Calculated Bond Lengths in Some Cyclic Compounds. Part III. Benzoic Acid.*

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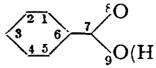
Energy levels, bond orders, and bond lengths have been deduced as accurately as possible for benzoic acid by the molecular-orbital method with both neglect and inclusion of overlap. The results have been compared with the *X*-ray measurements by Sim, Robertson, and Goodwin (*Acta Cryst.*, 1955, **8**, 157) and show a mean deviation from these of only $| \Delta | = 0{\cdot}014$ Å although it has usually been supposed that with heterocyclic compounds the calculations cannot be relied on to nearer than 0·05 Å.

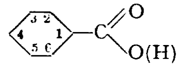
Wave-mechanical studies of benzene, naphthalene, and other aromatic hydrocarbons have been made during several years by both the valency-bond and the molecular-orbital method. Although the qualitative use of the valency-bond method by organic chemists in the form of " resonating structures " to explain the properties of hydrocarbons and their derivatives is well established, in this Series the molecular-orbital technique is being applied to calculate bond lengths for comparison with experimental measurements made chiefly by *X*-ray crystallography. The crystal structure of benzoic acid has recently been published by Sim, Robertson, and Goodwin (*Acta Cryst.*, 1955, **8**, 157) who have measured the interatomic distances with a standard deviation of about 0·020 Å. The present work was carried out to compare these experimental results with the most accurate values calculable by the molecular-orbital technique.

Parameters for Secular Equations

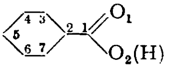
Three sets of calculations are presented. In the first two, described as methods 1 and 2, different values were used for the Coulomb integrals α, but the resonance (exchange) integrals *H* were the same and the overlap integrals *S* were neglected. In method 3 the α's were given the same values as in method 2, the *H*'s were modified slightly in the light of the results of method 2, and the overlap integrals were included. The values of these parameters were selected as follows.



(I*a*) (Numbering used in these calculations.)



(I*b*) (Standard numbering.)



(I*c*) (Numbering used by Sim, Robertson, and Goodwin.)

(a) *Coulomb Integrals.*—In benzoic acid (I) each of the seven carbon atoms and one oxygen atom supplies one p_z electron to the π-molecular-orbital system, while the hydroxyl-oxygen atom supplies its two p_z electrons. Thus nine molecular orbitals accommodate ten electrons. Now, in applying the molecular-orbital treatment to the π-electron system of benzoic acid, we suppose all these ten electrons to have been removed from the molecule. The Coulomb integral α of an atom then represents the net attraction of its nucleus and other electrons (σ-binding and non-binding) for the π-electrons which are to be fed in in pairs to each π-molecular orbital in succession. This attraction differs with the kind of atom and with the number of p_z electrons which it has lost. Thus $| \alpha_{\text{oxygen}} | > | \alpha_{\text{C}} |$, where C represents a standard aromatic carbon atom and, in particular, $\alpha_8 = \alpha_{\text{C}} + m\beta$ and $\alpha_9 = \alpha_{\text{C}} + m'\beta$, where $m' \approx 2m$ since atom 9 contributes two and atom 8 only one electron to the π-system. However these electron-affinity differences between oxygen and carbon induce changes in the Coulomb terms of the carbon atoms throughout the molecule. These changes (cf. Dewar, *Nature*, 1950, **166**, 790) have been supposed to be given by $\delta_i = 0{\cdot}6^n\beta$ in method 1 and by $\delta_i = 2 \times 0{\cdot}3^n\beta$ in methods 2 and 3, *n* being the number of bonds separating the *i*th (carbon) atom from oxygen. In setting up the secular equations these corrections were rounded to the second place of decimals. However it was not discovered

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* Part II, *J.*, 1955, 1689.

until the calculations of method 1 were complete that a slip had been made in writing the coefficient for the induced Coulomb effect as $0{\cdot}6^n\beta$, which is much too high. The results are therefore presented here simply as a demonstration of the consequences of using this coefficient; no discussion will be given of them.

