the molecule. The SECC's of the two benzofulvenes, 0·2284 eV in V and 0·2729 eV in VI, illustrate the benzostabilization, where the 1,2-benzo- is more stable than the 2,3-benzo-molecule,

II. *Molecular geometry*

The calculated bond lengths of the fulvenes I–VII are shown in Table 2. The *experimental* bond lengths of 6,6-dimethylfulvene,[11] E1 and 1,2,3-tribromo-6-(O-methoxy phenyl)fulvene,[12] E2 are also shown in order to facilitate comparison with the calculated bond lengths in the fulvene unit ((A)) of I and II (Fig. 1 and Table 2). The fulvene skeleton in E1 is planar[11] with average double and single bond lengths of 1·345 and 1·438 Å. The calculated average bond lengths are 1·350 and 1·465 Å. The bond lengths (a–d) of the fulvene unit in II are similar to the experimental bond lengths of E2, but there are large deviations in the phenyl ring bond lengths, attributable to the perturbation of the methoxy group on the phenyl ring and the peculiar crystal packing effects caused by this unsymmetrical group in E2.

TABLE 2. BOND LENGTHS (IN Å) OF THE FULVENES

Molecule	Unit*	a	b	c	d	e	f
[I]	A	1·469	1·352	1·457	1·348		
*E*1†	expt.	1·439	1·346	1·435	1·343		
[II]	A	1·462	1·356	1·453	1·368	x = 1·465	
*E*2†	expt.	1·46	1·32	1.48	1·36	x = 1·49	
[II]	Ph.	1·407	1·397	1·402	1·400	1·400	1·405
E2†	expt.	1·43	1·36	1·42	1·42	1·44	1·38
[III]	A	1·466	1·359	1·460	1·349	x = 1·467	
	Ph	1·406	1·398	1·402	1·399	1·400	1·404
[IV]	A	1·466	1·353	1·451	1·357	1·465	1·341
[V]	A	1·466	1·366	1·455	1·350		
	B	a′ = 1·459	b′ = 1·355	c′ = 1·452			
[VI]	A	1·468	1·349	1·463	1·347	1·470	1·408
	B	a′ = 1·407	b′ = 1·396	c′ = 1·404	d′ = 1·397	e′ = 1·406	
[VII]	A	1·462	1·352	1·461	1·367	1·450	1·409
	Ph	1·407	1·397	1·402	1·399	1·400	1·405
	B	a′ = 1·408	b′ = 1·396	c′ = 1·405	d′ = 1·396	e′ = 1·408	x = 1·465
$[VII]^{2-}$	A	1·398	1·411	1·414	1·467	1·424	1·441
	Ph	1·426	1·392	1·407	1·414	1·385	1·429
	B	a′ = 1·427	b′ = 1·385	c′ = 1·427	d′ = 1·387	e′ = 1·419	x = 1·420

* Composite units: A = fulvene; B = benzo; Ph = phenyl (bonds a′ to f′ labelled around the ring) Fig. 1.

† Based on the X-ray data of 6,6-dimethylfulvene,[11] E1, and of 1,2,3-tribromo-6-(o-methoxy-phenyl) fulvene,[12] E2.

The exocyclic bond "d" in these fulvenes gives a measure of the *dipolar resonance* contribution; a higher π-electron shift toward the ring results in a lowering of the bond order of "d", and consequently a smaller bond stretching frequency and a longer bond. The calculated and experimental bond lengths for "d", Table 2, agree very well: 1·348 Å in I with 1·343 Å in E1, and 1·368 Å in II with 1·36 Å in E2. The total net π-charge of the cyclopentadienyl ring is directly related to the lengthening of bond length "d", in a series of substituted fulvenes with substituents of varying electron-releasing power:

Molecule	Effect of substituent	Bond "d" in Å	Total net π-charge of cyclopentadienyl ring
I	Standard	1·348	−0·0762
IV	6-Vinyl	1·357	−0·0909
II	6,6-Diphenyl	1·368	−0·1287

The stretching frequency of the exocyclic bond in 6,6-dicyclopropylfulvene[13] is very similar to 6,6-diphenyl fulvene II, which implies that the cyclo propyl group is as effective as the phenyl group in electron-releasing power. Thus the bond lengths "d" in these two molecules would be expected to be almost identical.

Saturated alkyl or polymethylene[14] substituents have little influence on the π-system of the ring; a marked localization of the three double bonds persists in these fulvenes, as shown by their olefinic NMR absorptions, which resemble the double bond protons of cyclopentadiene.[5] The *calculated* bond length substantiate these conclusions, since the variations from I to IV are minor in the "A" unit, and all show strong bond alternations, while the phenyl bond lengths in Ph in II and III are also similar and close to 1·402 ± 0·005 Å.

The benzo bond lengths in 2,3-benzofulvene V *alternate*, as do those in the fulvene unit, and contrast sharply with the bond lengths in the benzo group of 1,2-benzofulvene VI, Fig. 1, which do not alternate. This variation explains the greater stability of VI, as established in section A-I. The bond lengths of VII° Fig. 1, Table 2, differ from those in the dianion VII^{2-}; VII^{2-} has more uniform bond lengths in the central 5-membered ring than VII°, due to the higher total π-electron density (5·6222 π-electrons) in this unit, which cause it to have a cyclopentadienyl-anion-like structure in VII^{2-}.

