Calculated Bond Lengths in Some Cyclic Compounds. Part I. Methods of Calculation.

By T. H. Goodwin and V. Vand.

[Reprint Order No. 5900.]

A description is given of new methods of expanding secular determinants and solving the resulting equation for the energy levels in molecular-orbital calculations of bond orders as well as for evaluating the secular coefficients (c_r^i). A new curve for correlating bond order and bond length is also proposed.

A refinement of the simplest valency bond counting method is described and a correlation curve for use with it is suggested.

Determinations of the crystal structures of condensed ring compounds made in these laboratories under the direction of Professor J. M. Robertson have established the bond lengths in many such substances with considerable or very great accuracy. Complementary to these practical investigations have been wave-mechanical studies of the theoretical values to be expected for the bond orders and hence for the bond lengths in some of the compounds examined by X-rays [see, for example, Coulson, Daudel, and Robertson (*Proc. Roy. Soc.*, 1951, *A*, **207**, 306) who discuss the results for naphthalene, anthracene, coronene, ovalene, pyrene, etc., and Coulson (*ibid.*, p. 91)]. In the present series of papers calculations are presented on a number of substances. For some of them the interatomic distances have already been measured and so can profitably be compared with the calculations. For others the calculations have been made in the hope of using the resulting bond lengths in setting up molecular models for use in refining the crystal structures. This first Part describes what are believed to be new methods of carrying out the calculations for very large molecules, of which benzanthrone, to which the technique was first applied, may be taken as typical.

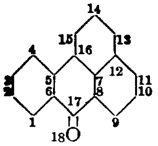
Molecular-orbital Calculations

Benzanthrone (I), $C_{17}H_{10}O$, has 18 π-electrons, and the 18 secular equations

$$\sum c_r^i(H_{rs} - ES_{rs}) = 0 \qquad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (1)$$

were set up in the usual way.

As the determinant Δ formed by the coefficients of the c_r^i is of the eighteenth order and has no simplifying symmetry, inclusion of overlap would greatly increase the labour of evaluating the coefficients c_r^i of the normalised atomic orbitals ϕ_r making up the molecular orbitals $\psi_i = \sum_r c_r^i \phi_r$ and so it was decided that the overlap integrals $S_{rs} = \int \phi_r \phi_s d\tau$ should be placed equal to zero, except for $S_{rr} = 1$. The following further simplifications were adopted: for all carbon atoms the Coulomb integral $H_{rr} = \alpha$; for the oxygen atom $H_{18,18} = \alpha + \beta$; resonance integrals H_{rs} between adjacent carbon atoms $= \beta$, between adjacent carbon and oxygen atoms $= 2\beta$, between other atoms $= 0$. The molecular orbital energy levels E_i were obtained in terms of β by writing $x_i = (\alpha - E_i)/\beta$ and solving the equation $\Delta = 0$.



(I) (Numbering used for mathematical calculations for benzanthrone.)

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 0 \\ 0 & 1 & x & 1 & 0 \\ 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 1 & x \end{vmatrix}$$

(*A*)

This and subsequent stages of the work are very conveniently carried out by use of determinants of the variety known as continuants of which P_5, in inset (*A*), is an example. The following are some properties of continuants which are useful for the present purpose :

$$P_n = xP_{n-1} - P_{n-2} \text{ with } P_0 = 1;\ P_1 = x;\ P_2 = x^2 - 1, \text{ etc.} \quad . \quad . \quad (2)$$

$$P_n.P_m = P_{n+m} + P_{n+m-2} + P_{n+m-4} + \ldots\ldots + P_{n-m+2} + P_{n-m} \quad . \quad . \quad (3)$$

where $n > m$.

$$P_n^2 = P_{2n} + P_{2n-2} + \ldots\ldots. + P_2 + P_0 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\mathrm{d}P_n/\mathrm{d}x = nP_{n-1} + (n-2)P_{n-3} + (n-4)P_{n-5} + \ldots\ldots + 2P_1 \text{ or } P_0 \quad . \quad (5)$$

according as n is even or odd. Continuants are, in fact, the Tschebysheff polynomials

$$P_n = x^n - \frac{n-1}{1}x^{n-2} + \frac{(n-2)(n-3)}{1.2}x^{n-1} \ldots\ldots \quad . \quad . \quad . \quad (6)$$

and may also be written as

$$P_n = 2[\cos n\theta + \cos(n-2)\theta + \cos(n-4)\theta + \ldots\ldots(\cos\theta \text{ or } \tfrac{1}{2})] \quad . \quad . \quad (7)$$

