

### 591. *Conjugation across a Single Bond.*

By C. A. COULSON and (Miss) J. JACOBS.

Calculations are made, using the method of molecular orbitals, of the partial bond order associated with the "single" bond connecting two resonating groups such as vinyl, phenyl, or naphthyl. This bond order increases when the size of either, or both, of the attached groups, increases. A careful study of the various phenyl- and diphenyl-ethylenes shows a close relation between the donor character of the ethylene link and the acceptor property of the adjacent single bonds. An appendix deals with the mathematical technique involved.

It was pointed out some years ago by Pauling, Springall, and Palmer (*J. Amer. Chem. Soc.*, 1939, **61**, 927) that when two conjugated groups are joined together by a "single" bond, as, *e.g.*, two phenyl groups to form diphenyl, this central bond partakes of some double-bond character: this is shown experimentally by a preference for a totally coplanar structure, in so far as steric conditions permit, and by a shortening of the bond length. The matter has been more fully discussed theoretically by Coulson and Longuet-Higgins (*Proc. Roy. Soc.*, 1948, *A.*, **195**, 188) (referred to as C.L.-H.) who have shown, in certain simple cases, how this bond order may be calculated according to the method of molecular orbitals, and how its value, together with the resulting extra resonance energy, may be related to the self-polarisabilities of the atoms which are thus joined together, and to their "conjugating powers." It is our object in this present paper to extend these calculations, and to draw certain general conclusions, not fully stated in the earlier work. We first give our numerical results without any detailed explanation of the technique which we found most appropriate, which is relegated to the Appendix. Our definitions and symbols have, where possible, the same significance as in the earlier paper. The results themselves fall naturally into four groups: the polyenes, condensed hydrocarbons, polyphenyls, and phenylethylenes.

*Results of Calculations.*—Group 1. *Polyenes.* It seemed probable from a study of the

numerical values in C.L.-H. that the double-bond character of the connecting "single" bond would be greater the larger the two units which it was joining together. This conjecture may easily be tested for the case where the two end-groups are polyene units of form  $\cdot\text{CH}[\cdot\text{CH}\cdot\text{CH}\cdot]_r\text{CH}_2$ , since for polyene chains the bond orders have been calculated by Coulson (*Proc. Roy. Soc.*, 1939, *A*, **169**, 413) in algebraic form. Table I shows that if we conjugate two equal groups in this way, the central bond order increases steadily from  $r = 0$  (butadiene) and  $r = 1$  (octatetraene) to  $r = \infty$  (infinite polyene chain).

TABLE I.

*Mobile bond order of central link with equal groups  $\cdot\text{CH}[\cdot\text{CH}\cdot\text{CH}\cdot]_r\text{CH}_2$  on each end.*

$r$ .....	0	1	2	3	$\infty$
Mobile bond order, $p$ .....	0.447	0.529	0.561	0.592	0.636

A similar result is obtained if we place a vinyl group at one end and a polyene of varying length at the other, as shown in Table II.

TABLE II.

*Mobile bond order with  $\cdot\text{CH}\cdot\text{CH}_2$  at one end and  $\cdot\text{CH}[\cdot\text{CH}\cdot\text{CH}\cdot]_r\text{CH}_2$  at the other.*

$r$ .....	0	1	2	3	$\infty$
$p$ .....	0.447	0.483	0.495	0.500	0.510

It will be noticed that, in both cases,  $p$  increases with the size of the group, though corresponding values in Table II are smaller than in Table I. It also appears that the entry in Table II for any value of  $r$  is very close to the geometrical mean of the values for  $r = r$  and  $r = 0$  in Table I. Even for the infinite molecule the discrepancy is only 4%. This confirms a conclusion stated in the earlier paper (C.L.-H.).