(b) *Resonance Integrals.*—The parameters H_{rs} selected in methods 1 and 2 are adequately set out in Table 1 and call for no further comment. In method 3 the standard value $\beta_{1\cdot39}$ (written β in Table 1) was used for all neighbouring atoms of the benzene ring because the bond lengths in this ring were likely to be very closely similar to those in benzene and to show very little variation among themselves. Following Lennard-Jones (*Proc. Roy. Soc.*, 1937, *A*, **158**, 280), Mulliken, Rieke, and Brown (*J. Amer. Chem. Soc.*, 1941, **63**, 48) give a Table showing the variation of β with interatomic distance and, this being used, H_{67} was set equal to $0{\cdot}72\beta_{1\cdot39}$. For the bonds involving oxygen β_{78} was again taken as $\sqrt{2}\beta_{1\cdot39}$(C–C) as in method 2 but β_{79} was evaluated as follows : the orders of bonds 7—8 and 7—9 obtained by method 2 were 0·542 and 0·723 respectively. Had these been between carbon atoms they would have corresponded to lengths of 1·373 and 1·427 Å and so to β values of $1{\cdot}05\beta_{1\cdot39}$ and $0{\cdot}87\beta_{1\cdot39}$. The same law of variation of β with distance being assumed for C–O and C–C bonds, this leads to $\beta_{79} = 0{\cdot}87\sqrt{2}\beta_{1\cdot39}/1{\cdot}05 = 1{\cdot}17\beta_{1\cdot39}$.

(c) *Overlap Integrals.* (*Method* 3 *only.*)—For the ring bonds S_{rs} was taken as 0·25. By using a linear interpolation between the values of 0·25 and 0·19 given by Mulliken, Rieke, Orloff, and Orloff (*J. Chem. Phys.*, 1949, **17**, 1257) for carbon atoms respectively 1·39 and 1·54 Å apart a figure of 0·22 was adopted for S_{67} on the basis of the length calculated in method 2. In a similar way interpolation between 0·23 and 0·14 for carbon and oxygen atoms respectively 1·22 and 1·43 Å apart gave $S_{78} = 0{\cdot}23$ and $S_{79} = 0{\cdot}20$.

These various sets of parameters are summarised in Table 1.

TABLE 1. *Parameters for benzoic acid.*

	Method		
	1	2	3
Coulomb integrals a_r			
α_C	—	—	$-3{\cdot}52\beta$
$\alpha_1 - \alpha_C = \alpha_5 - \alpha_C$	$0{\cdot}22\beta$	$0{\cdot}05\beta$	$0{\cdot}05\beta$
$\alpha_2 - \alpha_C = \alpha_4 - \alpha_C$	$0{\cdot}13\beta$	$0{\cdot}02\beta$	$0{\cdot}02\beta$
$\alpha_3 - \alpha_C$	$0{\cdot}08\beta$	0	0
$\alpha_6 - \alpha_C$	$0{\cdot}36\beta$	$0{\cdot}18\beta$	$0{\cdot}18\beta$
$\alpha_7 - \alpha_C$	$0{\cdot}6\beta$	$0{\cdot}6\beta$	$0{\cdot}6\beta$
$\alpha_8 - \alpha_C$	$0{\cdot}5\beta$	$1{\cdot}25\beta$	$1{\cdot}25\beta$
$\alpha_9 - \alpha_C$	β	2β	2β

	Method		
	1	2	3
Resonance integrals H_{rs}			
r and *s* Neighbours within ring	β	β	β
H_{67}	β	β	$0{\cdot}72\beta$
H_{78}	$\sqrt{2}\beta$	$\sqrt{2}\beta$	$\sqrt{2}\beta$
H_{79}	$\sqrt{2}\beta$	$\sqrt{2}\beta$	$1{\cdot}17\beta$
All others	0	0	0
Overlap integrals S_{rs}			
r and *s* Neighbours within ring	0	0	0·25
S_{67}	0	0	0·22
S_{78}	0	0	0·23
S_{79}	0	0	0·20
All others	0	0	0

EVALUATION OF BOND ORDERS WHEN OVERLAP IS INCLUDED

The inclusion of the induced Coulomb terms in methods 1 and 2 makes the expansion and solution of the secular determinant slightly more laborious than usual but by employing such of the techniques described in Part I (*J.*, 1955, **1683**) as are applicable some reduction in the work is possible. Thereafter the calculation of bond orders, etc., calls for no comment.

For a hydrocarbon the bonds of which are all of approximately the same order and hence have the same value of the overlap integral the secular determinant with overlap differs from that without only in that the non-zero elements lying off the leading diagonal are $\beta - SE$ instead of β. A simple transformation then gives the energy levels and the delocalisation energy in units of $\gamma = \beta - \alpha S$ instead of β. However, with heteromolecules this is not possible because of the inequality of the overlap, Coulomb, and exchange integrals involved. In particular, in the present case, it was necessary to express the Coulomb term of a standard carbon atom as a multiple of $\beta_{1\cdot39}$. This was done as follows.

