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The Crystal and Molecular Structure of Salicylic Acid*

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Bond lengths and the charge distribution in the dimeric molecule of salicylic acid have been measured with standard deviations of less than 0·01 Å and 0·1 e.Å^{-2} respectively. The results are interpreted in terms of the contributions of various 'resonance structures' to the state of the molecule. The small departure of covalently-bonded atoms from circular symmetry has been estimated to involve a transfer of about 0·05 electrons per carbon or oxygen atom.

1. Introduction

A recent study of adenine hydrochloride (Cochran, 1951*a*) has shown that when X-ray intensities have been measured with sufficient accuracy and when the technique of the $(F_o - F_c)$-synthesis is used, electron density can in favourable circumstances be measured to within 0·1 e.Å^{-2}, so that hydrogen atoms can be located in electron-density maps. It seemed worthwhile to apply similar methods to other compounds containing various types of hydrogen bond. Salicylic acid (*o*-hydroxybenzoic acid) is a very suitable example; it may be expected to show hydrogen bonds linking the carboxyl groups so as to form dimers; it also provides an example of an intramolecular, or chelate, hydrogen bond. The comparatively short length of the crystallographic *c* axis (4·92 Å) means that these bonds can be studied in projection on (001).

In previous work, the departure from spherical symmetry of covalently-bonded atoms was found to be unexpectedly small. In the adenine molecule it amounted to no more than 0·2 e.Å^{-2}. In the present investigation, a small departure of bonded atoms from spherical symmetry, of the same order of magnitude as that reported previously, has been confirmed and measured more accurately.

2. Experimental

Weissenberg photographs showed the space group of crystals of salicylic acid to be $P2_1/a$. The unit cell dimensions are

$$a = 11{\cdot}52,\ b = 11{\cdot}21,\ c = 4{\cdot}92\ \text{Å}(\pm 0{\cdot}1\%),$$
$$\beta = 90^\circ\ 50'(\pm 2').$$

The intensities of those (*hk*0) reflexions for which $s = \sin\theta < 0{\cdot}7$ were measured with Cu $K\alpha$ radiation, using a Geiger-counter spectrometer. The experimental technique has been described previously (Cochran, 1950). Four sets of measurements were made, using needle-shaped specimens having the following rectangular cross-sections: (*a*) 0·30×0·30 mm., (*b*) the same specimen after it had been dipped in liquid air, (*c*) 0·12×0·14 mm., (*d*) 0·05×0·05 mm. The relative magnitudes of the stronger reflexions increased slightly on liquid-air treatment, and more markedly when a smaller crystal was used (see Fig. 1). For the ten strongest reflexions the intensity from the smallest crystal was taken to be correct; for the others an average was taken. Comparison of independent measurements gave the mean standard deviation of the 91 structure factors in this range as $\sigma(F_o) = 0{\cdot}11$, ($F(000) = 288$). The intensities of a further 48 rereflexions in the range $0{\cdot}7 < s < 1{\cdot}0$ were measured photographically. A comparison of photographic and counter measurements in the first range gave $\sigma(F_o) =$ 0·36 for structure factors in this second range. The mean standard deviation of an (*hk*0) structure factor is therefore at least 0·20, and may be greater if systematic errors have passed undetected. An attempt to measure with the counter spectrometer the intensities of reflexions beyond $s = 0{\cdot}7$ was not successful, since the relatively large temperature factor of the crystals resulted in these reflexions being little above background level when filtered Mo radiation was used.

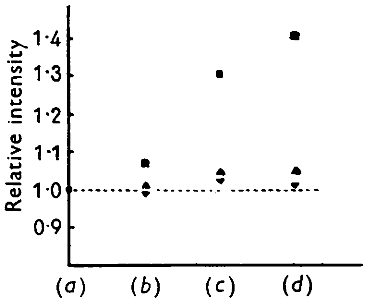

Fig. 1. Intensities from four specimens (*a*), (*b*), (*c*), (*d*) (described in the text), relative to that from specimen (*a*). Points marked ■ refer to a reflexion of intensity 27·6 × 10^4, points marked ▲ refer to a reflexion of intensity 5·8 × 10^4, points marked ▼ refer to a reflexion of intensity 2·08 × 10^4 arbitrary units.

The intensities of 40 (*h*0*l*) reflexions in the range

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* A note describing the results of preliminary work on this compound has been published (Cochran, 1951*b*).