*Group 2. Condensed hydrocarbons.* Our next group of molecules extends the previous idea by considering the conjugations of two naphthyl, or two anthryl, radicals and also the conjugation of either of these with a phenyl radical. In these calculations, and in our later ones, we have assumed that all such molecules are coplanar. This is extremely unlikely except perhaps in the crystalline form, though as Friedel, Orchin, and Reggel (*J. Amer. Chem. Soc.*, 1948, **70**, 199) have shown, this is very nearly true at least for 2 : 2'-dinaphthyl. In the cases of those other molecules which are not coplanar (particularly in ortho-conjugation), it seems most probable that the calculated mobile bond orders  $p$  should be multiplied by a factor approximately equal to  $\cos \theta$ , where  $\theta$  is the angle between the two parts of the composite molecule. We have thought it best to leave our results without this factor, treating the molecules as if they were planar; for this illustrates our general conclusions regarding the conjugation of radicals of different size without the complication due to steric hindrance. Table III shows the results obtained.

TABLE III.

*Bond orders in dinaphthyls, dianthryls, etc.*

Dinaphthyl .....	1 : 1'	2 : 2'	1 : 2'	
$p$ .....	0.404	0.375	0.389	
Dianthryl .....	1 : 1'	2 : 2'	1 : 2'	9 : 9'
$p$ .....	0.413	0.380	0.396	0.464
Phenyl-naphthalene .....	1-Phenyl	2-Phenyl		
$p$ .....	0.385	0.372		
Phenylanthracene .....	1-Phenyl	2-Phenyl	9-Phenyl	
$p$ .....	0.389	0.375	0.407	
Diphenyl : $p =$ .....	0.370			

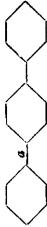
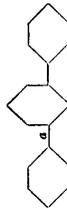
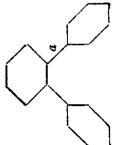
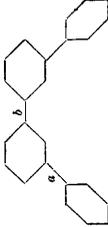
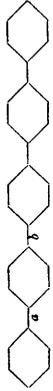
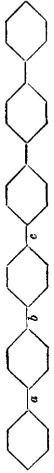
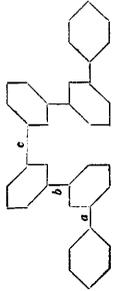
Several conclusions may be drawn from this table :

(a) Increasing the size of the units invariably increases the value of  $p$ ; and this is true whether the two conjugating units are the same or different.

(b) The 1-positions in naphthalene and anthracene are more effective than the 2-positions, in agreement with their conjugating powers defined in C.L.-H. When these positions are mixed, as in the 1 : 2'-compounds, the bond order is closely the mean of the 1 : 1'- and the 2 : 2'-bond orders.

(c) The *meso*-position in anthryl is much more susceptible than any of the other positions in any of these molecules, again in agreement with C.L.-H.

TABLE IV.  
Bond orders in polyphenyls.

	<i>para</i> -	<i>meta</i> -	<i>ortho</i> -
Diphenyl	 $p_a = 0.370$		
Terphenyl	 $p_a = 0.375$	 $p_a = 0.369$	 $p_a = 0.379$
Quaterphenyl	 $p_a = 0.375$ $p_b = 0.380$	 $p_a = 0.369$ $p_b = 0.363$	
Quinquephenyl	 $p_a = 0.375$ $p_b = 0.380$		
Hexaphenyl	 $p_a = 0.374$ $p_b = 0.381$ $p_c = 0.381$	 $p_a = 0.369$ $p_b = 0.368$ $p_c = 0.368$	
<i>s</i> -Triphenylbenzene		(Spokes)	$p = 0.368$ (Central ring) $p = 0.622$
Hexaphenylbenzene		"	$p = 0.371$ " " $p = 0.576$
Hexadiphenylbenzene		"	$p = 0.399$ " " $p = 0.572$

*Group 3. Polyphenyls.* The interest in this group arises from the fact that phenyls can combine in *o*-, *m*-, or *p*-positions. It is also known that a phenyl group will conjugate, though somewhat inefficiently, in the same way as a vinyl group. Table IV shows the results obtained. We have omitted the higher *o*-polyphenyls because, as Karle and Brockway have shown experimentally (*J. Amer. Chem. Soc.*, 1946, **68**, 1974), three phenyls in *o*-positions relative to each other are at a mutual angle of nearly 90°. Steric effects here predominate over resonance ones. The conclusions from this table are :

(d) Conjugation in the polyphenyls is almost independent of the number of rings conjugated together (cf. terphenyl with hexaphenyl, and *s*-triphenylbenzene with *m*-terphenyl).