according as n is odd or even. This transformation depends on the substitution $x = 2\cos\theta$ and means that a sum of continuants $aP_n + bP_m + \ldots\ldots$ can readily be expressed as a Fourier series and so evaluated very rapidly by any of the strip, stencil, or other methods (*e.g.*, Lipson and Beevers, *Proc. Phys. Soc.*, 1936, **48**, 772; *Acta Cryst.*, 1952, **5**, 670; Robertson, *Phil. Mag.*, 1936, **21**, 176; *J. Sci. Instr.*, 1948, **25**, 28) used by crystallographers and others for computing Fourier syntheses, provided the argument x ($\cos\theta$) lies between ± 2 (± 1).

The expansion of the determinant Δ is, then, carried out by expressing it as a sum of continuants since it is, in fact, a continuant with various " decorations," *viz.*, the terms not on the leading and immediately adjacent diagonals and such of these terms as are not x (leading diagonals) or 1 (adjacent diagonals). If there are decorations, b, in the original determinant at (pq) and (qp), *i.e.*, at the intersections of column p with row q and of column q with row p, then one of these (say that at pq) may be removed by writing

$$\Delta = \Delta'_1 + (-1)^{p+q}b\Delta'_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where Δ'_1 is derived from Δ by suppressing the b at (pq) and Δ'_2 is the minor of the b at (pq) in Δ. To remove both b's simultaneously write

$$\Delta = \Delta_1 + 2(-1)^{p+q}b\Delta_2 - b^2\Delta_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where Δ_1 is derived from Δ by suppressing both b's, Δ_2 is the minor of the b at (pq) in Δ but with the b at (qp) also suppressed, and Δ_3 is the " double minor " of the b's, *i.e.*, columns p and q and rows p and q of Δ are all suppressed. Note that if Δ is of order n, so are Δ_1 and Δ'_1; Δ_2 and Δ'_2 are of order $n - 1$, and Δ_3 is of order $n - 2$. Also Δ_1 and Δ_3 are, like Δ, axially symmetrical but Δ_2 is not. Δ_2 is, however, often found to be immediately factorised and is frequently zero. If not zero it or its factors may be treated by (8) to break it up further; factors are multiplied out by means of (3). Δ_1 and Δ_3 are of course treated as in (9). This process is repeated until all " decorations " have been removed. Thus, in quite a short time the eighteenth order determinant of benzanthrone was expanded to

$$\begin{aligned}&P_{18} + P_{17} - 7P_{16} - 4P_{15} + 8P_{14} - P_{12} - 5P_{11} + 29P_{10} + 10P_9 - 13P_8 + \\ &\qquad + 5P_7 + 6P_6 + 17P_5 - 52P_4 + 7P_3 - 9P_2 + 8P_1 - 36P_0 = 0 \quad . \quad (10)\end{aligned}$$

a simpler form than the equivalent

$$\begin{aligned}&x^{18} + x^{17} - 24x^{16} - 20x^{15} + 233x^{14} + 161x^{13} - 1197x^{12} - 681x^{11} + \\ &\qquad + 3571x^{10} + 1655x^9 - 6391x^8 - 2367x^7 + 6831x^6 + 1947x^5 - 4170x^4 + \\ &\qquad\qquad - 842x^3 + 1290x^2 + 146x - 144 = 0 \quad . \quad (11)\end{aligned}$$

An important feature of all work of this kind is the application of checks on accuracy. When the method of continuants is used these are particularly simple, as the following table of values of P_n for $x = 0, 1, 2$ shows:

x	n: 0	1	2	3	4	5	6	7	8
0	1	0	-1	0	1	0	-1	0	1
1	1	1	0	-1	-1	0	1	1	0
2	1	2	3	4	5	6	7	8	9

Also $P_{2n}(x) = +P_{2n}(-x)$, and $P_{2n+1}(x) = -P_{2n+1}(-x)$

Expansion (10) having been reached, inspection shows that $(x - 1)$ and $(x + 1)$ and therefore $(x^2 - 1)$ are factors of the left-hand side. Since $P_2 = x^2 - 1$ these factors are removed by division, using (3). Actually P_2 can also be removed again and finally $(x + 1)$ which is written as $P_1 + P_0$.

