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Valency-Bond Studies of Some Conjugated Hydrocarbons

V. Naphthalene

By

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A valency bond study of naphthalene has been made in which, assuming the molecular symmetry to be D_{2h}, successively more canonical structures up to the total of 42 have been included. All four chemically differentiable bonds have been independently varied in length to find the minimum molar energy and thus the equilibrium ground state molecular structure. The result is remarkably close to the observed structure and also agrees well with those deduced by other types of calculation.

Une étude du naphtalène a été faite par la méthode de la mésomérie. On a supposé que la symétrie soit D_{2h} et on a compris successivement de plus en plus formules canoniques jusqu'au total de 42. On a fait varier indépendamment les longueurs de toutes les quatre liaisons qu'on peut distinguer chimiquement afin qu'on peut estimer l'énergie moléculaire minimale et ainsi la structure stable de la molécule en état fondamental. Le résultat s'approche remarquablement de la structure observée et s'accorde bien à celles qu'on a déterminées par des autres types de calculs.

Im Rahmen der Methode der Valenzstrukturen wurde eine Untersuchung des Naphthalins durchgeführt, wobei als Symmetriegruppe des Moleküls D_{2h} angenommen wurde. Die Anzahl der einbezogenen Strukturen wurde schrittweise auf die Gesamtzahl von 42 erhöht. Bei der Minimisierung der molekularen Energie zur Bestimmung der Gleichgewichtsstruktur des Grundzustandes wurden auch die Längen aller vier chemisch unterscheidbaren Bindungen variiert. Diese Gleichgewichtsabstände stimmen sowohl mit den Meßwerten als auch mit den Ergebnissen anderer Rechenverfahren gut überein.

Valency-bond studies of aromatic hydrocarbons were made very early in the applications of wave-mechanics to chemical problems. Thus the first volume of the Journal of Chemical Physics includes three papers by PAULING and collaborators [16, 18, 19] on this subject. Among the many assumptions made in those early days was that that all bonds were equal in length and hence that Coulomb and exchange integrals Q and J were equal for all C-C bonds having some π-character.

As a matter of fact this could scarcely have been otherwise for, when PAULING and WHELAND [19] reported their work on the resonance energies of benzene and naphthalene on 21st March 1933, the latest experimental evidence on aromatic bond lengths was to be found in the statement of ROBERTSON [21] communicated to the Royal Society on 17th October 1932 on his investigation of anthracene that, "··· This is a very satisfactory result, because it shows in a more precise way that the molecule is built from regular hexagon rings." Again in reporting his study of naphthalene shortly afterwards the same author [22] says, "Careful measurement shows that the carbon rings are almost certainly in the form of two regular plane hexagons." It was later claimed [17] that deviations up to 2%

could be detected in these bond lengths as shown in the electron density maps [22, 23]. Such variations could not really be established until three-dimensional X-ray work was completed in 1948 [1a].

In the succeeding thirty years, beginning perhaps with the work of JAMES, KING and HORROCKS [13], it has become abundantly clear that aromatic C-C bond lengths do vary over a considerable range [2, 10, 14, 24]. Nevertheless improved valency-bond treatments have not kept pace with improved measurements, first because there were no means of allowing for the variations of Q and J with bond length, and secondly because even modern computers can scarcely cope with the very large number of resonating structures in the canonical set of a system of twelve or more π-electrons unless sufficient symmetry is assumed to permit the use of group theoretical methods and so reduce substantially the dimensions of the matrices involved.

The work of COULSON and DIXON [9] has now removed the first difficulty and since, by assuming D_{2h} symmetry, group theory enables the 42×42 matrices arising from the 42 canonical structures of naphthalene to be reduced to 16×16, the present paper reports on a new theoretical study of this hydrocarbon.