(e) Conjugation in the *p*-position is a little more effective than in the *m*-position. These two results are in close accord with experimental observations by Gillam and Hey (*J.*, 1939, 1170) who found that the ultra-violet spectra of these compounds showed only a very gradual shift to the red with increasing number of rings (a "convergent" series), and that this shift was a little greater for the *p*- than for the *m*-compounds. Now, ultra-violet absorption spectra arise through transitions from the ground level to an excited level. It would appear from the experimental facts that the conjugation is almost independent of the number of rings, both in the ground and in the excited levels of these molecules.

(f) A comparison of diphenyl with butadiene ( $\nu = 0$  in Table I) shows that a phenyl group is less efficient than a vinyl group in conjugation. This agrees with C.L.-H., who showed that their conjugating powers were 0.398 and 0.500, respectively, and with some valence-bond calculations by Pauling and Sherman (*J. Chem. Physics*, 1933, **1**, 679) who state that "a phenyl group is 20 or 30% less effective in conjugation than a double bond." It also agrees with some unpublished calculations by one of the authors (C. A. C.), who showed that in the infinite *p*-polyphenyl, the extra conjugation energy per phenyl group was 0.388 $\beta$ \* and in the infinite polyene chain it amounted to 0.548 $\beta$  per double bond; the ratio of these two quantities is 0.71, which is very similar to the ratio found by Pauling and Sherman, and in C.L.-H. These values relate to the energy of the molecule in its ground state. One must be careful not to apply them to excited states, with a view to the prediction of ultra-violet spectra. Here the effect of a phenyl group often exceeds that of a vinyl group: Lewis and Calvin (*Chem. Rev.*, 1939, **25**, 273), for example, in a study of the diphenylpolyenes Ph·[CH:CH]<sub>n</sub>·Ph, concluded that each Ph was the equivalent of 2.35 of the central units; and in a similar connection Hausser (*Z. techn. Physik*, 1934, **15**, 10) has taken the value 1.5.

(g) The diphenyl radical, being larger than the phenyl, is able to conjugate more effectively, so that the "spokes" in hexadiphenylbenzene have a bond order greater than those in hexaphenylbenzene. There is a kind of compensation here, showing that the enhanced bond order is partly taken from the central benzene ring, for in the less conjugated molecule the order of the central ring bonds is a little greater than in the other. But when only three phenyls, instead of six, are conjugated with the central ring, the bond order in this ring is distinctly higher.

*Group 4 Vinyl compounds.* These compounds are obtained by conjugating a double bond with some other larger radical. One or two particular cases of this have already occurred in Group 1, and some others have been given in C.L.-H. The rest are given in Tables V and VI for the first time. Here, in addition to the bond order  $p_s$  of the "single" bond, we also give

TABLE V.

*Bond orders in vinyl compounds.*

( $p_s$  and  $p_d$  refer to "single" and "double" bonds respectively. In the diphenyl compounds  $p_c$  refers to the central bond of the diphenyl group.)

Compound.	$p_s$ .	$p_d$ .	Compound.	$p_s$ .	$p_d$ .	$p_c$ .
Naphthyl .....	1-	0.425	Diphenyl .....	<i>o</i> -	0.417	0.381
	2-	0.409		<i>m</i> -	0.405	0.369
Anthryl .....	1-	0.429		<i>p</i> -	0.412	0.376
	2-	0.412	Vinyl .....		0.447	0.894
	9-	0.451	1-Butadienyl .....		0.483	0.871
Phenyl .....		0.406	2-Butadienyl .....		0.408	0.908
			1-Hexatrienyl .....		0.495	0.862
			3-Hexatrienyl .....		0.435	0.891
			Infinite polyene chain		0.509	0.849

\*  $\beta$  is the conventional resonance integral for  $\pi$ -orbitals on adjacent carbon atoms.