$s < 0{\cdot}7$ were also measured, using the counter spectrometer. Two specimens of quite different shapes were used, and some measurements were made using a third very small crystal. No effects attributable to secondary extinction were observed in this case, possibly because the two larger specimens had been lightly ground in the course of preparation. Comparison of independent measurements, after correction for absorption by the method of Albrecht (1939), gave $\sigma(F_o) = 0{\cdot}17$.

3. Determination of the structure

Relative values of $F^2(hk0)$ were modified through multiplication by a factor $\exp [Bs^2]$. The value of B was chosen so that the average modified value of $F^2(hk0)$ near $s = 1$ was one-tenth of the average value near $s = 0$. A 'sharpened' Patterson function $P(x, y)$ was then evaluated. Peaks representing vectors between adjacent atoms, and between next-but-one atoms, were clearly resolved and gave the orientation of the benzene ring in this projection. A model of the molecule was then projected on to structure-factor graphs until a position was found which resulted in moderately good agreement between low-order observed and calculated structure factors. This very rough structure required two molecules to be associated through their carboxyl groups across a centre of symmetry. The idealised structure shown in Fig. 2 was now taken to represent the structure of the dimer. By taking the lengths of all covalent bonds as 1·36 Å, and of the hydrogen bonds as 2·72 Å, the X coordinates of all atoms were made multiples of 0·68 Å, while all Y coordinates are multiples of 1·18Å. With these lengths as units of distance along their respective axes, the Fourier transform of a single dimer was evaluated. The ratio of the atomic scattering factors of oxygen and carbon was assumed to be constant and equal to 1·4. The function evaluated was therefore

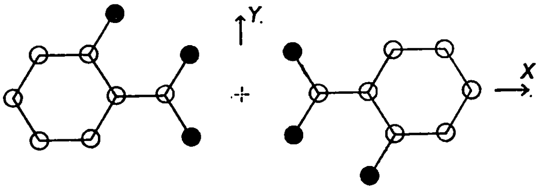

Fig. 2. Idealized structure for which the Fourier transform was calculated.

$$\begin{aligned} T(\xi, \eta) = {} & 1{\cdot}4 \cos (2\xi+\eta)+\cos (5\xi-2\eta)+\cos (2\xi-\eta) \\ & +\cos 3\xi+\cos 5\xi+\cos 9\xi+\cos (6\xi+\eta) \\ & +\cos (8\xi+\eta)+\cos (6\xi-\eta)+\cos (8\xi-\eta) \end{aligned}$$

(cf. Knott, 1940).

The evaluation was made at an interval of 6° in the ξ direction and 12° in the η direction; that is, on a rectangular lattice in reciprocal space whose translations were 0·0245 and 0·0282 Å^{-1} respectively. The ($hk0$) section of the reciprocal lattice of the crystal was now drawn in on this function in an orientation corresponding to the assumed orientation of the molecule relative to (001). Agreement between values of F_o, and values of F_c obtained from the transform, was sufficiently good to show that the postulated structure was essentially correct. The signs of about 70% of all observed $F(hk0)$'s were determined from the transform, and an approximate electron-density projection was calculated.

The signs of most of the $F(h0l)$'s were also read off from the transform, and an electron-density projection on (010) was calculated. The structure determined in this way is shown in Figs. 3 and 4.

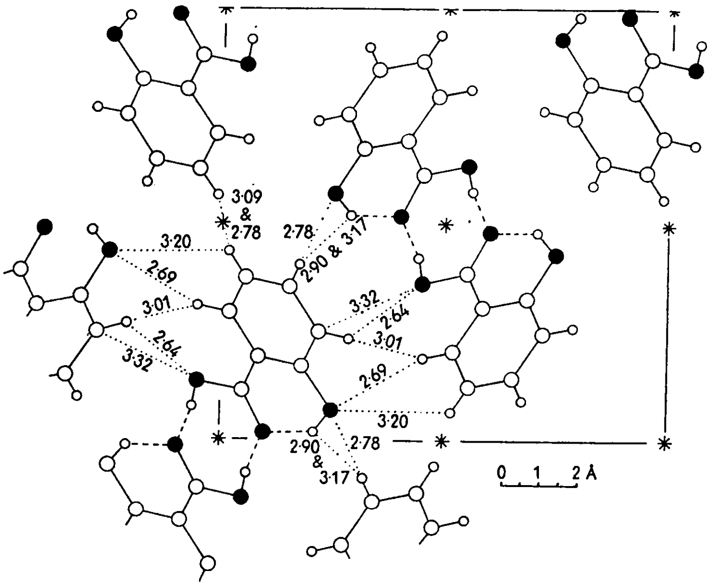

Fig. 3. Structure projected on (001). The lengths of van der Waals bonds are shown.