The method used has been described in Parts I to III [7, 4, 5] of this series of papers, but the technique indicated there has been applied as follows. Four distinct bond lengths can be recognised as shown at II. The forty-two canonical

(I)   II   III
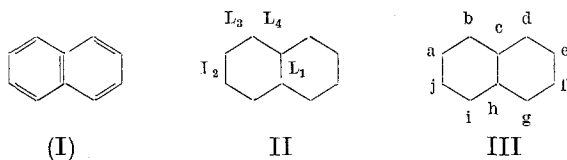
structures fall into groups of not more than four members according to the symmetry of each member. These groups are summarised below by enumerating the π-bonds of a representative member, the symbol ij implying a bond between the π-orbitals on atoms i and j of III.

1	ab	ch	de	fg	ij		20	aj	bi	ch	dg	ef
2, 3	ab	cd	ef	gh	ij		21, 22	ad	bc	ef	gj	hi
4, 5	ab	cd	ej	fg	hi		23—26	ab	cd	ej	fi	gh
6, 7	aj	bc	di	ef	gh		27—30	ab	cf	de	gj	hi
8, 9	ab	ch	dg	ef	ij		31—34	ab	cj	dg	ef	hi
10, 11	aj	bc	dg	ef	hi		35—38	ab	cj	di	ef	gh
12—15	ab	cd	ef	gj	hi		39, 40	ab	cj	di	eh	fg
16—19	ab	cd	eh	fg	ij		41, 42	ad	bc	ej	fi	gh

Setting up the appropriate matrix elements in terms of $R_1, \cdots R_4, J_1, \cdots J_4$ where $R(L) = Q(L) + E_\sigma(L)$ and giving the R's and J's the values [9] corresponding to the lengths $L_1, \cdots L_4$, the molar energy E for naphthalene was determined by the following steps.

A. 3 Kekulé structures (1—3) only, varying L_1 from 1.35 by intervals of 0.01 to 1.46 A; $L_2 = 1.35\ (0.01)\ 1.54$; $L_3 = 1.35\ (0.01)\ 1.46$; $L_4 = 1.35\ (0.01)$ 1.54 A.

B. Structures 1—3 *plus* 16 structures (4—19) with one long or formal bond ("first excited structures").

$L_1 = 1.35\ (0.01)\ 1.46\ \text{A}$; L_2, L_3 and L_4 all varied independently 1.35 (0.01) 1.54 A.

C. Structures $1-19$ *plus* 19 structures $(20-38)$ with two long bonds. $L_1 = 1.37\ (0.01)\ 1.43$; L_2 and L_4 1.41 (0.01) 1.47; $L_3 = 1.35\ (0.01)\ 1.41$ A.

D. All 42 structures. $L_1 = 1.37\ (0.01)\ 1.43$; $L_2 = 1.40\ (0.01)\ 1.46$; $L_3 = 1.35\ (0.01)\ 1.41$; $L_4 = 1.40\ (0.01)\ 1.47$ A.

Tab. 1 gives E, the optimum lengths L_1, $\cdots L_4$ and the Penney-Dirac bond orders p_1, $\cdots p_4$. In the series A, B, C the lengths are given, as actually obtained, only to 0.01 A. In the last series graphical interpolation of each length as obtained permitted statement of the length to 0.001 A and the values of R and J corresponding to this length were derived by substitution in the formulae given by COULSON and DIXON [9], followed by adjustment designed to make their formulae agree perfectly for the neighbouring values each way in their table. These "improved" intermediate values were then used in the computer calculations to give the remaining lengths.

A number of points arise from Tab. 1.

Table 1

Series Structures	$-E$ (kcal/mol)	L_1	p_1	L_2	p_2	L_3	p_3	L_4	p_4
A $1-3$	1314.79	1.38 A	0.74	1.47 A	0.25	1.36 A	0.87	1.47 A	0.25
B $1-19$	1333.22	1.40	0.63	1.44	0.40	1.37	0.81	1.44	0.40
C $1-38$	1334.28	1.40	0.63	1.43	0.45	1.38	0.74	1.43	0.45
D $1-42$	1334.37	1.407	0.588	1.428	0.466	1.377	0.760	1.434	0.433

1. The inclusion of further structures continually tends towards the equality of the optimum bond lengths. A similar effect is seen in the calculations of DEN BOER, DEN BOER, COULSON and GOODWIN [4] on pentalene, and of DEN BOER, DEN BOER and GOODWIN [5] on heptalene.