TABLE VI.

Bond orders in phenyl- and diphenyl-ethylenes.

( $p_s$ ,  $p_d$ , have the same significance as in Table V;  $\phi$  denotes a phenyl radical, D denotes a diphenyl radical.)

Molecule.	$p_s$ .	$p_d$ .	Molecule.	$p_s$ .	$p_d$ .
$\phi\text{HC}=\text{CH}_2$	0.406	0.911	$\text{DHC}=\text{CH}_2$	0.412	0.908
$\phi\text{HC}=\text{CH}\phi$	0.431	0.820	$\text{DHC}=\text{CHD}$	0.440	0.811
$\begin{array}{c} \phi \\ \diagdown \\ \text{C}=\text{CH}_2 \\ \diagup \\ \phi \end{array}$	0.376	0.843	$\begin{array}{c} \text{D} \\ \diagdown \\ \text{C}=\text{CH}_2 \\ \diagup \\ \text{D} \end{array}$	0.381	0.836
$\begin{array}{c} \phi \quad \phi \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \phi \quad \text{H} \end{array}$	(a) 0.396	0.752	$\begin{array}{c} \text{D} \quad \text{D} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{D} \quad \text{H} \end{array}$	(a) 0.403	0.739
$\begin{array}{c} \phi \quad \phi \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \phi \quad \text{H} \end{array}$	(b) 0.450		$\begin{array}{c} \text{D} \quad \text{D} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{D} \quad \text{D} \end{array}$	(b) 0.462	
$\begin{array}{c} \phi \quad \phi \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \phi \quad \phi \end{array}$	0.410	0.685		0.417	0.668

the order  $p_d$  of the vinyl, or "double" bond. As a result of the conjugation, this is decreased below 1.0. We draw the following conclusions from these tables:

(h) The conjugation of a naphthyl, anthryl, or phenyl radical with a vinyl group is similar to their conjugation with each other, so that both in the matter of the dependence on size and in the choice of conjugating position (*e.g.*, 1- or 2-naphthyl) the conclusions (a), (b), and (c) apply equally well to Table V as to Table III.

FIG. 1.

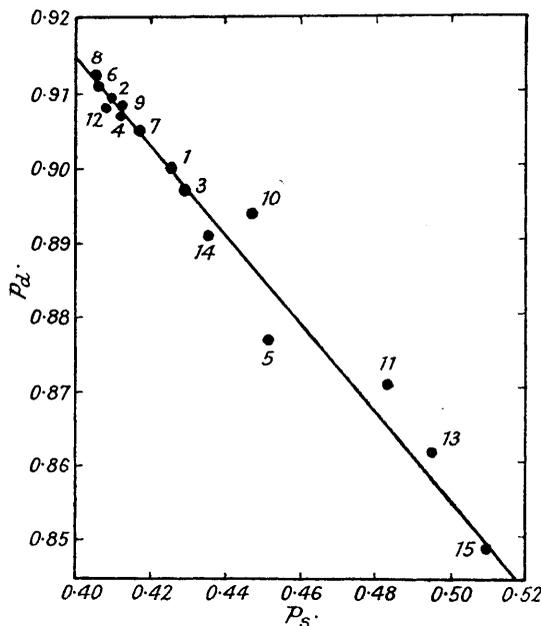
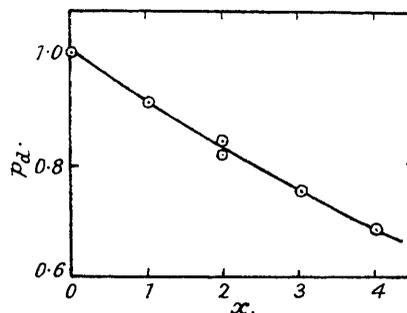


FIG. 2.



(i) So far as the *o*-, *m*-, and *p*-diphenylethylenes of Table V are concerned, the situation is exactly comparable with that summarised in (e) for the three corresponding terphenyls.