The calculated bond lengths of these fulvenes are related to their minium energy planar structures.[1] The low resonance stabilization of fulvene I is reflected by the strong bond alternations, whereas the higher stabilities in its derivatives and ions are associated with uniform benzenoidal bond lengths.

III. *Reactivities*

The reactivities of the fulvenes are investigated in terms of the "isolated molecule" approach,[16] where the calculated π-electron density distributions and molecular geometries in their ground state are used as sensitive detectors of *potential* reaction sites. The theoretical basis of this approach has been discussed elsewhere.[16, 17] The main intention is to complement the organic chemist's classical approach to reaction mechanism, by furnishing relable ground state properties, to which these qualitative arguments can be more satisfactorily applied.

(i) *Diels–Alder reaction.* Diphenylfulvene II, acting as a diene, participates in a four-centre reaction with maleic anhydride. Endo- and exo-adducts at C-1 and C-4 in the fulvene skeleton are formed. The kinetics and the stereochemistry of the addition products have been studied.[18] The SCF π-electron densities, Fig. 1, are highest at the symmetrical C-1 and C-4 positions, so that the C-1 and C-4 positions would interact with the electron-deficient centres of the carbonyl groups of the dienophile. The predicted geometry of II shows a diene-like unit, with bond lengths b, 1·356 Å and c, 1·453 Å in the cyclopentadienyl ring (Table 2). The combination of the calculated charge and the calculated geometry indicates the feasibility of formation of these adducts. Similarly, benzyne adds at the 1,4 positions to form the adduct 7-isopropylidene benzonorborna-diene.[5]

(ii) *Electrophilic and nucleophilic reactions.* The polar character of the exocyclic double bond, Fig. 1, in the fulvenes exhibits parallel properties to those of a carbonyl group. 6,6-disubstituted fulvenes react with electrophilic reagents, such as, Vilsmeier's complex, $[HC(N(CH_3)_2)_2]^+$, diazomethane, $CH_2{=}N{=}N$[5], and undergo protonation H^+, alkylation CH_3^+ and nitrosation NO^+[6], all of which occur at the C-1, position. The SCF π-electron density is the highest at C-1, Fig. 1, in agreement with these observed reaction sites.

Nucleophilic reagents,[6] for example $LiAlH_4$ and organolithium compounds, add to fulvene at the exocyclic carbon C-6, whose π-electron density is the lowest in the molecule. The driving force of this reaction is the gain in energy, originating from the transition of the "*cross*-conjugated" fulvene to the "*cyclic*-conjugated" anion.

The calculated energies of the reactants and products in the addition reaction of a hydride ion to fulvene is shown in Fig. 2.

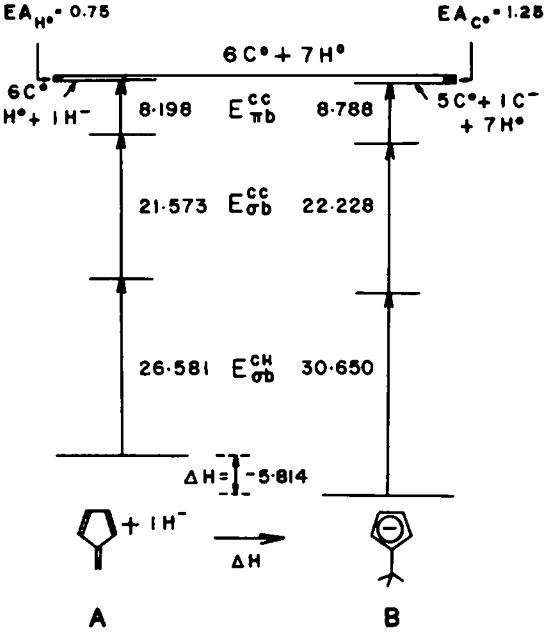

FIG. 2 Bond energy contributions to fulvene A, and methyl cyclopentadienyl anion B, relative to six ground state neutral carbons C° and seven hydrogen H° atoms. EA_{H° and $EA_{C^\circ}^{1c}$ the electron affinities of H° and C°, are used so that the total energies of A and B can be compared on a common basis (6C° + 7H°). All energies are in eV.

The bond energies of the reactants [A and $1H^-$] and the adduct B are calculated realtive to [$6C^\circ + 6H^\circ + 1H^-$] and [$5C^\circ + 1C^- + 7H^\circ$] respectively, according to the definition of the bond energies of a neutral conjugated hydrocarbon[1a] and of its ion.[1c] There are favourable energy gains in all the three types of bond energies $E^{CC}_{\pi b}$, $E^{CC}_{\sigma b}$ and $E^{CH}_{\sigma b}$ in the anion. The stability of the cyclopentadienyl anion is reflected by the higher $E^{CC}_{\pi b}$ than that of fulvene, both of which have 6 π-electrons. The large increase in $E^{CH}_{\sigma b}$ is the result of the formation of one additional CH bond in the adduct B.