Inspection of a table such as Hartmann's ("Theorie der chemischen Bindung," Springer, Berlin, 1954, pp. 267, 268) shows that the ratio of the delocalisation energy in units of β to that in units of γ is roughly constant over a wide range of hydrocarbons and closely constant over a smaller range of very similar compounds such as benzene, naphthalene, and anthracene. An even wider range of similar information, closely correlated with molecular size and constitution and leading to the same conclusion is obtainable from Bradburn, Coulson, and Rushbrooke's work (*Proc. Roy. Soc. Edinburgh*, 1948, **62**, 336) in which the delocalisation energies *per carbon atom* in units of β and γ can be derived by subtracting unity from each entry in their Table 1 and 0·8 from each entry in their Table 4, the π-energy per carbon atom in ethylene being 1β and $0{\cdot}8\gamma$ respectively. If it is then assumed as a first approximation that the delocalisation energies calculated by both these methods represent the same thing, *viz.*, the difference between observed and calculated heats of formation, they may be used to evaluate α. Thus, benzene being selected for an obvious reason, though styrene might have been better, the delocalisation energies are $2{\cdot}00\beta = 1{\cdot}067\gamma = 1{\cdot}067(\beta - \alpha S)$. Writing $S = 0{\cdot}25$ as usual this gives $\alpha = -3{\cdot}52\beta$ (styrene would have given $\alpha = -4{\cdot}01\beta$), a value agreeing with the ratio α/β implied by Mulliken, Rieke, and Brown (*loc. cit.*). If it is then reasonable to suppose that this value of α can be taken as applying to the " standard aromatic arbon atom " in benzoic acid the elements of the secular determinant can be expressed in terms of β and E alone, and hence the energy levels can be deduced as in methods 1 and 2. Incidentally, the change in the origin of energy does not affect the ratio of β/γ as might at first sight be expected.

Table 2 gives these energy levels for the molecular orbitals of the π-electrons in benzoic acid as calculated for each set of parameters while Tables 3 and 4 give the corresponding electron distributions, q, mobile bond orders, p, etc. The quantities q and p for method 3 were calculated as indicated by Chirgwin and Coulson (*Proc. Roy. Soc.*, 1950, *A*, **201**, 196). Since resonance and overlap integrals have been neglected except between nearest neighbour orbitals the combined effect of the carbonyl-oxygen atom 8 and the hydroxyl-oxygen atom 9 is the same at both atoms 1 and 5. Hence the ring shows axial symmetry about the line joining atoms 3 and 6. The theoretical bond lengths L_1 and L_2 in Table 4 are derived from the bond orders by the correlations indicated in Part I (*loc. cit.*) while L_M gives the measured lengths reported by Sim, Robertson, and Goodwin (*loc. cit.*); $\Delta = L_M - L_2$.

TABLE 2. *π-Electron molecular-orbital energy levels (E_i) for benzoic acid in order of increasing energy.*

	Method				Method		
i	1	2	3	i	1	2	3
1	$\alpha + 2{\cdot}9836\beta$	$\alpha + 3{\cdot}3816\beta$	$-0{\cdot}2948\beta$	6	$\alpha - 0{\cdot}6157\beta$	$\alpha - 0{\cdot}5601\beta$	$-5{\cdot}0967\beta$
2	$\alpha + 2{\cdot}0946\beta$	$\alpha + 2{\cdot}0513\beta$	$-1{\cdot}0031\beta$	7	$\alpha - 0{\cdot}8285\beta$	$\alpha - 0{\cdot}9651\beta$	$-5{\cdot}9460\beta$
3	$\alpha + 1{\cdot}1774\beta$	$\alpha + 1{\cdot}6024\beta$	$-1{\cdot}8043\beta$	8	$\alpha - 1{\cdot}4876\beta$	$\alpha - 1{\cdot}3951\beta$	$-7{\cdot}4967\beta$
4	$\alpha + 1{\cdot}1758\beta$	$\alpha + 1{\cdot}0923\beta$	$-1{\cdot}9879\beta$	9	$\alpha - 1{\cdot}9986\beta$	$\alpha - 2{\cdot}0723\beta$	$-11{\cdot}6932\beta$
5	$\alpha + 0{\cdot}7390\beta$	$\alpha + 1{\cdot}0351\beta$	$-2{\cdot}0074\beta$				