(j) A glance at Table V shows that, whenever the "single" bond has a high mobile order, the "double" bond order is reduced. This is shown more clearly in Fig. 1, which shows the values of  $p_s$  and  $p_d$  in this table plotted against one another and numbered according to their sequence in Table V. The points lie quite closely on one straight line, the only serious exceptions being the 9-anthrylethylene and butadiene, both of which are somewhat different from the other compounds in this table. This figure makes it very clear that the single bond acquires at least part of its double-bond character at the expense of the vinyl group; the terms "donor" and "acceptor" could very naturally be used to describe this phenomenon. On the other

hand, the slope of the line in Fig. 1 is not unity, so that, as the three values of  $p_c$  in Table V illustrate, the central bond accepts from both groups to which it is attached.

(k) The diphenyl radical is always more effective than the phenyl in increasing the bond order  $p_s$  and at the same time in lowering  $p_d$ , though the effect on  $p_d$  is quite small. This shows that a bond which has become acceptor from one side is able also to become acceptor from the other side. On the other hand, there is a slight saturation effect, in that if two single bonds receive from the same end of the ethylene double bond, as in  $\phi_2C=CH_2$ , their order is lower than when only one single bond competes for the donor power of the C=C bond (0.376 instead of 0.406). But if the two single bonds receive from opposite ends of the C=C link, as in  $\phi CH=CH\phi$ , their order is increased (0.431 instead of 0.406). In the latter case it is evident that the longer the conjugation path, the more exalted will be the bond order of the "single" bonds. An interpretation of these effects can be given without difficulty in the language of bond fixation and valence-bond resonance, as can soon be seen by writing down a few likely structures showing the "single" bond as double.

(l) The values of the double-bond order  $p_d$  in Table VI may be summarised by saying that the greater the phenylation of the original ethylene bond, the lower its bond order becomes. The case of the phenylethylenes is shown in Fig. 2, where the bond order of the double bond in  $C_2H_{4-x}Ph_x$  is plotted against  $x$ . When  $x = 0$  we have ethylene, and when  $x = 4$ , tetraphenylethylene. There are two values for  $x = 2$ , corresponding to the symmetrical and the unsymmetrical molecule; fortunately they do not differ very greatly. It will be seen that the graph in Fig. 2 is almost a straight line. The corresponding curve for  $C_2H_{4-x}D_x$ , where D is diphenyl, is very similar to that for the phenylethylenes.

We may say, in general terms, that the conjugation of an ethylene double bond will always lead to a certain loss of double-bond character, and thus a weakening of the bond. Each successive additional conjugation weakens it further, though the weakening is a little less noticeable if the second group is substituted at the same end as the first. It is important to recognise that this weakening of the bond does not correspond to any actual flow, or migration, of charge: for all the molecules considered are alternant (*i.e.*, crossable) hydrocarbons in the language of Coulson and Rushbrooke (*Proc. Camb. Phil. Soc.*, 1940, **36**, 193) so that the charges associated with the different nuclei are all equal, in this approximation. There may be—and probably is—a polarity effect in addition to the conjugation effect which we have described. But since polarity effects (Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **192**, 16, and especially pp. 23 and 24) may be shown to exert no first-order effect on bond orders in alternant hydrocarbons, it is unlikely that any such effects would be large. The most easily visualised interpretation of this weakening of the bond seems to be that increasing the conjugation of this bond with other resonating groups has the effect of loosening the pairing of the spins of the two electrons, so that they are no longer completely anti-parallel, and consequently (Penney, *ibid.*, 1937, *A*, **158**, 306) the bond strength is reduced. In molecular orbital language we could say that the larger the region over which the mobile electrons may move without any particular preference to concentrate around any of the atomic centres, the more closely will all the bonds tend to be equal, and approach the value appropriate to graphite. This will be more true if the original double bond is in the middle of the complete system than if its conjugations are all at one end.

