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REMARKS ON THE ω-TECHNIQUE IN SIMPLE MO CALCULATIONS

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Abstract—The ω-technique of the simple MO method has been slightly modified with the following consequences: (1) the self-consistent charge distribution can be obtained with just a few iterations beyond the first, and (2) a convergent series is obtained for benzyl and related cations using $\omega = 1{\cdot}4$. Self-consistent ω-charge densities are given for the cations of several hydrocarbons and radicals; and the case of acenaphthylene cation, which does not lead to a self-consistent charge distribution, is discussed.

Streitwieser and others have shown that the ω-technique[1] is an effective method for incorporating some electron repulsion within the framework of the simple LCAO method. In a number of cases the ω-technique has led to improved energy levels for organic cations, and has thereby been applied to studies of charge distribution in carbonium ions,[2] and to predictions of ionization potentials[3,4] and reactivities[5] in aromatic hydrocarbons.

The usual application of the ω-technique is as follows: The charge densities obtained from a Hückel molecular orbital (HMO) treatment are used to calculate a new set of Coulomb integrals according to the linear adjustment:

$$\alpha_i = \alpha_0 + q_i\omega\beta_0$$

where q_i denotes the charge on the i-th atom, α_0 and β_0 refer to the standard Coulomb and bond integrals, respectively, and ω is a dimensionless parameter whose value is generally taken to be about 1·4. A new energy matrix is constructed from the α_i's, rediagonalization yields a new charge distribution, and the whole process is repeated until the charge system becomes self-consistent. In actual practice, the foregoing scheme may require a dozen or more iterations to approach self-consistency, or it may not converge at all. After ten iterations,[3] the charge on the central carbon of allyl cation still deviates by 0·006 from its final self-consistent value. In other cases such as benzyl and related cations, Streitwieser[3,4] notes that successive iteration gives progressive divergence using $\omega = 1{\cdot}4$, although convergence was obtained with smaller values of the parameter. He observed that the self-consistent charge densities

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[1] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists.* p. 115. Wiley, New York (1961).

[2] Ref. 1, Ch. 12.

[3] A. Streitwieser, Jr. and P. M. Nair, *Tetrahedron* **5**, 149 (1959).

[4] A. Streitwieser, Jr., *J. Amer. Chem. Soc.* **82**, 4123 (1960).

[5] A. Streitwieser, Jr., J. I. Brauman and J. B. Bush, *Tetrahedron* **19**, Suppl. 2, 379 (1963).

fall between those from the Hückel treatment and the first iteration, and found that a single iteration sufficed for the purposes of his ionization potential calculations.

Streitwieser *et al.*[5] have used an alternative procedure to estimate the self-consistent charge distribution and corresponding π-energy. Starting from a series expansion due to Coulson and Longuet-Higgins,[6] they relate δE and $\delta\alpha_s$ to the second approximation, and $\delta\alpha_s$ and δq_r to a first approximation. Introducing the effect of the ω-technique on these relations, they derive a set of simultaneous equations:

$$q_r = \left(\frac{1}{\omega} + \pi_{rr}\right) \delta\alpha_r + \sum_{s \neq r} \pi_{rs}\, \delta\alpha_s$$

where the π_{rs} are the atom–atom polarizabilities given, along with the q_r, by the HMO treatment. The preceding equations may be solved for the matrix of $\delta\alpha_s$-values, and, hence, for the changes in charge density and energy required by this ω-approximation