The remaining thirteenth-order equation, R, is then solved by writing it as a Fourier series by use of (7) and summing and plotting it between $\theta = 0$ and π $(x = \pm 2)$. The nodes of this curve are at those roots of R which lie between $x = \pm 2$ but will only be given approximately by this method. To obtain them more accurately an iterative process is used. The values of P_n for $0 < n < 13$ were calculated by (2) and checked by (6), using Horner's method. These results are then used to evaluate accurately R and its derivatives R' and R'' at the approximate values of the roots; application of Taylor's theorem in the form

$$R(x + h) = R(x) + \frac{h}{1!}R'(x) + \frac{h^2}{2!}R''(x) = 0 \quad . \quad . \quad . \quad . \quad (12)$$

gives, to this approximation, the increment h by which x may be increased to get a better value of the root for further iteration.

Since the parameter β in units of which x is obtained is negative, only the negative roots of R are required in studying the ground state of the molecule. The rest may, of course, be obtained to use as a check on their correct extraction. To determine the roots lying outside the limits $x = \pm 2$ the accurate factors were removed from R and the residue, a function containing P_5, was examined by a combination of guess work, Taylor's theorem, and experience. The last shows that for hydrocarbons nearly all the roots are between $+2$ and -2 and so the Fourier technique described above is very helpful. It becomes less useful as the compound contains more and more heteroatoms.

The c_r^i are also easily evaluated by means of continuants as may readily be illustrated by means of the simple example of benzene, the secular equations of which are those indexed *a* to *f* below.

	c_1	c_2	c_3	c_4	c_5	c_6		
a	x	1	0	0	0	1	$= 0$	$a - xb$ gives g
b	1	x	1	0	0	0	$= 0$	$b - xc$ gives i
c	0	1	x	1	0	0	$= 0$	$c - xd$ gives l
d	0	0	1	x	1	0	$= 0$	
e	0	0	0	1	x	1	$= 0$	
f	1	0	0	0	1	x	$= 0$	$f - b$ gives h
g	0	$-P_2$	$-P_1$	0	0	1	$= 0$	$g + P_2c$ gives j
h	0	$-P_1$	$-P_0$	0	P_0	P_1	$= 0$	$h + P_1c$ gives k
i	1	0	$-P_2$	$-P_1$	0	0	$= 0$	$i + P_2d$ gives m
j	0	0	P_3	P_2	0	P_0	$= 0$	
k	0	0	P_2	P_1	P_0	P_1	$= 0$	
l	0	1	0	$-P_2$	$-P_1$	0	$= 0$	
m	1	0	0	P_3	P_2	0	$= 0$	

The object is to write a simple expression for each coefficient in terms of as few others as possible and the method is sufficiently illustrated by the notes given beside the equations. The final set of equations is given as *p* to *u* from which it is seen that they are in fact relatively simple to write down and a simple equation gives c_5 in terms of c_6 and the rest simiarly. Incidentally the determinant of the coefficients of c_5 and c_6 in *t* and *u* is equivalent to the secular determinant Δ. The larger set of equations for benzanthrone is given in (13) in which

	c_1	c_2	c_3	c_4	c_5	c_6	
p	0	0	0	1	P_1	1	$= 0$
q	0	0	1	0	$-P_2$	$-P_1$	$= 0$
r	0	1	0	0	P_3	P_2	$= 0$
s	1	0	0	0	$-P_4$	$-P_3$	$= 0$
t	0	0	0	0	P_5	$1 + P_4$	$= 0$
u	0	0	0	0	$1 + P_4$	$P_3 + P_1$	$= 0$

$A = P_8 - P_4 - 1$; $B = -(P_3 + P_1)$; $C = P_8 + P_4 + 1$; $D = P_7 + P_3$; $E = P_7 + 2P_3 + P_1$; $F = -P_7 + P_5 + P_3 + P_1$; $G = P_4 + 2P_2$; $H = -P_8 + P_4 + P_1$. Hence, from equations *f, h, i, q, r* and a Table of P_n for x = the root, the values of c_5, c_6, c_7, c_{17}, c_{18} for each energy

