205. *Structure and Properties of Mesomeric Systems. Part I. Resonance Energies.*

By David Peters.

A simple perturbation method is used to derive the Hückel resonance energies of a large number of mesomeric hydrocarbons from the resonance energies of the corresponding straight-chain polyenes.

The Hückel L.C.A.O. molecular-orbital method,[1] despite its shortcomings,[2] remains the only one of wide applicability in problems of structure, chemical reactivity, and ultraviolet spectra of mesomeric systems. The more sophisticated methods, successful though they are with a small group of molecules, fail to provide the organic chemist with the versatile method required in practice. The Hückel method itself, however, is not always free from arithmetical complexity and there is now described a perturbation method whereby the resonance energy of mesomeric hydrocarbons can be determined with a minimum of labour.

Conceptually, the method is derived from Dewar and Pettit's demonstration [3] that the properties of mesomeric hydrocarbons can be derived from those of the cyclic polyenes, the formation of the cross-links being treated as a perturbation. The latter method is limited, however, in that the highly condensed benzenoid hydrocarbons (pyrene, perylene, and coronene), the vinyl substituted benzenoids (styrene, stilbene), and the non-alternant hydrocarbons having exocyclic bonds (fulvene, fulvalene) are all outside of its scope. A simple method for the hydrocarbons of the last category would be particularly useful owing to the complexity of their normal secular equations. Lacking symmetry, such hydrocarbons present formidable problems in calculation.

A variant on Dewar and Pettit's cyclic-polyene method is now described, the properties of the mesomeric hydrocarbons being derived from those of the open-chain linear polyenes. Most hydrocarbons in the above three classes then come within range, the few exceptions being listed below. Perturbation methods, in addition to eliminating the labour involved in computation, also bring out relations between classes of hydrocarbons which are less evident from the results obtained by solution of the secular equations.

Method.—The mathematical properties of the linear polyenes, investigated by Lennard-Jones [4] and by Coulson,[5] are required. The energy (e_j) of the jth molecular orbital (ψ_j) of a linear polyene (C_nH_{n+2}) is given [1] by

$$e_j = 2\beta \cos [j\pi/(n + 1)], j = 1, 2, \ldots . n \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

and the atomic-orbital coefficient (c_{rj}) of the jth molecular orbital at the rth carbon atom by

$$c_{rj} = [2/(n + 1)]^{\frac{1}{2}} \sin [rj\pi/(n + 1)] \quad . \quad . \quad . \quad . \quad . \quad . \qquad (2)$$

The occupied molecular orbitals are $j = 1, 2 \ldots . n/2$ and β is the standard carbon–carbon bond resonance integral, overlap being neglected.

Now consider the formation of a cross-link between atoms r and s. Denote the change in the Hamiltonian of the system by δH and the energy of the perturbed jth molecular-orbital by e_j', then first-order perturbation theory gives

$$e_j' = e_j + \int \psi_j \, . \, \delta H \, . \, \psi_j \, . \, d\tau \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

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[1] Hückel, *Z. Physik*, 1930, **60**, 423; 1931, **70**, 204; 1931, **72**, 310; 1932, **76**, 628.
[2] Coulson and Dewar, *Discuss. Faraday Soc.*, 1947, **2**, 54.
[3] Dewar and Pettit, *J.*, 1954, 1617.
[4] Lennard-Jones, *Proc. Roy. Soc.*, 1937, *A*, **158**, 280.
[5] Coulson, *ibid.*, 1938, *A*, **164**, 383.

Expand the ψ_j's in terms of the constituent atomic orbitals (ϕ_s) from $\sum_r c_{rj} \,.\, \phi_r = \psi_j$ and suppose that the only non-vanishing terms in the expansion are $\phi_r \,.\, \delta\mathrm{H} \,.\, \phi_s(\beta_{rs})$ [3, 6, 7] then

$$e_j' = e_j + 2c_{rj}c_{sj} \,.\, \beta_{rs} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

i.e.,

$$E_{\mathrm{a}} = 2\sum^{\mathrm{occ}} e_j' = E_{\mathrm{l.p.}} + 4\beta \sum_{j=1-(n/2)} \,.\, c_{rj}c_{sj} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (5)$$