A distinction should be made at this point on the different natures of the SECC values and the total bond energies, as measures of molecular stability. The SECC is defined only for closed-shell conjugated hydrocarbons and hydrocarbon-ions. It is an average measure of stability within these conjugated systems. However, for conjugated systems with *saturated substituents*, SECC's cannot be defined, and *total bond energies* have to be used to distinguish the stabilities of geometrical isomers and to trace out the energetics of a reaction, (see later sections).

(iii) *Reductive coupling.* 6,6-Diphenyl 2,3-benzo fulvene VII is reduced polarographically to its dianion, which reacts with two moles of acrylonitrile (CH_2 =

CHCN) at the C-6 and C-2 positions,[19] Fig. 1. The SECC of this dianion, 0·4644 eV compared to 0·3267 eV of the neutral molecule VII, demonstrates the ease of reduction. The highest π-electron densities C-6, 1·2522 and C-2, 1·2865 are the most probable positions for electrophilic addition, in agreement with experiment. The first mole of acrylonitrile adds to C-6, followed by a second mole to C-2. The calculated π-electron density on VII^{2-} at C-2 is higher than C-8, and would therefore suggest a reverse order for these additions. However, extension of the energy considerations used above, Fig. 2, shows that the stability of the C-6 addition product is greater than that of the C-2 adduct which has disrupted conjugation.

(iv) *Halogen addition.* Two molecules of chlorine add to the endocyclic double bonds "b" of fulvene I to give a blue 1,2,3,4 tetrachloro addition product. Diphenyl benzofulvene VII reacts with two molecules of chlorine; the first substitutes in bond "b", to give the 1,2-dichloro substituted molecule, followed by halogen addition by the second molecule of chlorine to the same bond[5] to give the 1,2-tetrachloro derivative. These chemical properties support the double bond character of bonds "b" in the cyclopentadienyl ring of these fulvenes, as predicted by their geometries, Table 1.

(v) *"Active" methyl group in 6-methylfulvene* VIII_a *Fig.* (3) The polarity of the exocyclic double bond in 6-methyl fulvene permits VIII_a and VIII_b to exist in tautomeric forms,[5] analogous to the ketone and enol tautomers of carbonyl compounds, Fig. 3.

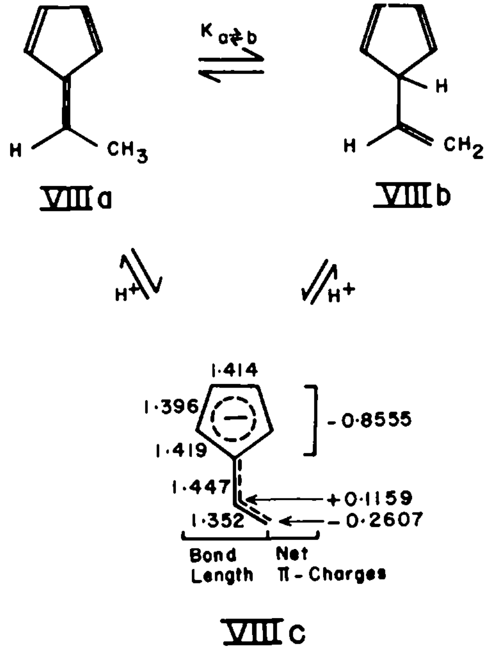

FIG. 3 Tautomeric equilibrium of 6-methylfulvene.

The "electronegative" cyclopentadienyl ring of VIII_a functions as the oxygen of the carbonyl group, while VIII_b with disrupted cyclic conjugation is equivalent to the enol form. The relative stability of these tautomers is determined by the difference in their ΔH_a's, 68·617 eV* in VIII_a and 67·744 eV in VIII_b.

These ΔH_a are evaluated by considering VIII_a as a composite structure of fulvene plus a methyl group, and VIII_b as one ethylene unit linked by a saturated sp^3 C to a *cis*-1,3-butadiene. The $E^{CC}_{\pi b}$ and $E^{CC}_{\sigma b}$ of the unsaturated units have been given before: fulvene in Table 1, and the linear polyenes,[1a] $E_{\sigma b}(C_{sp^2} - C_{sp^3})$ and $E_{\sigma b}(C_{sp^3} - H)$ are 86·809 and 99·355 kcal/mole,* as described in Section (B-II).

The thermodynamic relation between the equilibrium constant $K_{a \rightleftarrows b}$ and the enthalpy difference between VIII_a and VIII_b, $^{\ominus}H^{\circ}$ of 20·1 kcal/mole, is[15]

$$K_{a \rightleftarrows b} = Ae^{-\Delta H^{\circ} \cdot RT}$$

where A the entropy ratio, is assumed to be unity favouring both tautomers; $K_{a \rightleftarrows b}$ is thus estimated to be $1{\cdot}8 \times 10^{-15}$, highly favouring VIII_a. Obviously, the absolute magnitude of this estimated $K_{a \rightleftarrows b}$ is open to many uncertainties,[17] nevertheless, it does give a "*semi-quantitative*" description of this tautomeric equilibrium.