We have found that the latter procedure is obviated by a slight modification of the original version of the ω-technique. In our version the following advantages have been realized: (1) the self-consistent charge distribution (i.e., self-consistent to better than 0·001 in all q_i) can be obtained with just a few iterations beyond the first, and (2) a convergent series is obtained for the benzyl and related cations employing $\omega = 1{\cdot}4$. This modified ω-technique simply exploits the fact that the charges calculated in each successive iteration tend to oscillate about their final self-consistent values. The zero-th (HMO) and first iterations are performed exactly as in the original application. However, the charge densities derived from these iterations, $q_i^{(0)}$ and $q_i^{(1)}$, are then averaged:

$$Q_i^{(1)} = (q_i^{(0)} + q_i^{(1)})/2$$

and the $Q_i^{(1)}$ become the input charges for the next cycle. The charge densities resulting from the second iteration, $q_i^{(2)}$, are averaged with the preceding $Q_i^{(1)}$ to form $Q_i^{(2)}$, and the third iteration is initiated. In general:

$$\alpha_i = \alpha_0 + Q_i^{(n)}\, \omega\beta_0 \qquad (n + 1)\text{-th iteration}$$

where

$$Q_i^{(n)} = (q_i^{(n)} + Q_i^{(n-1)})/2.$$

This process is continued until the $q_i^{(n+1)}$ differ from $Q_i^{(n)}$ for all atoms i by less than some predetermined amount (0·001 in this work). Thus, the oscillation of the calculated charges at each step becomes damped, and self-consistency has generally been attained on the fourth iteration with the examples attempted so far. (The fifth iteration, where required, involves only a possible minor adjustment in the third decimal place.) Further, the use of "averaged" charge densities at each iteration maintains the term $q_i\omega\beta_0$ ($\omega = 1{\cdot}4$) within the range of values necessary for convergence in the benzyl cation problem, and we have not had to resort to smaller values of ω. Table 1 shows the results of successive iterations in the benzyl cation calculation using the present method.

In Fig. 1 we have summarized the self-consistent ω-charge densities for the cations

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[6] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* **A191**, 39 (1947).

of thirty-two hydrocarbons and hydrocarbon radicals. Fig. 2 depicts the same information for three non-alternant hydrocarbons, which have uneven charge distributions. These charge densities should find useful application in various contexts. In particular, those given for the molecule cations of even systems may enable one to predict the effects of various substituents on ionization potentials or their equivalent.[7]

The energies of the cations and their parent compounds may be expressed in the form: $E_\pi = n\alpha_0 + M\beta_0$ (n is the total no. of π-electrons) and the coefficients of β_0 are listed in Table 2. In all the molecular orbital calculations, the bond integrals between adjacent carbons were assumed to be $1{\cdot}00\beta_0$ except as noted at the bottom of Table 2. The difference in bonding energy between the positive ion and the neutral molecule corresponds to the ionization potential:

$$I = E\,(\text{cation}) - E\,(\text{hydrocarbon}) = -\alpha_0 + \chi\beta_0$$

As may be seen from Table 2, our self-consistent χ_ω is only slightly larger in every case than χ obtained from a single iteration. Re-evaluation of Streitwieser's linear correlation[3,4] between χ and I_{exp}, using χ_ω from this work and the same electron impact data, leads to calculated ionization potentials which are essentially unchanged from those reported by him. His use of χ from a single iteration has thus been vindicated. We have taken this opportunity, however, to establish a new correlation based on the more recent electron impact measurements of Lossing *et al.*, and on some available photoionization results. The correlation is based on the first twelve entries of Table 2, of which five are special cases included so as to achieve a wide range of eV values. For methyl radical, $\chi \equiv 0$; for the cases of ethylene, benzene, cyclopentadienyl and tropylium, one starts with an even distribution of positive charge in the cation, and obtains the "self-consistent" χ from a single iteration. Our least-squares result is presented in Eq. (1), in which the uncertainties in slope and intercept are given as the standard deviations:

$$I(\text{eV}) = (-1{\cdot}947 \pm 0{\cdot}079)\chi_\omega + 9{\cdot}681 \pm 0{\cdot}070. \tag{1}$$

The average deviation between I_{calc} and I_{exp} for the twelve examples is about 0·1 eV; with the exception of naphthalene, the agreement is remarkably good. All our values of χ_ω in Table 2 have been converted to I_{calc} via Eq. (1).