where $E_{\mathrm{l.p.}}$ and E_{a} are the total π-electron energies of the linear polyene and the cross-linked polyene (aromatic) respectively. All β's are taken equal. From eqns. (2) and (5)

$$E_{\mathrm{a}} = E_{\mathrm{l.p.}} + \frac{8\beta}{n+1} \sum_{j=1-(n/2)} \left(\sin\frac{rj\pi}{n+1} \,.\, \sin\frac{sj\pi}{n+1} \right) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

$$= E_{\mathrm{l.p.}} + \frac{4\beta}{n+1} \sum_{j=1-(n/2)} \left(\cos\frac{(r-s)j\pi}{n+1} - \cos\frac{(r+s)j\pi}{n+1} \right) \quad . \quad . \quad . \qquad (7)$$

and since

$$\sum_{p=1-q} \cos(p\theta) = \sin\left[(q+\tfrac{1}{2})\theta\right] \Big/ \left(2\sin\frac{\theta}{2}\right) - \tfrac{1}{2} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

$$E_{\mathrm{a}} = E_{\mathrm{l.p.}} + \frac{2\beta}{n+1}\left(\frac{\sin[(r-s)\pi/2]}{\sin\{(r-s)\pi/[2(n+1)]\}} - \frac{\sin[(r+s)\pi/2]}{\sin\{(r+s)\pi/[2(n+1)]\}} \right) \,. \qquad (9)$$

First-order perturbations being additive, the formation of several cross-links is given by the sum of each determined from eqn. (9).

Before we proceed to explicit calculations, certain interesting general results can be obtained from eqn. (9). If $(r - s)$ and $(r + s)$ are even integers, the expression in large parentheses vanishes for all such values of r, s, and n. Physically, this means that cross-linking of atoms of like parity * does not change the π-electron energy of the system (see p. 1027). The $(4\gamma + 2)$ rule of aromaticity[1] can also be deduced from eqn. (9) as follows. First consider the denominators in the term in braces. Both $(r - s)$ and $(r + s)$ are less than $2(n + 1)$ and both denominators are thus positive. Now let $s = 1$. If $r = (4\gamma + 2)$, then $(r - s) = 4\gamma + 1$ and the first sine term in the braces is positive, the second negative. The resonance energy is thus high. When $r = 4\gamma$, however, it is easily seen that the first sine term is negative, the second positive, and the resonance energy is low.

The π-electron energy ($E_{\mathrm{l.p.}}$) of the polyene must be computed. From eqn. (1),

$$E_{\mathrm{l.p.}} = 4\beta \sum_{j=1-(n/2)} \cos[j\pi/[\mathrm{n}+1)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

$$= 2\beta \operatorname{cosec}\{\pi/[2(n+1)]\} - 2\beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

The resonance energy of the cross-linked aromatic hydrocarbon is then

$$\mathrm{R.E_a.} = 2\beta \operatorname{cosec}\{\pi/[2(n+1)]\} - (n+2)\beta$$
$$+ \frac{2\beta}{n+1}\left(\frac{\sin[(r-s)\pi/2]}{\sin\{(r-s)\pi/[2(n+1)]\}} - \frac{\sin[(r+s)\pi/2]}{\sin\{(r+s)\pi/[2(n+1)]\}} \right) \,. \qquad (12)$$

It is convenient to classify the mesomeric hydrocarbons in three groups: (*a*) alternants,