$$\left.\begin{array}{cccccccccccccccccccc}
 & c_1 & c_2 & c_3 & c_4 & c_5 & c_6 & c_7 & c_8 & c_9 & c_{10} & c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} & c_{17} & c_{18} & \\
(a) & 0 & 0 & 0 & 0 & P_5 & P_4+1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_4 & 0 & 0 & =0 \\
(b) & 1 & 0 & 0 & 0 & -P_4 & -P_3 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -P_3 & 0 & 0 & =0 \\
(c) & 0 & 1 & 0 & 0 & P_3 & P_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_2 & 0 & 0 & =0 \\
(d) & 0 & 0 & 1 & 0 & -P_2 & -P_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -P_1 & 0 & 0 & =0 \\
(e) & 0 & 0 & 0 & 1 & P_1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & =0 \\
(f) & 0 & 0 & 0 & 0 & P_4+1 & P_3+P_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_3 & 1 & 0 & =0 \\
(g) & 0 & 0 & 0 & 0 & 0 & 0 & P_1 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 & 0 & =0 \\
(h) & 0 & 0 & 0 & 0 & A & B & C & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & P_9-P_3 & 0 & 0 & =0 \\
(i) & 0 & 0 & 0 & 0 & D & 0 & E & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & C & 0 & 0 & =0 \\
(j) & 0 & 0 & 0 & 0 & P_6 & 0 & P_6+P_2 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & P_7 & 0 & 0 & =0 \\
(k) & 0 & 0 & 0 & 0 & -P_5 & 0 & -P_5-P_1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & -P_6 & 0 & 0 & =0 \\
(l) & 0 & 0 & 0 & 0 & P_4 & 0 & P_4+1 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & P_5 & 0 & 0 & =0 \\
(m) & 0 & 0 & 0 & 0 & -P_3 & 0 & -P_3 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & -P_4 & 0 & 0 & =0 \\
(n) & 0 & 0 & 0 & 0 & P_2 & 0 & P_2 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & P_3 & 0 & 0 & =0 \\
(o) & 0 & 0 & 0 & 0 & -P_1 & 0 & -P_1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & -P_2 & 0 & 0 & =0 \\
(p) & 0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & P_1 & 0 & 0 & =0 \\
(q) & 0 & 0 & 0 & 0 & F & G & -D & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & H & 0 & -2 & =0 \\
(r) & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & P_1+1 & =0
\end{array}\right\}(13)$$

level can be expressed in terms of c_{16}. From these the rest are readily obtained also in terms of c_{16} and then evaluated by use of the normality condition $\sum_r (c_r^i)^2 = 1$ and the orthogonality condition $\sum_r (c_r^i c_r^j) = 0$. The electron distribution q and mobile bond orders p can then be deduced from

$$q_r = \sum_i n(c_r^i)^2$$

and

$$p_{rs} = \sum_i n c_r^i c_s^i$$

summation being over all the occupied energy levels, usually with $n = 2$ electrons in each.

To determine the bond lengths L_1 reference was made to a curve drawn through the following points :

		Mobile bond order	Bond length
D	Diamond corrected to sp^2 hybridisation	0	1·50
G	Graphite	0·525	1·421
B	Benzene	0·667	1·39
E	Ethylene	1·00	1·34

This curve (Fig. 1) is almost rectilinear and so interpolation is simple. The arguments for the diamond point are given by Coulson (Victor Henri Memorial Volume, " Contribution à l'Étude de la Structure Moleculaire," Desoer, Liège, 1948) ; the others are long established. However, Cox and Smith's work (*Nature*, 1954, **173**, 75) suggests a benzene point of (0·667, 1·378) with an uncertainty of 0·003 Å in the bond length. This measurement, made on crystals at −3°, is significantly different from Stoicheff's value 1·396—1·401 Å (*J. Chem. Phys.*, 1953, **21**, 1410) derived from Raman spectrum data on the vapour at 61°. Even after allowance for the difference of state this discrepancy is so great that temporary use of the old intermediate value of 1·39 Å seems to be the correct course.

Alternatively, conversion of bond orders into bond lengths might be effected by use of Coulson's " best correlation curve " (*Proc. Roy. Soc.*, 1951, *A*, **207**, 95, Fig. 26) which is derived from the generally very accurate measurement of thirty-six distinct bond lengths in nine hydrocarbons, the bond orders being obtained by the molecular-orbital approximation. This curve (Fig. 1) passes through the points (measured from the figure) (0·466, 1·46) ; (0·5, 1·443) ; (0·6, 1·406) ; (0·7, 1·378) ; (0·8, 1·361) ; (0·9, 1·351) ; (1·0, 1·34). Unfortunately the extrapolation of this to mobile bond orders lower than 0·4, such as are obtained for some of the compounds to be discussed, is not practicable as it would lead to a length of *ca.* 1·495 for order 0·4 and *ca.* 1·58 for order 0·3. However, by using the same parameters as for benzanthrone, it is found that in benzoquinone the bonds adjacent to the keto-group have mobile orders of 0·310 and, according to the measurement reported by Robertson (*Proc. Roy. Soc.*, 1935, *A*, **150**, 106), a length of 1·50. This value, obtained twenty years ago, is not, of course, known with the precision of modern measurements. It is, therefore, being measured again in this Department but. in the meantime, we may recognise that it is reliable to within a few hundreds of an Ångström. In particular if we take its length to be 1·485 Å the Coulson curve may be extrapolated through (0·310, 1·485) to (0, 1·50) to provide a graph for correlations at low order to within a few hundredths of an Angstrom unit.