Our modified ω-technique should facilitate the calculation of self-consistent ω-localization energies,[5,8] L_ω, which are a measure of the π-energy change between the aromatic hydrocarbon and the σ-complex intermediate in aromatic substitution. Two examples are given below, employing the results in Table 2:

$$\begin{aligned} L_\omega\,(\text{benzene}) &= M\,(\text{benzene}) - M_\omega\,(\text{pentadienyl cation}) \\ &= 8{\cdot}000 - 6{\cdot}509 = 1{\cdot}491\ (1{\cdot}490^{5}) \end{aligned}$$

$$\begin{aligned} L_\omega\,(\text{naphthalene, pos. 1}) &= M\,(\text{naphthalene}) - M_\omega\,(\text{cinnamyl cation}) \\ &= 13{\cdot}683 - 12{\cdot}511 = 1{\cdot}172\ (1{\cdot}180^{5}) \end{aligned}$$

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[7] A. Streitwieser, Jr., *Ionization Potentials in Organic Chemistry* in *Progress in Physical Organic Chemistry* Vol. 1, p. 1. Interscience, New York (1963).

[8] Ref. 1, p. 335.

Acenaphthylene cation (with $\beta_{1,2} = 1{\cdot}07\beta_0$ and $\beta_{1,9} = \beta_{2,10} = 0{\cdot}9\beta_0$) has not proved amenable to our modified ω-technique, and the reason for this is readily analyzed. After four iterations the charge densities of acenaphthylene cation appear to be converging to the approximate values:

$$\begin{array}{llll} q_1 = 0{\cdot}168 & q_3 = 0{\cdot}094 & q_4 = 0{\cdot}035 & q_5 = 0{\cdot}099 \\ q_9 = 0{\cdot}041 & q_{11} = 0{\cdot}084 & q_{12} = 0{\cdot}042. & \end{array} \quad (2)$$

Yet, the charge distribution obtained from the fifth iteration is entirely different, and the equality between q_1 and q_2, q_9 and q_{10}, etc. is lost despite the demands of symmetry. The difficulty is traced to the fact that the highest two occupied orbitals, which are close to degeneracy in the HMO approximation ($m_{m-1} - m_m = 0{\cdot}0721$, where $\alpha_0 + m_m\beta_0$ is the energy of the highest occupied orbital), have become completely degenerate on the fifth iteration. The situation now resembles that of benzene, coronene, and triphenylene cations in the HMO treatment, where, in principle, a variety of π-electron distributions are possible. At this juncture, we could follow Streitwieser's suggestion[4] and seek convergence for acenaphthylene cation with values of ω less than 1·4. Self-consistent charge densities corresponding to $\omega = 1{\cdot}4$ may then be defined by extrapolation. If we employ $\omega = 1{\cdot}0$ and 1·2, convergence is virtually obtained after five iterations. Extrapolation to $\omega = 1{\cdot}4$ essentially yields the charge distribution given in (2). Of the several examples in Table 2 which led to convergence, the smallest energy separation of the highest bonding orbitals, in the zero approximation, occurs in 3,4-benzphenanthrene. In this case, $m_{m-1} - m_m = 0{\cdot}0946$, and the latter drops to 0·0483 when self-consistency has been attained.

TABLE 1. SUCCESSIVE ITERATIONS FOR THE BENZYL CATION ($\omega = 1{\cdot}4$)

Iteration no.	q_1	q_2	q_3	q_4	q_7
0 (HMO)	0·000	0·143	0·000	0·143	0·571
1	0·189	0·127	0·094	0·200	0·170
2	0·076	0·132	0·061	0·135	0·402
3	0·084	0·137	0·054	0·153	0·382
4	0·084	0·135	0·054	0·153	0·384

TABLE 2. IONIZATION POTENTIALS OF π-SYSTEMS, USING SELF-CONSISTENT CHARGES ($\omega = 1\cdot4$)