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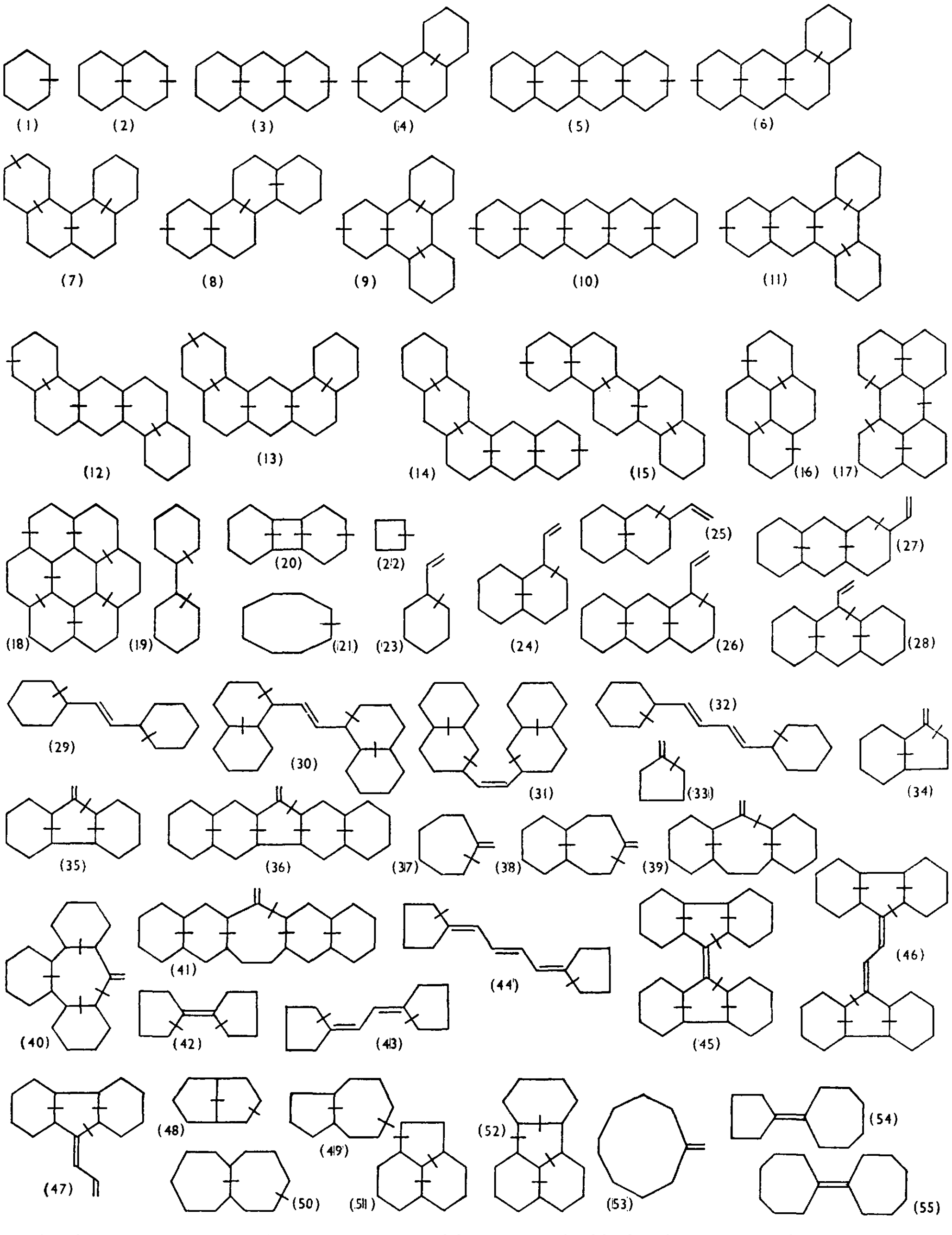
* Atoms are of like parity when both are starred or unstarred.

[6] Longuet-Higgins and Sowden, *J.*, 1952, 1404.

[7] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.



All these compounds are formally aromatic, although the double bonds are omitted for convenience. The cross-lines represent the points at which the rings are regarded as being " closed " from the linear polyenes.

(*b*) vinyl derivatives of alternants, (*c*) non-alternants. In the Table (all quantities in units of β) are listed the resonance energies (R.E.$_a$) calculated by the perturbation methods [eqn. (12)], the resonance energies (R.E.$_{s.e.}$) obtained by solution of the secular equations,[8]

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[8] Pullman and Pullman, " Les Théories Electroniques de la Chimie Organique," Masson et Cie., Paris, 1952, p. 226; p. 632 *et seq.*

and the errors in the estimated resonance energies. The manner of division of the aromatic hydrocarbons into polyenes is shown.

Discussion.—From the Table, it is clear that the resonance energies calculated by the perturbation method differ from those calculated from the secular equations. Nevertheless, there is a linear relation between the two sets of resonance energies, and this is the same situation as that found by Dewar and Pettit[3] in their cyclic-polyene method.