Throughout this series of papers, therefore, bond lengths will be described as L_1 when derived from the curve *DGBE* and as L_2 when derived from the Coulson curve extended through benzoquinone *Q* to diamond. The latter curve will be called *DQCE*. This extrapolation is rather arbitrary but fortunately orders less than 0·5 are seldom required and unfortunately there are no other points available. Nowhere do these two curves differ by more than 0·026 Å and in the most important region (orders greater than 0·55) by more than 0·008 Å.

It is of interest that graphite (0·525, 1·421) lies below this curve by about 0·01 Å and the benzene point *B* above it by 0·005 Å while the newer crystallographic benzene point is below it by 0·008 Å. It is also clear that benzene and graphite are unsatisfactory standards for correlating orders and lengths in polycyclic compounds since graphite, considered as an infinite sheet has no " edge effects," *i.e.*, no carbon atoms linked to only two others, while benzene is all edge effects, *i.e.*, has no carbon atoms linked to three others. It amounts to the same thing to say that the approximations used in calculating bond orders are, in fact, too naïve to cover all types of compound adequately.

FIG. 1. *Correlation curves for molecular-orbital method.*

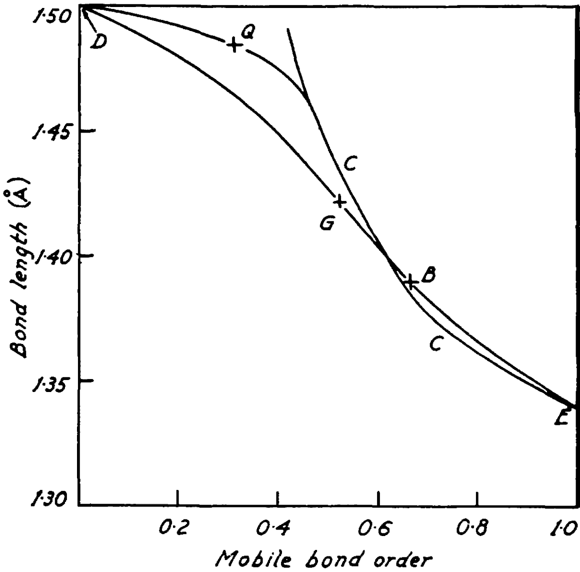
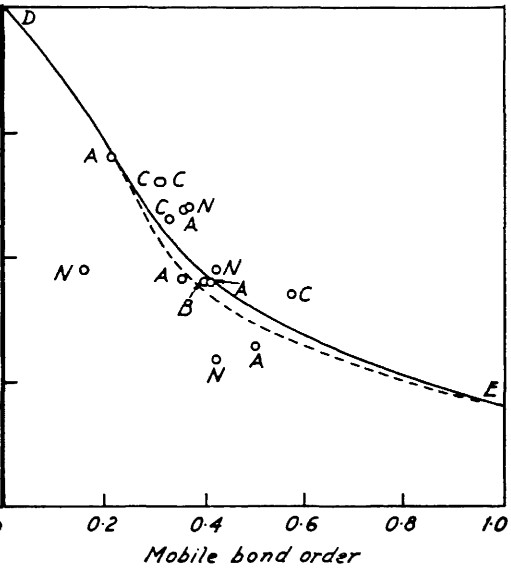


FIG. 2. *Correlation curves for second valence-bond approximation.*



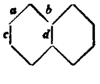
The correlation of orders and lengths for C=O is much less satisfactory, as Cox and Jeffrey have pointed out (*ibid.*, 1951, *A*, **207**, 110). For the compounds discussed in this paper a linear interpolation has been made between 1·185 Å for a double bond and 1·437 Å for a single bond on the basis of data given by these authors, but with the note that the calculated bond order of a pure double bond is 0·895 Å as shown by Coulson (*Trans. Faraday Soc.*, 1946, 42, 106). As the orders calculated are all greater than 0·85 the uncertainties are not very serious. For C–N bonds Cox and Jeffrey's linear correlation curve (*loc. cit.*, p. 115) was used.