Compound	Iterations required	M compound	M_ω cation	χ_ω this work	χ single iter.[a]	$I_{ca}^{(eV)}$ this work[b]	$I_{exp}^{(eV)}$ [c]
Methyl	*d*				—	9·68	9·82 (PI)[e]
Ethylene[i]	*d*				−0·37	10·40	10·516 (PI)[f]
Benzene	*d*				0·167	9·36	9·245 (PI)[f]
Cyclopentadienyl	*d*				0·502	8·70	8·69 (EI)[g]
Tropylium	*d*				1·645	6·48	6·60 (EI)[g]
Allyl	4	2·828	3·656	0·827	0·785	8·07	8·16 (EI)[h]
Benzyl	4	8·721	9·768	1·047	1·001	7·64	7·76 (EI)[h]
Benzhydryl	4	17·301	18·498	1·198	1·164	7·35	7·32 (EI)[h]
α-Naphthylmethyl	5	14·495	15·645	1·150		7·44	7·35 (EI)[h]
β-Naphthylmethyl	6	14·427	15·536	1·109		7·52	7·56 (EI)[h]
Naphthalene	4	13·683	14·289	0·606	0·592	8·50	8·12 (PI)[f]
Butadiene[j]	3	4·651	4·969	0·319	0·310	9·06	9·07 (PI)[f]
Pentadienyl	4	5·464	6·509	1·045	1·018	7·65	
Styrene[k]	5	10·484	10·943	0·459	0·445	8·79	
Phenanthrene	4	19·448	20·112	0·664	0·653	8·39	
Anthracene	4	19·314	20·166	0·852	0·839	8·02	
Tetracene	4	24·931	25·925	0·994	0·982	7·75	
Stilbene[l]	5	18·848	19·546	0·698	0·687	8·32	
Biphenyl[m]	4	16·293	16·817	0·525	0·517	8·66	
β-Phenylallyl	5	11·190	12·054	0·864	0·798	8·00	
Cinnamyl	4	11·385	12·511	1·126	1·094	7·49	
Fulvene[n]	5	7·488[q]	7·938	0·450	0·385	8·81	
Triphenylmethyl	5	25·800	27·061	1·261	1·239	7·23	
Azulene[o]	5	13·207[q]	14·033	0·825	0·74	8·08	
Perinaphthenyl	5	17·827	19·063	1·236	1·217	7·28	
Pyrene	4	22·505	23·342	0·836	0·826	8·05	
Chrysene	4	25·192	25·970	0·778		8·17	
Fluoranthene[p]	4	22·340[q]	22·996	0·656	0·632	8·40	
1,2-Benzanthracene	4	25·101	25·935	0·834		8·06	
Perylene	4	28·245	29·206	0·961		7·81	
1,2-Benzpyrene	4	28·222	29·151	0·930		7·87	
1,2,5,6-Dibenzanthracene	4	30·880	31·715	0·835		8·06	
Anthanthrene	4	31·253	32·267	1·014		7·71	
3,4-Benzphenanthrene	4	25·188	25·918	0·730	0·721	8·26	
Picene	4	30·943	31·758	0·815		8·09	
1-Phenylbutadiene[r]	5	13·018	13·678	0·660	0·648	8·40	
2-Phenylbutadiene[s]	5	12·970	13·538	0·568	0·545	8·58	

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[a] Taken from Refs. 3 and 4.

[b] Calculated from Eq. (1).

[c] Experimental data used to derive Eq. (1); EI = electron impact, PI = photoionization.

[d] These are special cases included in the derivation of Eq. (1). See discussion in text.

[e] F. A. Elder, C. Giese, B. Steiner and M. Inghram, *J. Chem. Phys.* **36**, 3292 (1962).

[f] K. Watanabe, *J. Chem. Phys.* **26**, 542 (1957).

[g] A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr. and F. P. Lossing, *J. Amer. Chem. Soc.* **82**, 5593 (1960).