Hydrocarbon	R.E.$_a$	R.E.$_{s.e.}$	Corr. R.E.	Error
Class (*a*) (alternants).				
Benzene (1)	1·59	2·00	2·00	0·00
Naphthalene (2)	2·88	3·68	3·73	0·05
Anthracene (3)	4·10	5·31	5·36	0·05
Phenanthrene (4)	3·83	5·45	5·40	0·05
Naphthacene (5)	5·28	6·93	6·94	0·01
1 : 2-Benzanthracene (6)	5·07	7·10	7·30	0·20
3 : 4-Benzophenanthrene (7)	5·08	7·19	7·31	0·12
Chrysene (8)	5·07	7·19	7·30	0·11
Triphenylene (9)	4·94	7·27	7·10	0·17
Pentacene (10)	6·45	8·54	8·51	0·03
1 : 2-3 : 4-Dibenzanthracene (11)	6·19	8·94	9·01	0·07
1 : 2-5 : 6-Dibenzanthracene (12)	6·10	8·88	8·87	0·01
1 : 2-7 : 8-Dibenzanthracene (13)	6·10	8·88	8·87	0·01
Pentaphene (14)	6·10	8·76	8·87	0·11
Picene (15)	6·10	8·94	8·87	0·07
Pyrene (16)	4·55	6·51	6·50	0·01
Perylene (17)	5·78	8·25	8·38	0·13
Coronene (18)	7·07	10·57	10·35	0·22
Diphenyl (19)	3·55	4·38	4·63	0·25
Diphenylene (20)	2·04	4·51	—	—
*cyclo*Octatetraene (21)	1·06	1·66	—	—
*cyclo*Butadiene (22)	—0·42	0·00	—	—
Class (*b*) (vinyl derivatives of alternants).				
Styrene (23)	2·04	2·42	2·42	0·00
1-Vinylnaphthalene (24)	3·04	4·12	3·99	0·13
2-Vinylnaphthalene (25)	3·02	4·10	3·96	0·14
1-Vinylanthracene (26)	4·11	5·74	5·67	0·07
2-Vinylanthracene (27)	4·09	5·72	5·64	0·08
9-Vinylanthracene (28)	4·25	5·79	5·89	0·10
Stilbene (29)	4·07	4·88	5·61	0·73
1 : 2-Di-1′-naphthylethylene (30)	6·16	8·30	8·89	0·59
1 : 2-Di-2′-naphthylethylene (31)	6·08	8·25	8·76	0·51
1 : 4-Diphenylbutadiene (32)	4·59	5·40	6·42	1·02
Class (*c*) (non-alternants).				
Fulvene (33)	0·99	1·47	1·37	0·10
Benzofulvene (34)	2·51	3·33	3·31	0·02
Dibenzofulvene (35)	4·01	5·22	5·23	0·01
Dinaphthofulvene (36)	6·59	8·60	8·54	0·06
Heptafulvene (37)	1·52	1·99	2·04	0·05
Benzoheptafulvene (38)	3·02	3·84	3·97	0·13
Dibenzoheptafulvene (39)	4·54	5·73	5·91	0·18
Tribenzoheptafulvene (40)	5·96	7·62	7·73	0·11
Dinaphthoheptafulvene (41)	7·12	9·41	9·21	0·20
Fulvalene (42)	2·05	2·78	2·72	0·06
Di-6-fulvenyl (43)	2·59	3·47	3·42	0·05
1 : 2-Di-6′-fulvenylethylene (44)	3·13	4·09	4·10	0·01
1 : 2-Bisdiphenylene-ethylene (45)	7·97	10·52	10·31	0·21
1 : 4-Bisdiphenylenebutadiene (46)	8·51	11·07	10·99	0·08
Vinyldibenzofulvene (47)	4·52	5·76	5·88	0·12
Pentalene (48)	1·06	2·46	1·46	1·00
Azulene (49)	2·42	3·36	3·20	0·16
Heptalene (50)	2·28	3·62	3·02	0·60
Acenaphthylene (51)	3·40	4·62	4·45	0·17
Fluoranthene (52)	4·89	6·50	6·36	0·14