DISCUSSION

In the crystallographic study of benzoic acid it was found that though the benzene ring may be regarded as strictly planar the carbon atom numbered 7 in this paper and the oxygen atom numbered 9 are 0·042 and 0·068 Å respectively from the plane of the ring. These deviations, though small, appear to be significant because they are several times as great as the standard deviation of position of a carbon or an oxygen atom. The molecular-orbital treatment adopted here is based on the assumption of an entirely planar molecule, first, because this is the most obvious molecular structure resulting from maximum overlap of neighbouring atomic orbitals throughout the molecule, secondly, because the extra delocalisation energy of benzoic acid over that of benzene (see, *e.g.*, Pauling, " Nature of the Chemical Bond," Cornell Univ. Press, New York, 1944, p. 139) indicates that the

TABLE 3. *π-Electron distribution (q) in benzoic acid.*

Atom, numbered according to			Method			Atom, numbered according to			Method		
I*a*	I*b*	I*c*	1	2	3	I*a*	I*b*	I*c*	1	2	3
1, 5	2, 6	3, 7	0·991	0·949	0·976	7	C	1	0·981	0·810	0·838
2, 4	3, 5	4, 6	0·987	0·999	1·000	8 *	=O	O_1	*1·402*	*1·538*	*1·447*
3	4	5	0·949	0·943	0·976	9 *	–O–	O_2	*1·646*	*1·746*	*1·751*
6	1	2	1·067	1·070	1·036						

* Oxygen atoms.

π-electron system must extend into the carboxyl group which one would therefore expect to be coplanar with the ring, and, thirdly, because the calculations were well under way before the *X*-ray results were completed. In any case it is not unreasonable to suppose that the small deviations from planarity noted experimentally are, if genuine (as they appear to be), the results of crystal packing rather than fundamental to the isolated molecule.

The most obvious thing about the data in Table 4 is, perhaps, the close agreement between L_M and the values of L_2 calculated by methods 2 and 3. Coulson (*Proc. Roy. Soc.*, 1951, *A*, **207**, 91) and Coulson, Daudel, and Robertson (*ibid.*, p. 306) show that for aromatic hydrocarbons molecular-orbital calculations and good *X*-ray work both permit 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 heteromolecules the agreement is not usually closer than 0·05 Å. In Table 4 the agreement is much better the average $|\Delta|$ for the nine bonds, being only 0·017 Å in method 2 and 0·014 Å in method 3. Clearly the reliability of the calculations must depend on the extent to which the system can be regarded as a hydrocarbon perturbed by heteroatoms. In benzoic acid three of the ten electrons in the nine-atom π-orbital system are supplied by the two oxygen atoms, so that a profound effect would be expected. Actually, by comparison with styrene (Pullman and Pullman, " Les Théories Électroniques de la Chimie Organique," Masson et Cie., Paris, 1952, p. 598) it seems that the effect of the oxygen atoms scarcely extends into the ring. This is shown by the following bond orders, the hydrocarbon being numbered in accordance with the scheme used in this paper for benzoic acid :

TABLE 4. *Mobile bond orders* (p) *with calculated and observed bond lengths* (L) *in benzoic acid.*

Bond, numbered according to			Method 1		Method 2				Method 3				
I*a*	I*b*	I*c*	p_{12}	L_2	p_{12}	L_1	L_2	Δ	p_{12}	L_1	L_2	Δ	L_M
1–2	2–3	3–4	0·740	1·370	0·677	1·388	1·383	0·03	0·671	1·389	1·385	0·02	1·41
1–6	1–2	2–3	0·632	1·395	0·620	1·400	1·399	−0·01	0·640	1·396	1·393	0·00	1·39
2–3	3–4	4–5	0·661	1·387	0·659	1·391	1·387	−0·03	0·664	1·390	1·386	−0·03	1·36
6–7	1–C	1–2	0·303	1·486	0·346	1·459	1·482	0·00	0·291	1·468	1·487	−0·01	1·48
7–8 *	C=O	C–O$_1$	*0·748*	*1·226*	*0·723*	*1·233*	*1·233*	*0·01*	*0·771*	*1·219*	*1·219*	*0·02*	*1·24*
7–9 *	C–O	C–O$_2$	*0·587*	*1·271*	*0·542*	*1·284*	*1·284*	*0·01*	*0·532*	*1·286*	*1·286*	*0·00*	*1·29*

* Oxygen atoms.