The methyl protons in VIII_a are acidic, since triphenyl methyl sodium converts VIII_a to its anion VIII_c^5, Fig. 3. The driving force of this reaction is the high stability of the anion. The SECC of VIII_c is 0·7168 eV relative to 0·2044 eV of VIII_a. the cyclopentadienyl ring absorbs a net π-charge of $-0{\cdot}8555$, as does the highly electronegative oxygen atom of a carbonyl group.[5] The bond lengths in the 5-membered ring of the anion are uniform, in contrast to the strong alternation in its precursor VIII_a, Fig. 3.

IV. *Magnetic susceptibility, proton NMR and aromaticity*

London's theory of diamagnetic susceptibility, used extensively with the HMO approximations for conjugated systems, has been refined to treat non-benzenoidal systems,[20] in which an additional term, the HMO resonance energy, contributes to the estimate of the resultant magnetic susceptibility. Diamagnetic or paramagnetic contributions are distinguished by the signs and magnitudes of these values. A qualitative measure of aromaticity of the fulvenes is then established by successively calculating the three inter-related terms: geometry, to give the π-electron resonance energy, which gives the magnetic susceptibility.

Recent developments[21] confirm that ring current is the most sensitive detector of aromaticity, but it does not give a direct measure of resonance energy. However, the ring current contributions to the proton chemical shifts are found to be small in the fulvenes, implying small aromaticity. Consequently, the vicinal (or ortho) proton coupling constants are used to assess this small aromatic character in these systems.[22, 23] For example, in 6-phenyl fulvene, the coupling constants J_{12}, J_{23} and J_{34} of the cyclopentadienyl ring are 5·57, 1·88 and 5·86 c/s,[22] indicative of the alternation of double-single bond lengths of the molecule and the low aromaticity. The π-electron density shift from the exocyclic double bond to the ring is reflected by the increased shielding of the ring protons.

In the present study of the aromaticity of the fulvenes, which encompasses and verifies such experimental criteria, the SECC values have been extensively used as an

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* The bond energy of a single bond and the heat of a reaction are conventionally expressed in kcal/mole, whereas the "total" bond energy of the molecule is expressed in eV

1 eV = 23·053 kcal/mole

average measure of molecular stability and aromaticity. The stabilizations due to *specific* structural units in a molecule, that contribute to the overall Empirical Resonance Energy, ERE, and hence of aromaticity, are investigated in the following section B-I.

B· *Dibenzofulvenes*

I. *Analysis of component stabilization* (ACS)

The Empirical Resonance Energy (ERE) of conjugated systems is, traditionally, defined as the difference in energy between a localized single and double bond reference structure and the minimum energy real molecule.[1] For example, the ERE of 1,4-bis(biphenylene)-1,3-butadiene is the estimated energy difference between the reference structure L and the minimum energy molecule IX, as illustrated schematically in Fig. 4. The ERE is the total overall molecular energy change due to π-electron delocalization, conjugation stabilization and σ-bond compression. Any stabilization due to specific structural components in the molecule is therefore hidden within the total energy change. Other *intermediate* hypothetical reference structures can be proposed to illustrate special effects, as shown in Fig. 4 for IX.