Greater accuracy is possible if slightly different equations are used for each class of hydrocarbon and the best straight lines are:

$$\text{Class }(a)\begin{cases}\text{R.E.}_{\text{s.e.}} = 1{\cdot}34\ \text{R.E.}_{\text{a}} - 0{\cdot}13 \text{ for linear acenes} & (13)\\ \text{R.E.}_{\text{s.e.}} = 1{\cdot}53\ \text{R.E.}_{\text{a}} - 0{\cdot}46 \text{ for bent acenes} & (14)\end{cases}$$

$$\text{Class }(b)\quad \text{R.E.}_{\text{s.e.}} = 1{\cdot}57\ \text{R.E.}_{\text{a}} - 0{\cdot}78 \qquad (15)$$

$$\text{Class }(c)\quad \text{R.E.}_{\text{s.e.}} = 1{\cdot}28\ \text{R.E.}_{\text{a}} + 0{\cdot}1 \qquad (16)$$

The corrected resonance energies reported in the fourth column of the Table are calculated from these equations.

The resonance energies of the common benzenoid hydrocarbons containing six-membered rings are estimated accurately. Different equations are required for the linear and the bent acenes, and this situation is again identical with that found in the cyclic-polyene method. Benzene is correctly found to be common to both lines. Pyrene, perylene, and coronene are of particular interest as they cannot be reached with the cyclic-polyene method. Diphenyl is a representative of another class of hydrocarbon whose resonance energy cannot be obtained from the cyclic-polyene approach, and the current treatment is of immediate interest for its analogues (dinaphthyl, etc.) where symmetry is rarely of help in reducing the order of the conventional secular equations. The points for *cyclo*octatetraene, *cyclo*butadiene, and diphenylene do not fall on the same line as those of the six-membered ring compounds and more data on the secular equation resonance energies of compounds of this type are required before the reliability of the perturbation method can be examined fully.

The resonance energies of the vinyl-substituted aromatic hydrocarbons are accurately reproduced and the perturbation method should find immediate application in predicting the position of Diels–Alder attack in molecules of this kind.[9] The disubstituted ethylenes evidently require a characteristic line since they do not fall on the line generated by the vinyl hydrocarbons, as is shown by their large deviations.

The most useful result of the linear-polyene method is the excellent behaviour of the non-alternant hydrocarbons. The tedious task of solving their secular equations can now be avoided and, in fact, calculation of their resonance energies is particularly easy owing to the fact that cross-links between atoms of like parity do not alter the π-electron energy of the system. The linear-polyene method exaggerates the higher resonance energy of azulene as compared with pentalene and heptalene but fortunately the cyclic-polyene method is available here and should be used for quantitative work.

It is noticeable that no rule analogous to the $(4\gamma + 2)$ rule of aromaticity for the cyclic polyenes emerges for the non-alternant hydrocarbons having exocyclic bonds. The resonance energies of the series fulvene (**33**), heptafulvene (**37**), and nonafulvene (**53**) and of the series (**42**), (**54**), and (**55**) are those of the corresponding open-chain polyenes and thus increase regularly with increasing number of carbon atoms.

There is a possibly ambiguity in the linear-polyene method in that there is often more than one way of dividing the cross-linked aromatic hydrocarbon into a linear polyene. No formal rule governing the manner of division can be given but when the larger members of a given class have only one possible mode of division, the smaller members should be divided in as similar a manner as possible. When only one or two representatives of a given type of hydrocarbon are known (*e.g.*, acenaphthylene, fluoranthene) the results must be accepted with caution until the reliability of the perturbation method can be checked on a larger number of representatives.

It is not, of course, correct to infer that the equality of the resonance energies of some of the non-alternant hydrocarbons and the corresponding cyclic or linear polyene leads to equality of chemical reactivity. The ability of these non-alternant hydrocarbons to be

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[9] R. D. Brown, *J.*, 1950, 691, 2730; 1951, 1612, 3129.

prepared is primarily a function of their chemical reactivity, and there is no simple connection between the latter property and the resonance energy. The point is taken up in detail in the following paper.

For obvious geometric reasons, certain mesomeric hydrocarbons are outside the scope of both the cyclic and the linear polyene methods. The more numerous of these exceptions are hydrocarbons containing either rings having more than one exocyclic bond, the exocyclic bonds not being joined elsewhere in the molecule (*e.g.*, *m*- and *p*-terphenyl), or a carbon atom bonded to three other carbon atoms not joined elsewhere in the molecule (*e.g.*, 1 : 1-diphenylethylene). These exceptions are comparatively unimportant and are not examined further.

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