2. The optimum lengths with the Kekulé structures alone differ in one important respect from those predictable by the simple superposition method of PAULING, BROCKWAY and BEACH [17]. This method indicates bond orders $p_1' = p_2' = p_4' = 1/3$, $p_3' = 2/3$, so that L_1, L_2 and L_4 should be equal and substantially longer than L_3. In the series A results L_3 is certainly the shortest bond length and L_2 and L_4 are equal and considerably longer than L_3, but L_1 is only slightly longer than L_3.

3. In Parts I to III of this series of papers [7, 4, 5] we have calculated the Penney-Dirac bond orders of the bonds in the various compounds discussed. The rather elaborate procedure for this purpose is now no longer necessary since DEN BOER and DEN BOER in Part IV [3] have shown how these may be determined directly from the bond lengths *of the equilibrium structure*. Using this technique the Penney-Dirac orders, p, for naphthalene are found to have the values set out in Tab. 1. The tendency to equality of bond lengths is, of course, reflected strikingly in these bond orders and it is not until all the canonical structures are included that bonds L_2 and L_4 (*i. e.*, 2−3 and 1−9) are distinguished. L_3 always has the highest order.

There is, of course, no suggestion that bond orders calculated by different methods should be identical unless their definitions are ultimately identical, which is not usually the case. In addition to the simple estimate p', based on Kekulé

structures only and referred to in the previous paragraph, Pauling, Brockway and Beach [17] gave a second definition $p'' = \Sigma_i' C_i^2 / \Sigma_i C_i^2$, where C_i is the coefficient of the ith structure orbital in the full wave function the primed sum being over those structures in which the bond in question is double and the unprimed over all structures. Using Sherman's wave function for naphthalene [23] this led to $p_1'' = 0.43$, $p_2'' = 0.33$, $p_3'' = 0.60$ and $p_4'' = 0.26$, overlap being neglected. Sherman had used equal Q's and equal J's. If this calculation is repeated using the coefficients given later (paragraph 9) and based on variable Coulomb and exchange integrals the following results are obtained: $p_1'' = 0.667$, $p_2'' = 0.209$, $p_3'' = 0.714$, $p_4'' = 0.184$. Permitting variation of these integrals with length has increased the order of the high order bonds and decreased that of the low order ones. A comparable change was noted in the Penney-Dirac orders for butadiene calculated by Clarkson, Coulson and Goodwin [7].

4. The inclusion of the sixteen "first excited structures" (having one long or formal bond) with the three Kekulé forms causes notable changes in the optimum bond lengths, while little further change results from the inclusion of the remaining twenty-three canonical structures. How safe it would be to neglect "higher" excited structures in studies of still larger molecules it is difficult to predict, since their number increases rapidly with increasing number of π-electrons⋆.

5. The changes in E consequent upon inclusion of excited structures parallel those in the optimum lengths. The inclusion of the sixteen structures with one long bond lowers E by 18.43 kcal/mol from the value for three Kekulé structures only. Inclusion of the remaining twenty-three structures leads to a further lowering of only 1.15 kcal/mol.

6. The molar energy E_{42} (with all 42 structures) is -1334.37 kcal/mol. The energy of the most symmetrical Kekulé structure (1) is given by

$$E_1' = R_1 + J_1 + 2 R_2 - J_2 + 4 R_3 + 4 J_3 + 4 R_4 - 2 J_4 = -1264.86 \text{ kcal/mol}$$