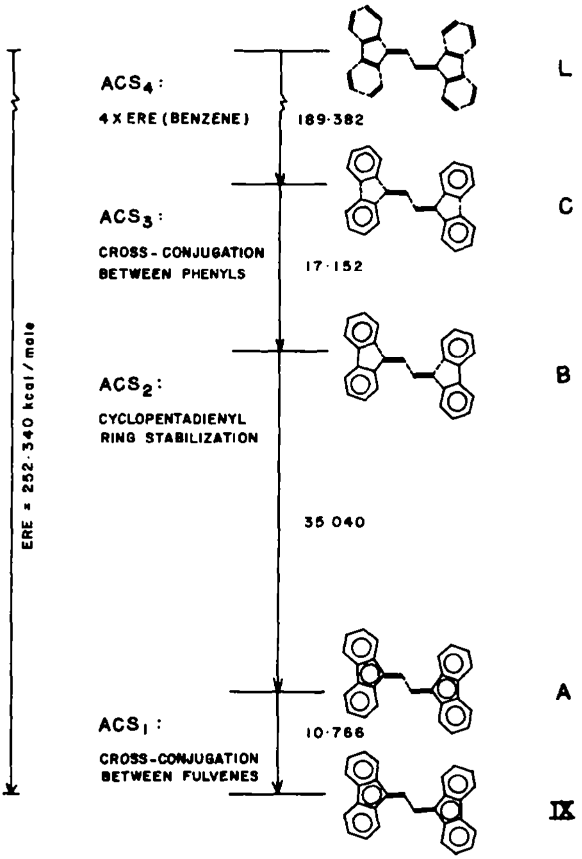


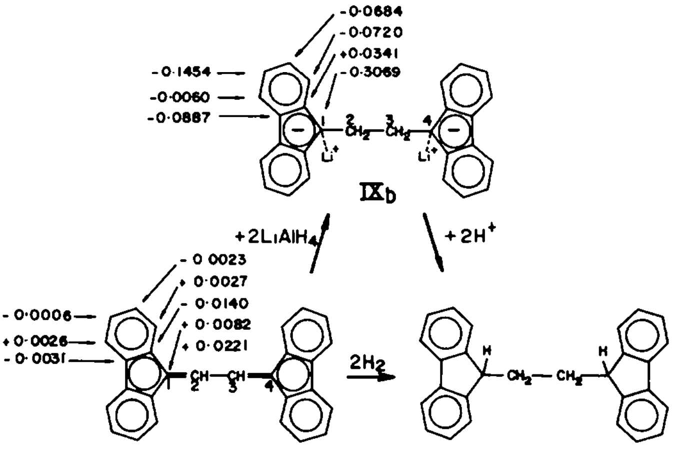
FIG. 4 Component stabilization energies (kcal/mole) in 1,4-bis(biphenylene)-1,3-butadiene IX.

The total π + σ bond energy corresponding to the minium energy ground state of

IX is determined from the present SCF method. The reference structure A, shown in Fig. 4 with two dibenzofulvenes linked by a *pure single bond* is now considered. $E^{CC}_{\pi b}$ and $E^{CC}_{\sigma b}$ of the dibenzofulvene component is given in Table 1. $E^{\rm single}_{\sigma b}$ ($C_{sp^2} - C_{sp^2}$) is 3·9115 eV.[1a] The energy change, ACS_1, from A to IX, 10·766 kcal/mole, measures the cross-conjugation stabilization energy between the two terminal fulvenic units. Successively, structures B and C are defined. The separate components in these structures are taken at their SCF mininum energy state. The stabilization energy, attributable to the conjugation of the cyclopentadienyl ring is given by ACS_2. The cross-conjugation energy between the phenyl rings is the energy ACS_3. ACS_4 is simply four times the ERE of benzene.

The ERE can now be analysed in terms of the ACS, the contributions of separate stabilization energies by individual structural units in the molecule. The present approach is "in principle" similar to Dewar's perturbation method,[17] where the molecular components are treated as unperturbed systems, onto which perturbations are applied, and the overall molecular properties obtained. The present *method operates in reverse, by analysing the final result as a sum of contributions from molecular fragments.* The theory is applied in section B-III to two other related molecules.

II. *The heat of hydrogenation*, ΔH_h (25°)



IXa		IXc
41·570	$E^{cc}_{\pi b}$	35·142
122·143	$E_{\sigma b}$ ($C_{sp^2} - C_{sp^2}$)	95·820
—	$E_{\sigma b}$ ($C_{sp^2} - C_{sp^3}$)	15·063
—	$E_{\sigma b}$ ($C_{sp^3} - C_{sp^3}$)	10·538
79·744	$E_{\sigma b}$ (C_{sp^2} - H)	70·884
—	$E_{\sigma b}$ (C_{sp^3} - H)	25·859
243·457	ΔH_a (e.v.)	253·306

FIG. 5 Hydrogenation of 1,4-bis(biphenylene)-1,3-butadiene. Bond energies for IX_a and IX_c and net π-charges for IX_a and IX_b.

In order to calculate the heat of hydrogenation of a molecule theoretically, it is necessary to know the bond energy of every σ bond in the molecule. The total π-bond energy of the conjugated molecule or molecular component can be calculated from the present SCF method.

The bond energies for $E_{\sigma b}$ (C_{sp^2}—H) has been established as 102·13 kcal/mole,[1a] and the $E^{CC}_{\pi b} + E^{CC}_{\sigma b}$ for ethylene and benzene were calculated to be 5·6033 eV and 30·595 eV previously.[1a] However, the energies $E_{\sigma b}(C_{sp^3}$—H), $E_{\sigma b}(C_{sp^2}$—$C_{sp^3})$ and $E_{\sigma b}(C_{sp^3}$—$C_{sp^3})$ are not known. In order to find them, it is necessary to use the experimental ΔH_a and ΔH_h[24] in a series of polyalkyl and polymethylene and substituted benzenes and polyenes, and to make a least squares fit of the unknown energies. It has been assumed that the conjugated part of the molecule is non-interacting energetically with the saturated substituents. The energies are calculated to be

$$\begin{aligned} E_{\sigma b}(C_{sp^3}\text{—H}) &= 99{\cdot}355 \text{ kcal/mole} \\ E_{\sigma b}(C_{sp^2}\text{—}C_{sp^3}) &= 86{\cdot}809 \text{ kcal/mole} \\ E_{\sigma b}(C_{sp^3}\text{—}C_{sp^3}) &= 80{\cdot}982 \text{ kcal/mole} \end{aligned}$$

These additive bond energy constants agree very well with their previous estimates[31] of 99·298 kcal/mole in $E_{\sigma b}(C_{sp^3}$—H) and 81·276 kcal/mole in $E_{\sigma b}(C_{sp^3}$—$C_{sp^3})$, with mean deviations of $\pm 1{\cdot}11$ kcal/mole, based on a series of alkanes.