Table 1. *Final atomic scattering factors*

s	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
f_O	8·26	7·80	6·80	5·60	4·57	3·75	3·10	2·58	2·20	1·90	1·71
f_C	5·89	5·41	4·23	3·20	2·55	2·20	1·99	1·83	1·71	1·63	1·55
f_H	1·00	0·90	0·72	0·50	0·34	0·21	0·14	0·09	(0·06)	(0·05)	(0·03)

The method used to refine the structure was essentially the same as that described in a previous paper (Cochran, 1951*a*), and will only be outlined here.

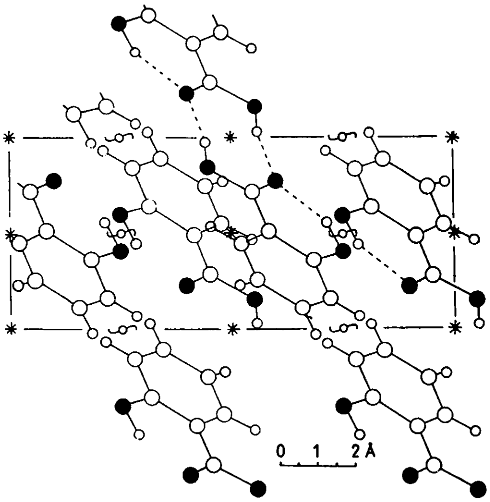

Fig. 4. Structure projected on (010).

Structure factors $\mathcal{F}_c$ were calculated for atoms at rest, using f's appropriate to 'Hartree' atoms. Calling the measured structure factors on a relative scale $\mathcal{F}_o$, constants K and γ were chosen so that the relation

$$\overline{F_o} = K\overline{\mathcal{F}_o} = \overline{\mathcal{F}_c} \exp\left[-\gamma s^2\right] = \overline{F_c} \qquad (1)$$

was most nearly satisfied over the whole range of observation. Successive $(F_o - F_c)$-syntheses were then calculated in order to improve the (xy) atomic coordinates. The value of $R = \Sigma|F_o - F_c| \div \Sigma|F_o|$, with the sum taken only over structure factors in the range $s < 0·7$ (the range of accurate measurement) was taken at each stage to be a measure of the improvement effected. Two successive corrections to atomic coordinates, and the inclusion of contributions to F_c from the four hydrogen atoms attached to the benzene ring, reduced R from an initial value of 0·24 to 0·12. At this stage it became clear that further changes in coordinates would effect little improvement, and that the disagreement arose mainly from the assumption that all atoms had the same isotropic temperature factor, γ of equation (1). Additional parameters were therefore introduced, so that for the jth atom

$$\gamma_j = \alpha_j + \beta_j \sin^2(\varphi - \psi_j)\,,$$

where $(2s, \varphi)$ are the polar coordinates of a reciprocal-lattice point and ψ_j is the angle which the direction of maximum thermal vibration makes with the a axis. The constants α, β and ψ were now chosen so as to reduce the value of $\varrho_o - \varrho_c$, at and near the centre of each atom, to zero. After a further five successive approximations had been made, involving changes of α, β and ψ, and further small changes ($\approx$ 0·01 Å) in x and y, the value of R was reduced to 0·065.

At this stage, certain anomalies in the electron distribution led to a closer investigation of the justification for the assumption that eight electrons were being subtracted from oxygen atom sites, and six from carbon atom sites. There is already a good deal of experimental and theoretical evidence that the Hartree f curve for carbon, derived by James & Brindley from Hartree's calculations on other atoms (see James, 1948) may be considerably in error. Application of a test, which will be described elsewhere, showed that in the range $0·1 < s < 1·0$, the range of experimental measurement in the work described here, the Hartree curve corresponds to an atom containing, not 6·0, but 5·7 electrons. The Hartree atomic scattering factors were therefore abandoned in favour of those in Table 1, which, except in the case of hydrogen, have only an empirical basis. However, they deviate from the Hartree curves by, at most, only 3·3%. The relative scattering factors for hydrogen, carbon, and oxygen were so little altered that the value of R was not changed from 0·065.

These scattering factors satisfy the following conditions:

(1) When temperature factors listed in Table 2 are taken into account, they represent closely the scattering by the atoms of salicylic acid in the range $0·1 < s < 1·0$.

(2) They are extrapolated to $s = 0$ in such a way that the electron density in the corresponding atom falls to zero in a reasonable distance.