if $L_1 \cdots L_4$ have the optimum values found in the series D calculations. This would appear to lead to a resonance energy $P' = 69.51$ kcal/mol, in very encouraging agreement with the thermochemical value $\mathscr{R} = 75$ kcal/mol [18]. Unfortunately this is not acceptable because the thermochemical value is based on comparison of the heat of combustion of naphthalene with that expected for a structure (1) in which the double and single bonds between carbon atoms are of optimum lengths to give minimum energy to that structure, i. e. pure ethylenic and pure ethanoid in type. Such a structure, which we may call "undistorted (1)", would have $(R_1 + J_1)$ and $(R_3 + J_3)$ minima i.e. with $L_1 = L_3 = 1.34$ A and $(R_2 - 1/2 J_2)$ and $(R_4 - 1/2 J_4)$ also minima i. e. with $L_2 = L_4 = 1.53$ A using the Coulson-Dixon curve [9]. The optimum E_1 is then found to be -1293.15 kcal/mol leading to $P = 41.22$ kcal/mol. $E_1' - E_1 = +28.29$ kcal/mol is the energy of distortion (compression of some bonds and stretching of others) [8] to give the isolated but

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⋆ For cyclic polyenes with $2 N$ π-electrons the numbers of structures with one and with two long bonds are

$2 N$	6	8	10	12	14	16	18
Structures with 1 long bond	3	8	15	24	35	48	63
Structures with 2 long bonds	4	20	60	140	280	504.	

The corresponding figures for acenes, phenes and other polycyclic hydrocarbons depend slightly on the number and positions of the cross linkages.

distorted (1), while $P' = 69.51$ kcal/mol is the energy of stabilisation or resonance when this "mixes" with the other 41 structures.

A similar effect is observed in calculations with benzene. As noted by COULSON and DIXON [9] and as easily demonstrated using their table and curves of R and J, the molar energy of benzene is a minimum with all bonds equal to 1.40 A and has the value $E_5 = -744.09$ kcal/mol. For a single Kekulé structure with bonds 1.40 A long, $E'_1 = -695.81$, and $P' = +48.28$ kcal/mol, while cyclo-hexatriene with bonds of 1.34 and 1.53 A gives $E_1 = -720.08$ and $P = +24.01$ kcal/mol compared with the empirical $\mathscr{R} = 37$ kcal/mol.

The explanation of these discrepancies lies in the fact that COULSON and DIXON used as their two reference compounds ethylene and benzene which have all their carbon atoms in the sp^2 hybridised state, while the thermochemical calculation of the molar energy of cyclo-hexatriene, with localised double and single bonds, uses for the bond energy of C-C a value appropriate to ethane in which both carbons are hybridised sp^3. Since three such bonds are involved, we may naively correct the theoretical resonance energy for benzene $P = +24.01$ to $+37$ kcal/mol by making

$$E_1 \text{ (corrected)} = E_1 + 3\ Y = -720.08 + 13.00$$
$$= -707.08 \text{ kcal/mol,}$$

Y being the change in bond energy

$$C_{sp^3} - C_{sp^3} \rightarrow C_{sp^2} - C_{sp^2} \qquad \Delta H = Y = +4.33 \text{ kcal}$$

due to change in hybridisation.

If this is applied to naphthalene, for which the thermochemical calculation of resonance energy involves six C-C bonds,

$$E_1 \text{ (corrected)} = E_1 + 6\ Y = -1267.15 \text{ kcal/mol} \quad \text{and} \quad P = 41.22 \quad \text{becomes}$$

$\mathscr{R}$ (calc) $= 41.22 + 26 = 67.22$ kcal/mol, which is reasonably close to the $\mathscr{R} = 75$ kcal/mol.

7. Reference has been made to the paper of PAULING and WHELAND [19] on naphthalene, in which all Q and all J were supposed equal. Improved calculations were made on this compound by SHERMAN [23] again with equal Q and J. Tab. 2 compares his results with those presented here and gives the minimum molar energies and the (all equal) bond lengths L obtained from his figures by use of the Coulson-Dixon curves and table. The energy is, at each stage, lower in the present calculations, as it should be, but the difference is astonishingly low except when only Kekulé structures are involved. The final difference of only 2 kcal/mol, if also observed with other compounds, may mean that the labour of varying bond lengths simply to minimise the energy is not worth while, though it may account in large measure for the success attending the use of the earlier calculations on naphthalene etc.