VALENCE-BOND CALCULATIONS

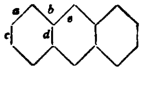
Calculations by the valence-bond method have been made by the two simplest approximations. In the first of these (Pauling, Brockway, and Beach, *J. Amer. Chem. Soc.*, 1935, **57**, 2705) only unexcited canonical structures were included. It follows that bonds 5–16, 6–17, and 8–17 (see I) of benzanthrone are necessarily single bonds so that ring 1,2,3,4,5,6 can have only the two canonical structures of benzene while the double ring 7,8,9,10,11,12,13,14,15,16 must have the three of naphthalene. By counting *N*, the number of times a given bond is double in the total of six structures, the bond order *p* is obtained as *N*/6 whence Pauling's correlation curve

(" Nature of the Chemical Bond," Cornell Univ. Press, New York, 1945, p. 174) modified for the sp^2 diamond leads at once to the bond lengths L_3.

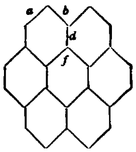
In the second valence-bond approximation unexcited and first excited structures, *i.e.*, structures with not more than one long bond, were included, with the proviso that no long bond should traverse more than two rings. There are fifty-four such structures, including the six referred to in the previous paragraph, and by the method indicated there the orders are readily obtained, equal weights being given to unexcited and excited structures. The authors know of no established order–length curves for use with such calculations and it is difficult to set up one using graphite as one of the standards. To get over this difficulty the corresponding calculations were made on naphthalene (II) and anthracene (III) for use with the measurements made by Abrahams, Robertson, and White (*Acta Cryst.*, 1949, **2**, 238) and by Sinclair, Robertson, and Mathieson (*ibid.*, 1950, **3**, 251), respectively, on these compounds. Additional points were diamond (0, 1·50), benzene (0·4, 1·39), and ethylene (1·0, 1·34) and the results are shown in the Table and in Fig. 2. The broken curve was drawn first as the best then possible. To check this computations were made for coronene (IV) in the same way, for comparison with the measurements by Robertson and White (*J.*, 1945, 607); these are also given in the Table.



(II)



(III)



(IV)

(Bond symbolism used for mathematical calculations.)

Mobile bond orders (p) *calculated by second valence-bond approximation, and observed bond lengths* (L) *in naphthalene, anthracene, and coronene.*

Bond	Naphthalene		Anthracene		Coronene	
	p_4	L	p_4	L	p_4	L
a	0·421	1·359	0·500	1·364	0·573	1·385
b	0·367	1·420	0·357	1·419	0·328	1·415
c	0·421	1·395	0·405	1·390	—	—
d	0·158	1·395	0·215	1·440	0·311	1·430
e	—	—	0·357	1·391	—	—
f	—	—	—	—	0·305	1·430

Every point for this compound lay above the broken curve, so the full curve was drawn. It passes through (0, 1·50); (0·2, 1·445); (0·4, 1·393); (0·6, 1·369); (0·8, 1·353) and (1·0, 1·34).

DISCUSSION

As to the general reliability of the molecular-orbital calculations, Coulson (*Proc. Roy. Soc.*, 1951, *A*, **207**, 91) and Coulson, Daudel, and Robertson (*loc cit.*) show that for aromatic hydrocarbons both molecular-orbital calculations and good *X*-ray work permit the estimation of bond lengths to about 0·02 Å, and that the results obtained by the two methods agree within the same limits. Coulson (*loc. cit.*) also indicates that for hetero-molecules the agreement is not generally closer than ±0·05 Å, but this will clearly depend on the perturbations caused by the hetero-atoms. Thus benzanthrone, considered in Part II, contains one hetero-atom out of eighteen supplying π-electrons. It is thus essentially a large aromatic hydrocarbon with a local perturbation. The molecular-orbital calculations ought, therefore, to be accurate to ±0·03 Å except, perhaps, for the C–C bonds attached to the keto-carbon atom, for which the order–length curve is less reliable. With more hetero-atoms or fewer carbon atoms the uncertainty is likely to be greater and so will be discussed for each compound in turn (see following paper).

The authors gratefully acknowledge the helpful interest of Professor J. M. Robertson, F.R.S., and Professor C. A. Coulson, F.R.S., in this work.

CHEMISTRY DEPARTMENT, UNIVERSITY OF GLASGOW.
(Present address of V. V.: PENNSYLVANIA STATE UNIVERSITY,
STATE COLLEGE, PENN., U.S.A.)

[*Received, November 22nd,* 1954.]