Bond	1–2	1–6	2–3	6–7	7–8
Benzoic acid	0·674	0·640	0·657	0·286	*0·783* *
Styrene	0·679	0·610	0·659	0·406	0·911

* Bond involving oxygen.

Thus, apart from the bonds in which they are directly concerned, the main effect of the oxygen atoms seems to be a slight lengthening of the extracyclic C–C bond compared with that in styrene. Experimental figures for this liquid are not, of course, available.

Sim, Robertson, and Goodwin (*loc. cit.*) give the standard deviations of the C–C and C–O bonds as 0·016 and 0·014 Å respectively, which could be regarded as accounting for all the discrepancies in Table 4 except those for the bonds 1–2 and 2–3. The calculations require the ring bonds to be scarcely distinguishable in length but the bond 1–2 is longer and 2–3 shorter than the calculated length, though by amounts which are only about twice the standard deviation and therefore not definitely significant. However the difference between 1–2 and 2–3 (0·05 Å) does appear to be significant as was recognised in the report on the measurements where it was pointed out that the difference could not be explained on the basis of any reasonable resonating structures which could be written for benzoic acid. This conclusion, taken with the present results, suggests that the problem is not likely to be resolved without a three-dimensional *X*-ray analysis.

The second point to notice about the figures in Table 4 is that the inclusion of overlap in the calculations has influenced only the extracyclic bonds. It is well known (Chirgwin and Coulson, *loc. cit.*) that the inclusion of overlap in calculations on hydrocarbons does not alter the bond orders though it must in heteromolecules. The present calculations indicate that the effect is local, reaching only to the first bonds of the ring. This suggests that some of the labour involved in these calculations could be avoided by including overlap only for the bonds nearest to the perturbing heteroatoms. Careful trials would be needed to establish this point since, although it is now established that there is little difference between the results when all overlap integrals are included and when none are, inclusion of some only might give quite wrong bond orders, etc.

In support of the arguments of Part I (*loc. cit.*), the length L_2 of the bond 6–7 obtained by method 2 agrees better with experiment than L_1, although in method 3 the two lengths straddle the experimental value.

Turning to Table 3 there is, of course, no change in the sequence of π-electron distributions when overlap is included, though the charges on all the atoms tend to be reduced. It will be noted that since only 1·751 (1·746) of the two p_z electrons are formally associated with the hydroxyl-oxygen atom 9 this atom carries a positive charge of 0·249 (0·254) due to this π-electron deficiency while there is a corresponding negative charge of 0·447 (0·538) on the carbonyl-oxygen atom 8.

If the charges recorded in Table 3 are used to calculate the contribution of the π-electrons to the dipole moment of the molecule a value of 3·84 D is obtained in a direction nearly along the bond 7→8. This may be contrasted with the following experimental results: 1·0 D in benzene at 25° (Williams and Allgeier, *J. Amer. Chem. Soc.*, 1927, **49**, 2416), 0·56 D in benzene at 22° (Briegleb, *Z. phys. Chem.*, 1930, *B*, **10**, 205), 1·71 D in dioxan at 25° (Wilson and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 1265), 1·78 D in dioxan at 30° (Brooks and Hobbs, *ibid.*, 1940, **62**, 2851), and 1·64 D in benzene at 30° (Pohl, Hobbs, and Gross, *Ann. New York Acad. Sci.*, 1940, **40**, 389). There are many possible causes of this discrepancy, particularly that, though the π-dipole moment would be expected to make the greatest contribution to the total moment, contributions would also be expected from the σ-bonds and from the non-bonding electrons. The σ-bond moment can be allowed for by using Orgel, Cottrell, Dick, and Sutton's data (*Trans. Faraday Soc.*, 1951, **47**, 116) and amounts to 1·2 D along the bond 6→7. This combines vectorially with the π-moment to give a total moment of 4·35 D at about 56° to the bond 6→7, but it seems unlikely that the contributions of the non-bonding electrons, etc., can account for this even larger discrepancy. However the calculations are for an isolated molecule whereas the measurements are for solutions from which the solvent effects cannot be satisfactorily eliminated and in which the molecules are dimeric. *X*-Ray examination of many carboxylic acids leads one to expect that in solution the dimers will be centrosymmetrical and hence will have no dipole moment or at most only a small one due to thermal disturbance of the centrosymmetrical ideal. Thus the observed and calculated moments are not strictly comparable but do in fact differ in the expected direction.

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