[h] A. G. Harrison and F. P. Lossing, *J. Amer. Chem. Soc.* **82**, 1052 (1960).

[i] $\beta_{1,2} = 1\cdot07\,\beta_0$

[j] $\beta_{1,2} = \beta_{3,4} = 1\cdot07\,\beta_0$; $\beta_{2,3} = 0\cdot91\,\beta_0$.

[k] $\beta_{7,8} = 1\cdot07\,\beta_0$; $\beta_{1,7} = 0\cdot91\,\beta_0$.

[l] $\beta_{7,8} = 1\cdot07\,\beta_0$; $\beta_{1,7} = \beta_{8,9} = 0\cdot91\,\beta_0$.

[m] $\beta_{1,7} = 0\cdot87\,\beta_0$.

[n] $\beta_{1,2} = \beta_{1,5} = \beta_{3,4} = 0\cdot9\,\beta_0$; $\beta_{1,6} = \beta_{2,3} = \beta_{4,5} = 1\cdot07\,\beta_0$.

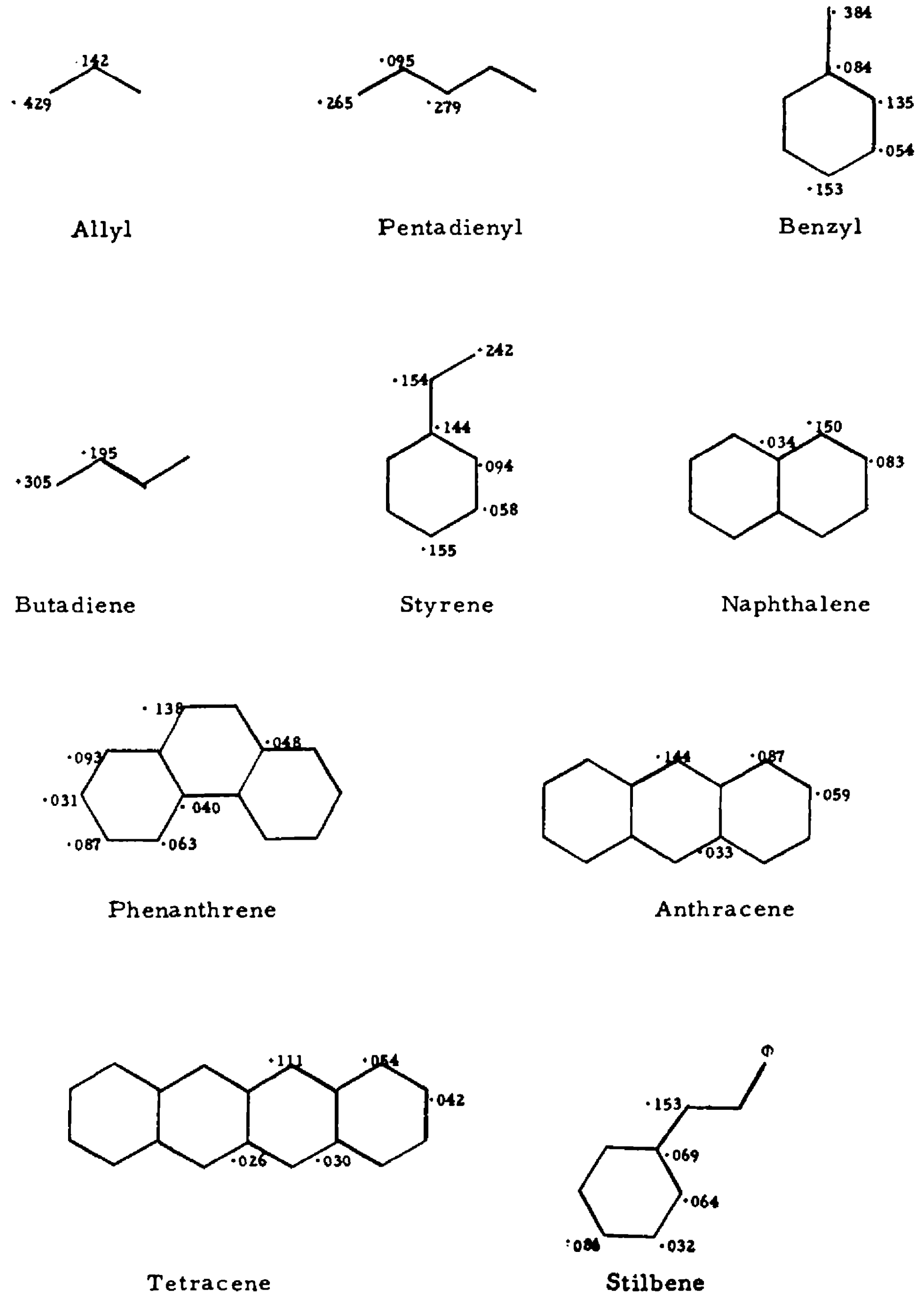
[o] $\beta_{9,10} = 0\cdot9\,\beta_0$.