The $E^{CC}_{\pi b}$ and $E^{CC}_{\sigma b}$ of the biphenyl unit in IX$_c$ are calculated from the present SCF method to be 17·571 eV and 47·910 eV. These bond energy data permit the calculation of ΔH_h (IX), the hydrogenation of the bridge bonds "d" in 1,4-bis(biphenylene)-1,3-butadiene, as follows:[24]

$$\begin{aligned} \Delta H_h\,(\text{IX}) &= \Delta H_a\,(\text{IX}_c) - \Delta H_a\,(\text{IX}_a) - 2\Delta H_a(H_2) \\ &= 18{\cdot}64 \text{ kcal/mole.} \end{aligned}$$

ΔH_h (IX) is a thermochemically assessible quantity from hydrogenation reactions, and can be compared with the experimental value, when available.

The hydrogenation can be achieved indirectly using LiAlH$_4$[5, 25], Fig. 5. Two moles of LiAlH$_4$ react with IX$_a$ to give an alkali-organic intermediate IX$_b$.[25] The calculated π-electron densities of IX$_a$ correlate with the experimental reaction sites. The hydride ions interact with IX$_a$ at C-2 and C-3, the highest electron deficient positions, while Li^+ ions react with the dianion IX$_b$ at the fluorenylic positions C-1 and C-4, which have the highest π-charges in the dianion. The π-electron densities of the fluorenyl anion have been determined experimentally from the NMR proton chemical shifts,[26] and confirm C-1 and C-4 as the highest π-electron density centres. Hydrolysis of IX$_b$ gives the product IX$_c$.[25]

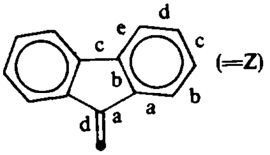
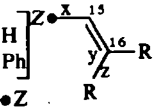
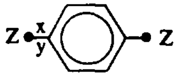
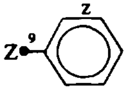
III. *Bond energies and bond lengths*

The bond energies of the dibenzofulvenes are tabulated in Table 3, and their geometries in Table 4. Two molecules XIII and XIV that are structurally similar to IX are considered. The *cross-conjugation stabilization energies* in IX, XIII and XIV are calculated by the ACS method to be 10·766, 19·457 and 19·733 kcal/mole, and the calculated ΔH_h's 18·64, 12·43, and 12·17 kcal/mole, corresponding to the hydrogenation of bonds "d" in IX, XIII and XIV. These results suggest XIII and XIV exhibit a more pronounced *cross* conjugation stabilization effect than IX and that the ethylene

TABLE 3. BOND ENERGIES (IN eV) OF DIBENZOFULVENES. GEOMETRIES GIVEN IN TABLE 4

	Molecule		$E_{\pi b}^{CC}$	$E_{\sigma b}^{CC}$	SECC
X	Dibenzofulvene	$C_{14}H_{10}$	20·625	59·042	0·3275
XI	9-Vinyl dibenzofulvene	$C_{16}H_{12}$	23·374	66·219	0·3139
XII	16,16-Diphenylvinyldibenzofulvene	$C_{28}H_{20}$	41·234	118·179	0·3299
IX	1,4-bis(Biphenylene)-1,3-butadiene	$C_{28}H_{18}$	41·570	122·143	0·3317
XIII	1,6-bis(Biphenylene)-hexatriene	$C_{30}H_{20}$	44·238	129·367	0·3235
XIV	*p*-difluorenyl benzene	$C_{34}H_{22}$	50·559	148·052	0·3347
XV^0	9-Benzal fluorene	$C_{20}H_{14}$	29·568	85·019	0·3349
XV^{2-}	Dianion	$C_{20}H_{14}$	30·440	85·402	0·4631
XVI^{1-}	1,5-bis(Biphenylene) pentadienyl anion	$C_{29}H_{11}$	45·848	126·278	0·4544

TABLE 4. BOND LENGTHS OF DIBENZOFULVENES

	Molecule	State	Unit*	R(Å)				
				a	b	c	d	e
X		0	A	1·469	1·409	1·466	1·347	
			B	1·405	1·398	1·402	1·398	1·405
	1,1-diphenyl ethylene[1]	0	A	1·469	1·405	—	1·347	
			B	1·404	1·400	1.400	1·401	1·398
XI	R = H 	0	A, C	$x = 1·465$	$y = 1·341$		1·356	
XII	R = Ph	0	A, C	$x = 1·459$	$y = 1·358$	$z =1·467$	1·359	
IX	$Z\bullet\overset{x}{\text{—}}\bullet Z$	0	C	$x = 1·459$				
XIII		0	C	$x = 1·459$	$y = 1·354$			
XIV		0	C	$x = 1·464$	$y = 1·407$	$z =1·397$		
XV^0		0	A	1·467	1·409	1·467	1·357	
XVI^{1-}		−1	A	1·446	1·415	1·455	1·400	
XV^{2-}		−2	A	1·415	1·438	1·429	1·461	
XV^0		0	B	1·406	1·398	1·403	1·398	1·405
XVI^{1-}		−1	B	1·416	1·390	1·411	1·393	1·412
XV^{2-}		−2	B	1·429	1·380	1·431	1·385	1·421

* Composite units: A = fulvene, B = benzo, C = vinyl or bridge. Molecular bond lengths not tabulated here have identical distances as their counterparts in molecule X.