The distinction which we have made between symmetrical and unsymmetrical conjugation with two phenyl groups is also shown in the reduction potentials for a double bond in various degrees of phenylation. Wawzonek and Laitinen's experimental values (in volts) (*J. Amer. Chem. Soc.*, 1942, **64**, 1767, 2365; quoted from Birch, *Faraday Soc. Discussions*, 1947, **2**, 246) are :

$PhCH=CH_2$ .	$PhCH=CHPh$ .	$Ph_2C=CH_2$ .	$Ph_2C=CHPh$ .	$Ph_2C=CPh_2$ .
-2.343	-2.140	-2.258	-2.118	-2.046

This table is extremely similar to the appropriate half of Table VI, and would give a curve very similar to that of Fig. 2. This shows again that two phenyl groups at the same end of a double bond have less effect than one at each end.

*Conclusion.*—We have shown that resonance across a "single" bond has a definite tendency to stabilise the molecule by giving a certain double-bond character to this link. We have given exhaustive tables of such bond orders and have shown how they may be related to the number and size of the conjugating groups. The value of such analysis seems to us to be threefold :  
 (a) In the physical sense, it describes the geometry, *e.g.*, bond length, of the molecule concerned.  
 (b) In a static chemical sense it provides us with a deeper insight into the nature and character of

$\pi$ -electron conjugation. (c) In the dynamic chemical sense it gives us a measure of reactivity for addition, for, as Gold (*Trans. Faraday Soc.*, 1949, 45, 191) has recently demonstrated by explicit calculation, there is a direct relation between the order of a bond and the energy change that takes place when the carbon atoms at the end of the bond are saturated. It is quite true that many other factors play some part as well, but this is certainly one important consideration, of particular application when one of the conjugating units is a double bond.

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WHEATSTONE PHYSICS LABORATORY,  
KING'S COLLEGE, LONDON.

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#### APPENDIX.

This appendix is solely concerned with the mathematical technique and calculations. It was shown (C.L.-H.) that if two resonating units A and B are conjugated by joining atom *a* of A to *b* of B to form a single resonating unit C, as in Fig. 3, then the mobile order of the bond *ab* is

$$p_{ab} = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\beta_{ab} A_{a,a} B_{b,b}}{AB - \beta_{ab}^2 A_{a,a} B_{b,b}} dy = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\beta_{ab} A_{a,a} B_{b,b}}{C} dy \quad (1) \quad \text{Fig. 3.}$$

$A(\epsilon)$ ,  $B(\epsilon)$ , and  $C(\epsilon)$  denote the secular determinants for the two separate units and the final molecule as functions of the energy  $\epsilon$ , and  $A_{a,a}$ ,  $B_{b,b}$  are similar determinants when atoms *a* and *b* have been removed.  $\beta_{ab}$  is the resonance integral across the bond *a-b*. In our work all resonance integrals have been given the single value  $\beta$ . In (1)  $\epsilon$  has to be given the value  $iy$  and the integration is between  $\pm \infty$ .

Now since all the structures considered are alternant hydrocarbons every secular determinant is of the form

$$\Delta(\epsilon) = \epsilon^n - f\beta^2\epsilon^{n-2} + g\beta^4\epsilon^{n-4} - \dots$$

with alternating signs, and only either odd, or even, powers of  $\epsilon$ . Thus  $\Delta(iy)$  has all its terms of the same sign, and the integrand in (1) is always of the form shown in Fig. 4. Only one half of the total range need be considered, because of symmetry around  $y = 0$ .

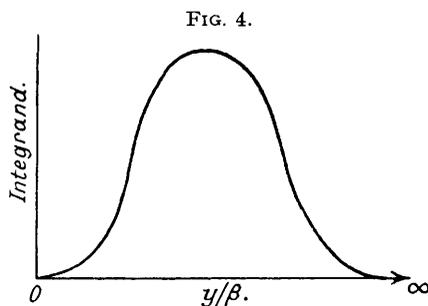


FIG. 4.