[p] $\beta_{1,14} = \beta_{8,9} = 0\cdot9\,\beta_0$.

[q] Includes energy correction, ΔE_ω, from application of ω-technique to uneven charge distribution of non-alternant hydrocarbon (Fig. 2).

[r] $\beta_{7,8} = \beta_{9,10} = 1\cdot07\,\beta_0$; $\beta_{1,7} = \beta_{8,9} = 0\cdot91\,\beta_0$.

[s] $\beta_{7,8} = \beta_{9,10} = 1\cdot07\,\beta_0$; $\beta_{1,8} = \beta_{8,9} = 0\cdot91\,\beta_0$.



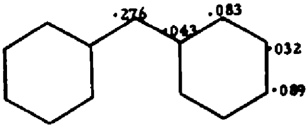
Allyl Pentadienyl Benzyl

Butadiene Styrene Naphthalene

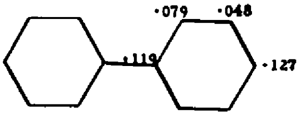
Phenanthrene Anthracene

Tetracene **Stilbene**

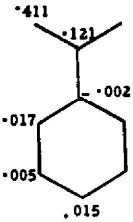
FIG. 1. Self-consistent charge distributions for various cations (by ω-technique, ω = 1·4).



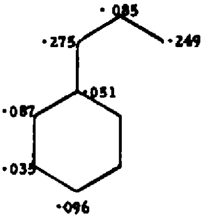
Benzhydryl



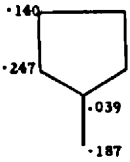
Biphenyl



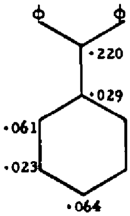
β-Phenylallyl



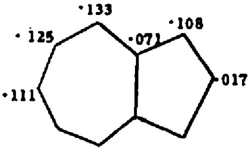
Cinnamyl



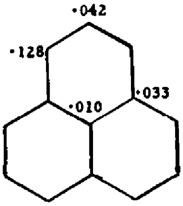
Fulvene



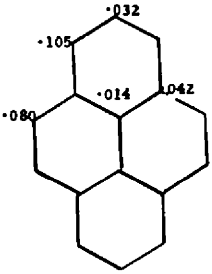
Triphenylmethyl



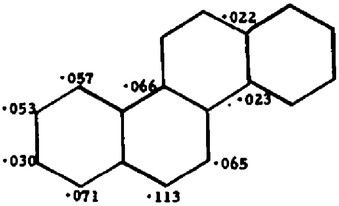
Azulene



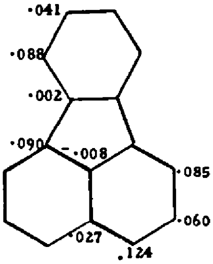
Perinaphthenyl



Pyrene

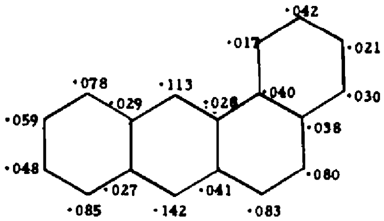


Chrysene.