(XIII) and benzene (XIV) bridge contributions to stability are approximately the same. The increase in polarity in bond "d", as illustrated by the total net π-charges of the cyclopentadienyl ring of −0·0259 in IX, −0·0284 in XIII and −0·0288 in XIV support the idea that the ethylene and benzene bridging units are equally effective in transmitting *cross*-conjugation.

The SECC's and geometries of XV° and XIV, Tables 3 and 4, are identical, suggesting they possess the same molecular stability. This is also evident from the ACS calculated cross-conjugation energy between the benzene ring with *one* dibenzofulvene unit in XV which is 9·52 kcal/mole, equal to half the 19·733 kcal/mole in XIV, which has two terminal dibenzo fulvenes. The total net π-charges of the electron- releasing benzene rings, +0·0110 in XIV and +0·0085 in XV are of comparable magnitude.

The variations of the dibenzofulvene bond lengths in XV°, XVI^{1-} and XV^{2-} follow an interesting pattern, Table 4. The first set of fulvenic bond lengths of 1·4 ± 0·05 Å in XV° increase, while the second set of 1·467 Å in XV° decrease, on going to the anions XVI^{-} and XV^{2-}. This is accompanied by a substantial increase in π-electron density in the cyclopentadienyl ring on going from XV° to XVI^{-} and XV^{2-} with total net-charges of −0·0330, −0·2283 and −0·3926, respectively.

The bond lengths of X, Table 4, are very similar to 1,1-diphenyl ethylene,[1a] except for bond "e" of the benzo group, which is directly linked to another "e" bond in X. The π-electron densities are uniform in the alternant hydrocarbon 1,1-diphenyl ethylene, but a polar exocyclic double bond "d" exists in X. The polarity of d is, however, much less than that of the bond d in fulvene I, due to the annelation of two benzo groups. The net π-charge of the exocyclic carbon in fulvene I, +0·0762 is over twice the +0·0317 of the exocyclic carbon in X.

The polarity of the exocyclic bond in X enables 6-bromofulvene to react with Grignard reagents,[27] and 9-benzal fluorene XV to act as an acceptor in a Michael reaction with a fluorenyl anion.[5]

The electron-withdrawing power of the cyclopentadienyl ring is transmitted through the extended vinylic bridge in XI, Table 4. A polar vinyl bond "y" in XI results in π-electron densities of 0·9885 at C-16 and 1·0048 at C-15. Thus the nucleophilic dialkylamines add to C-16 in XI.[5]

Polarographic reduction of 9-benzal fluorene XV with two electron up-take, results in the formation of the dianion XV^{2-}, which then reacts with acrylonitrile in a fast reaction at C-9,[19] with the highest net π-charge (−0·2959) in the dianion. XV^{2-} has a higher SECC than its neutral precursor, which might facilitate the ease of reduction. The well-known reaction of alkali metals with fulvenes[5] further illustrates the stability of the dianion.

C. *Heptafulvenes*

I. 8-*Vinyl heptafulvene* XVIII

The NMR and IR data for XVIII, in comparison with 8,8-dicyano heptafulvene and tropone, lead to the conclusion that the dipolar resonance interactions are minor in the ground state of XVIII, and the extension of conjugation in this vinylogue of heptafulvene only confers a slight enhancement of stability over heptafulvene XVII.[28] The total π-charge of the tropylium ring in XVIII, +0·0483 indicates a small, 4·83%, dipolar resonance contribution. The slight increase of SECC values in XVIII (0·1997 eV) over the 0·1985 eV of XVII agrees with the NMR and IR results.

TABLE 5. BOND ENERGIES (eV) OF HEPTAFULVENES

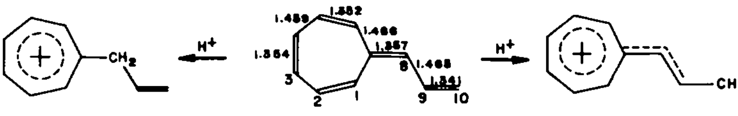
	Molecule		$E_{\pi b}^{CC}$	$E_{\sigma b}^{CC}$	SECC
XVII	Heptafulvene	C_8H_8	10·885	28·762	0·1985
XVIII	8-Vinylheptafulvene	$C_{10}H_{10}$	13·595	35·977	0·1997
XIX	3,4-Benzoheptafulvene	$C_{12}H_{10}$	17·112	47·473	0·2757
XX	1,2-Benzoheptafulvene	$C_{12}H_{10}$	17·125	47·493	0·2783
XXI	1,2.5,6-Dibenzoheptafulvene	$C_{16}H_{12}$	23·353	66·235	0·3137
XXII	8-vinyl Dibenzoheptafulvene	$C_{18}H_{14}$	26·095	73·419	0·3028
XXIII	8-Phenyl-1,2.3,4.5,6-tribenzo heptafulvene	$C_{26}H_{18}$	38·530	110·964	0·3385