It is therefore of interest to make the corresponding comparisons for fulvene, Tab. 3, and pentalene, Tab. 4, the subjects of Parts I and II of this series. Here the differences between the minimum energies with equal and unequal bond lengths are much greater, but such a result should have been anticipated since in both these compounds marked alternation of bond lengths (1.35 and 1.49 A in fulvene and 1.35 and 1.48 A in the pentalene periphery) is found when inequality is permitted, whereas with naphthalene the extreme bonds are 1.377 and 1.434 A by calculation and 1.364 and 1.421 A by (X-ray) measurement.

Table 2

SHERMAN

Structures	Min. Energy and Optimum Bond Length with all L's equal	Present work	
		E	L
1 only	$11\,R\,(L) + 2\,J\,(L)$ = -1248.02 kcal/mol with $L = 1.431$ A	-1293.15	1.444
1 – 3	$11\,R\,(L) + 3.3703\,J\,(L)$ = -1303.99 kcal/mol with $L = 1.414$	-1314.79	1.411
1 – 19	$11\,R\,(L) + 4.0036\,J\,(L)$ = -1330.80 kcal/mol with $L = 1.408$	-1333.22	1.411
1 – 42	$11\,R\,(L) + 4.0400\,J\,(L)$ = -1332.32 kcal/mol with $L = 1.408$	-1334.37	1.410

Table 3. *Fulvene*

Structures	Minimum Energy and Optimum Bond Lengths with all Lengths Equal	Minimum Energy with unequal Bond Lengths
1 Kekulé	$6\,R\,(L) + 1.5\,J\,(L) = -697.24$ kcal/mol with $L = 1.424$ A	-720.08 kcal/mol
5 Structures	$6\,R\,(L) + 2\ \ J\,(L) = -718.06$ kcal/mol with $L = 1.413$ A	-732.28

Table 4. *Pentalene*

Structures	Minimum Energy and Optimum Bond Lengths with all Lengths Equal	Minimum Energy with unequal Bond Lengths	
		D_{2h}	C_{2h}
1 Kekulé	$9\,R\,(L) + 1.5\,J\,(L)$ = -1015.72 kcal/mol with $L = 1.434$ A	-1042.2 kcal/mol	-1052.5 kcal/mol
2 Kekulés	$9\,R\,(L) + 2\,J\,(L)\star$ = -1035.73 kcal/mol with $L = 1.426$		-1054.8
14 Structures	$9\,R\,(L) + 2.597\,J\,(L)\star$ = -1060.22 kcal/mol with $L = 1.417$	-1067.5	-1070.5

★ Reference: CRAIG, D. P., and A. MACCOLL: J. chem. Soc. 1949, 964.

8. Perhaps the most interesting feature of the present work arises from comparison (Tab. 5) of the optimum bond lengths with those obtained by other methods. These other methods, with the key to their display in the table, are

(i) T. H. G; m. o. [12]. A calculation by the present writer using a refinement of the Hückel molecular orbital technique.

(ii) D. A. M-B; m. o. [15]. A calculation by D. A. MORTON-BLAKE of this laboratory using a modification of the procedure referred to in (i).

(iii) P. and S; s. c. m. o. [20]. PRITCHARD and SUMNER's self-consistent molecular orbital calculation.

(iv) P. N. S; P. P. P. [24]. P. N. SKANCKE's application of the Pariser-Parr-Pople technique.

(v) C. and S; X-R. [11]. Experimental results derived by CRUICKSHANK and SPARKS from the X-ray measurement of ABRAHAMS, ROBERTSON and WHITE [26].

(vi) A. B. and D; E. D. [1]. Experimental determination by electron diffraction by ALMENINGEN, BASTIANSEN and DYVIK.

With the exception of Pritchard and Sumner's length for the central bond, close agreement is shown among all five sets of calculations and their near concurrence with the experimental results is very satisfactory. The present study, in particular, leads to bond lengths always within 0.014 A of the mean experimental value and this by a method which is essentially simple to carry out.