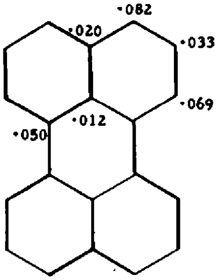


Fluoranthene

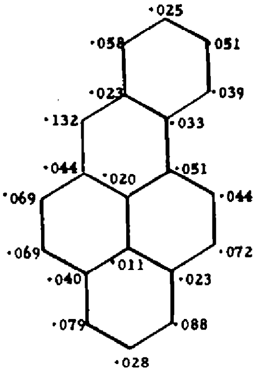
FIG. 1 (contd.)



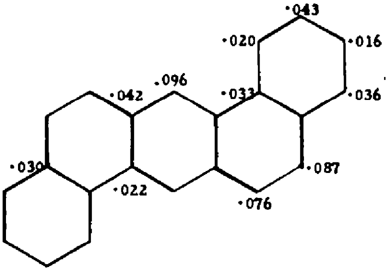
1, 2-Benzanthracene



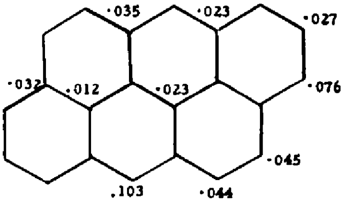
Perylene



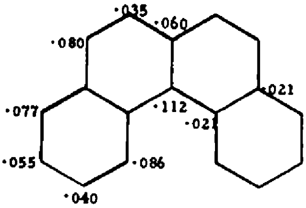
1, 2-Benzpyrene



1, 2, 5, 6-Dibenzanthracene

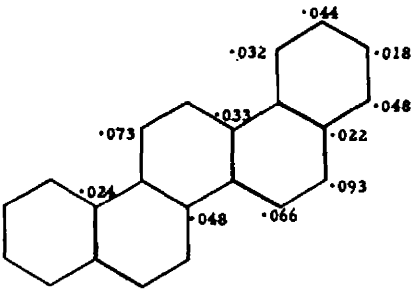


Anthanthrene

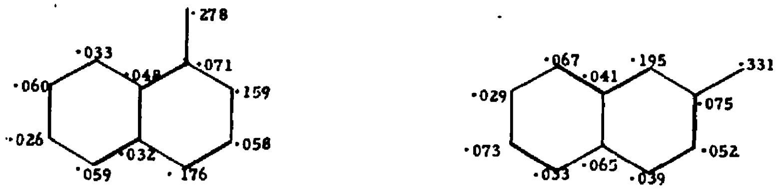


3, 4-Benzphenanthrene

FIG. 1 (contd.)



Picene



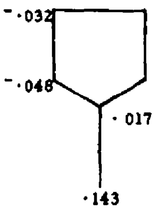
α-Naphthylmethyl

β-Naphthylmethyl

1-phenylbutadiene

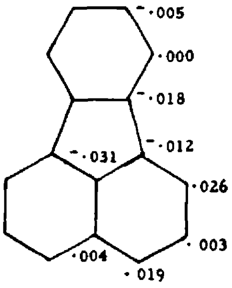
2-phenylbutadiene

FIG. 1 (contd.)



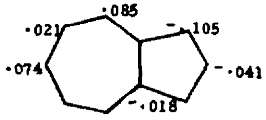
Fulvene

$\Delta E_\omega = -.052\ \beta_0$



Fluoranthene

$\Delta E_\omega = -.008\beta_0$



Azulene

$\Delta E_\omega = -.080\ \beta_0$

Fig. 2. Self-consistent charge distributions for non-alternant hydrocarbons (by ω-technique, $\omega = 1{\cdot}4$).