Heptafulvalene shows no dipolar character because of the two symmetrical tropylium rings. However, dipolar resonances occur in both heptafulvene XVII and 8-vinyl heptafulvene XVIII, because of the presence of a single electron-releasing tropylium ring. The net π-charges are consistent with their similar NMR chemical shifts for the ring protons, which occur at approximately the same high field region.[28]

	XVII	XVIII	heptafulvalvene
C-1	+0·0179	+0·0207	+0·0254
C-2	−0·0015	−0·0012	−0·0113
C-3	−0·0050	+0·0065	+0·0053

The calculated vinylic bond lengths in 8-vinyl heptafulvene XVIII are identical with those of 6-vinyl fulvene IV, despite the vinyl groups being electron-withdrawing in XVIII and electron-releasing in IV.

Protonation of XVIII can take place either at C-8 or C-10, Fig. 6 on the exocyclic chain. These sites have net π-charges of −0·0391 and −0·0154 respectively, and would therefore favour $XVIII_a$ as the major protonated species on charge considerations. However, the calculated total energies of $XVIII_a$ and $XVIII_b$, 98·922 eV and 99·596 eV reveal $XVIII_b$ to be favourable by 15·5 kcal/mole. $XVIII_b$ is experimentally confirmed to be the only product.[28]



XVIII_a XVIII XVIII_b

FIG. 6 Protonation of 8-vinyl heptafulvene.

Thus all electrophilic attacks will occur at C-10, since π-electron delocalization is favoured in the transition state for $XVIII_b$ in this reaction and $XVIII_b$ is more stable.

Protonation cannot take place in the tropylium ring, because of the unfavourable energy loss which would be caused by disruption of the cyclic conjugation in the cation.

II. *Annelation and the loss of fulvenic character*

In the higher benzologues of heptafulvene, the incorporation of the double bonds of the tropylium ring into the aromatic benzo groups deprives these systems of their pseudo-aromatic character:[5] the exocyclic double bonds exist as normal olefins and do not react with nucleophiles. The UV spectra of XXI and XXIII contain no absorptions typical of fulvenic structures but resemble the corresponding substituted 1,1-diphenyl ethylene[5] and triphenyl ethylene.[29] This loss of fulvenic character by annelation is shown theoretically by the increase of SECC values and the decrease of the total net π-charges on the tropylium rings, as illustrated by Fig. 7. As the number, N, of benzo groups in increased, N(0 → 3) in the sequence XVII, XX, XXI and XXIII, the SECC values smoothly increase and approach the polyphenyl SECC limit.[1a] The total net π-charge of the tropylium ring gradually loses its polarity in the same direction.

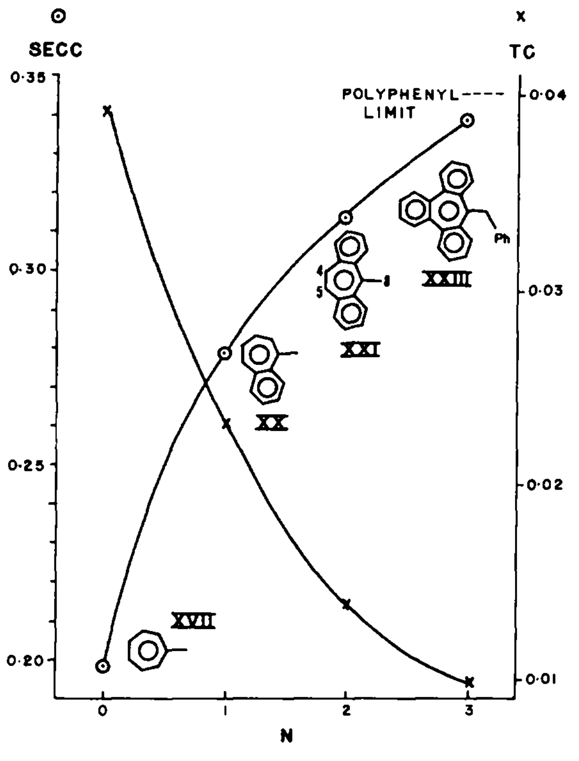


FIG. 7 SECC and total net π-charge of the tropylium ring, TC, as a function of benzo groups on the ring, N.

The extent of pseudo-aromaticity in a series of substituted dibenzo heptafulvenes has been analysed by NMR.[30] Aromaticity is measured by the H_4, H_5 proton absorptions and polarity from H_8 absorptions. These data are in agreement with the above conclusions.

CONCLUSION

The experimental chemical and physical properties of the fulvenes have been correlated with the calculated ground state properties of the fulvenes. Good agreements have been obtained in the predictions of reaction sites, geometry, molecular stability and dipolar resonance interaction.

By using the calculation results in these figures and tables, further correlations can be achieved depending on the nature of the specific problem.

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