We found it best to make the integrations numerically by direct evaluation of the integrands. This was considerably shorter than the possible alternative of solving the secular determinant  $C(\epsilon) = 0$  and using the standard definition of bond order in terms of the coefficients in the different molecular orbitals (Coulson, *Proc. Roy. Soc.*, 1939, A, 169, 413). The technique was the same as that already described by Coulson (*Proc. Camb. Phil. Soc.*, 1940, 36, 201) for calculation of the total mobile energy. A great advantage of this method was that once the fundamental polynomials  $A(iy)$ ,  $B(iy)$ ,  $A_{a,a}(iy)$ ,  $B_{b,b}(iy)$  had been

evaluated for a suitable set of values of  $y$ , any pair of radicals could be conjugated together and the bond order  $p_{ab}$  could be calculated in about an hour. In this way the whole process was systematised, and everything depended on the values of some  $30 \times 2 = 60$  polynomials.

It was found convenient to divide the complete range 0 to  $\infty$  of  $y$  into three ranges 0— $2\beta$ ,  $2\beta$ — $6\beta$ , and  $6\beta$ — $\infty$ . In each of the first two ranges a 9-ordinate rule of numerical integration was used. In the third range,  $6\beta$ — $\infty$ , the following asymptotic expansion was practicable.

$C(\epsilon)$  is the secular determinant for the complete molecule, and  $A_{a,a}(\epsilon)$ ,  $B_{b,b}(\epsilon)$  [ $\equiv D(\epsilon)$ , say] is the secular determinant for the whole molecule, from which the bond *a-b* has been removed. Let there be  $n$  carbon atoms in the complete molecule. Then we can expand C and D in the form

$$\begin{aligned} C(\epsilon) &= \epsilon^n - f_C \beta^2 \epsilon^{n-2} + g_C \beta^4 \epsilon^{n-4} - \dots \\ D(\epsilon) &= \epsilon^{n-2} - f_D \beta^2 \epsilon^{n-4} + g_D \beta^4 \epsilon^{n-6} - \dots \end{aligned} \quad (2)$$

The integral in (1) becomes, after a little reduction,

$$\frac{2}{\pi} \int_{-\infty}^{\infty} \left( \frac{1}{t^2} + \frac{c_1}{t^4} + \frac{c_2}{t^6} + \dots \right) dt \quad (t = y/\beta) \quad \dots \quad (3)$$

where

$$\begin{aligned} c_1 &= f_D - f_C \\ c_2 &= g_D - g_C + f_C(f_C - f_D) \quad \dots \quad (4) \end{aligned}$$

The contribution from  $t = 6$  to  $t = \infty$  is

$$\frac{2}{\pi} \left\{ \frac{1}{6} + \frac{c_1}{3 \times 6^3} + \frac{c_2}{5 \times 6^5} + \dots \right\}$$

Only the three terms shown are sufficient for an accuracy of 1 in 10,000. The first two terms alone give 1 in 1000.

Now there are particularly simple expressions for the coefficients  $f$  and  $g$ . Thus Coulson has shown (*Proc. Camb. Phil. Soc.*, in the press) that

$$f_C = \text{no. of bonds in the structure C,}$$

so that  $f_C - f_D$  is simply the number of bonds that are lost when atoms  $a$  and  $b$  are removed from the complete molecule. This must have one of the values 3, 4, or 5, and may be obtained by simple inspection without the need to evaluate any secular determinant.

Similarly  $g_C =$  no. of distinct pairs of bonds in structure C, which are non-adjacent to each other. Thus the coefficient  $c_2$  in (4) is easily found by inspection: it takes all values between 4 and 29, with a contribution to  $\mathcal{P}_{ab}$  that lies between 0.00007 and 0.00047. As a result of this, the calculations are nothing like so arduous as might have been expected.

An example will show how the method works. In diphenyl, the contributions are

range 0—2β .....	0.1307
range 2β—6β .....	0.1373
range 6β—∞ .....	0.1015
$\mathcal{P}_{ab}$ .....	0.3695

In this case a direct calculation from the coefficients in the molecular orbitals can fairly easily be made. It yields the accurate value 0.36968, showing that our technique is quite adequate if bond orders are wanted to not more than 3 decimal places. This is at least as accurate as is warranted by the idea of a fractional bond order.

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