9. The normalised ground state wave function for the 42-structure hybrid is $\Psi = \Sigma\, C_i\, \Phi_i$ with

$$C_1 = 0.29363 \qquad C_2 = C_3 = 0.13636$$
$$C_4 = C_5 = 0.05074 \qquad C_6 = C_7 = 0.03756$$
$$C_8 = C_9 = 0.10357 \qquad C_{10} = C_{11} = 0.03690$$
$$C_{12} = C_{13} = C_{14} = C_{15} = 0.05034$$
$$C_{16} = C_{17} = C_{18} = C_{19} = 0.06814 \qquad C_{20} = 0.03684$$
$$C_{21} = C_{22} = 0.01191$$
$$C_{23} = C_{24} = C_{25} = C_{26} = 0.00896$$
$$C_{27} = C_{28} = C_{29} = C_{30} = 0.02459$$
$$C_{31} = C_{32} = C_{33} = C_{34} = 0.01601$$
$$C_{35} = C_{36} = C_{37} = C_{38} = 0.01853$$
$$C_{39} = C_{40} = 0.01139 \qquad C_{41} = C_{42} = 0.00176$$

Table 5

	L_1	L_2	L_3	L_4
This work	1.407	1.428	1.377	1.434
T. H. G. (m. o.)	1.409	1.432	1.363	1.439
D. A. M-B. (m. o.)	1.413	1.418	1.371	1.423
P. and S. (s. c. m. o.)	1.396	1.418	1.364	1.424
P. N. S. (P. P. P.)	1.407	1.424	1.374	1.428
C. and S. (X-R.)	1.418	1.415	1.364	1.421
A. B. and D. (E. D.)	1.420	1.412	1.371	1.422
Mean experimental	1.419	1.414	1.368	1.422
$\Delta\star$	0.012	0.014	0.009	0.012

$\star$ Difference between the bond lengths found in the present work and their mean experimental values.

The weightings of the contributory structures, which these figures indicate, are of interest though one must, of course, not suppose the structures to represent real entities. One finds, as expected, that the Kekulé forms (1) and (2, 3) are of greatest importance. Now the chemical properties of naphthalene (see, for example, CLAR [6]) provide no indication that the central bond is double, dihalogenation, dihydrogenation and addition in general occurring at other bonds or atoms. One would, therefore, expect that (2) and (3) would be rather more important than (1). However although (1), (2) and (3), considered individually in equilibrium, would have the same energy $E(1) = E(2) = E(3) = E_1 = -1293.15$ kcal/mol the energies of the isolated structures after distortion to the 42-structure equilibrium bond lengths are $E'(1) = -1264.86$ and $E'(2) = E'(3) = -1242.48$. This, of course, gives greater weight to (1). In only one other structure, (20), is the central bond double; $C_{20} \sim 1/10\ C_1 \sim 1/4\ C_2$.

The structure wave functions $\Phi_4 \cdots \Phi_{19}$ for the structures having only one long bond all have coefficients lying between 0.03690 and 0.10357; only Φ_{20} among the remaining structures has $C \geq 0.036$. C_4 to C_{19} must be less than C_1 to C_3 because, when isolated but distorted to the 42-structure equilibrium bond lengths, their energies are appreciably higher (averaging -1178.27 kcal/mol, about 72 kcal/mol higher than the average of the three distorted Kekule structures) since the number of real bonds total four double and seven single. The structures with highest coefficients are (8, 9) which have formal bonds dg and bi respectively; direct addition of bromine to naphthalene gives the (unstable) 1:4 dibromo-derivative. It is, however, unwise to make much of this because (10) and (11) also have formal bonds dg and bi respectively, but C_{10} and C_{11} are the smallest among C_4 to C_{19}.

C_{20} to C_{38} for the structures with two long bonds are again generally substantially smaller than C_4 to C_{19}, and C_{39} to C_{42} for those with three long bonds smaller still.

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