Table 2. *Final atomic parameters*

Atom	x	y	α	β	$\gamma = \alpha + \frac{1}{2}\beta$	ψ
C_1	0·0841	0·1926	1·25	0·4	1·45	147°
C_2	0·1847	0·1697	1·3	0·4	1·5	147
C_3	0·2207	0·2512	1·5	0·6	1·8	135
C_4	0·1570	0·3520	1·45	1·2	2·05	147
C_5	0·0576	0·3755	1·5	0·8	1·9	180
C_6	0·0208	0·2977	1·55	0·4	1·75	180
C_7	0·0456	0·1094	1·4	0	1·4	—
O_1	−0·0514	0·1370	1·5	0·6	1·8	37
O_2	0·0990	0·0164	1·3	0·7	1·65	45
O_3	0·2503	0·0705	1·5	0·8	1·9	55
H_1	−0·060	0·075	1·7	0	1·7	—
H_2	0·213	0·020	1·7	0	1·7	—
H_3	0·286	0·233	1·7	0	1·7	—
H_4	0·188	0·399	1·7	0	1·7	—
H_5	0·017	0·431	1·7	0	1·7	—
H_6	−0·048	0·321	1·7	0	1·7	—

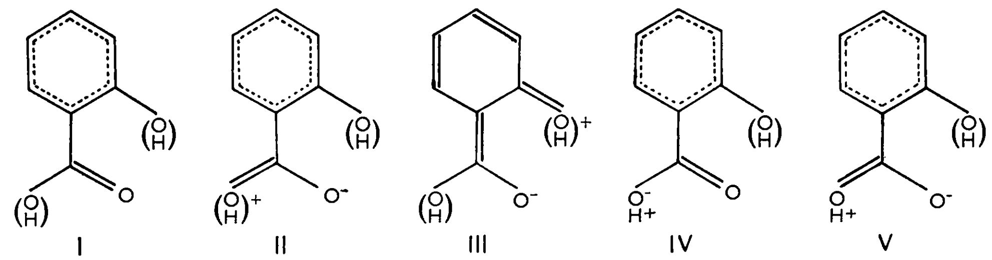

Fig. 5. Resonance 'structures' which contribute to the molecular state. A full line with a parallel dotted line indicates a bond having 50% double-bond character. The symbol $\left(\begin{smallmatrix}\mathrm{O}\\\mathrm{H}\end{smallmatrix}\right)^{+}$ is used to indicate that the transfer of electrons may be from either atom.

(3) The scale has been chosen so that the seven carbon and three oxygen atoms contain 66 electrons in all.

The use of these curves in no way prejudices the outcome of the investigation. Any deviations of the numbers of electrons in carbon and oxygen atoms from those assumed here, will show up in the $(\varrho_o-\varrho_c)$-map. This point is further considered in § 4. The atoms of ϱ_c have circular symmetry, apart from possible anisotropic thermal movement, and if those of ϱ_o do not have this symmetry, this too will be shown by the $(\varrho_o-\varrho_c)$-map. It would of course have been preferable to use atomic scattering factors with a better theoretical foundation, but those calculated by McWeeny (1951) were not available until this work was nearly completed.

Structure factors were calculated using the coordinates and temperature-factor parameters listed in Table 2, and the scattering factors listed in Table 1. Contributions from H_1 and H_2 were not included. (The atoms are numbered in Fig. 9.) The corresponding (F_o-F_c)-synthesis is shown in Fig. 6. It was the ninth successive synthesis. The only atoms not subtracted are H_1 and H_2. The (F_o-F_c)-synthesis shown in Fig. 7 corresponds to the same parameters as Fig. 6, but none of the hydrogens has been subtracted.

Structure factors corresponding to the data given in Tables 1 and 2 are given under $2F_{c1}$ of Table 6. (H_1 and H_2 were given reduced weight—see later.)

The projection on (010) was not refined as carefully as that on (001), as it was clear that, because of the smaller area of projection and the smaller range of experimental measurements, it would not be possible to obtain results of the same accuracy. In this projection all the atoms are resolved except C_5 and O_1. At each stage of the refinement the z coordinates of these two atoms were calculated from those determined from the other atoms, assuming the molecule to be planar. After three successive approximations, the value of R was reduced to 0·095. The final atomic parameters used in calculating the structure factors given in Table 7, are shown in Table 3. The x coordinates were not determined independently from this projection, but were taken to be as given in Table 2. Possible anisotropic temperature movement

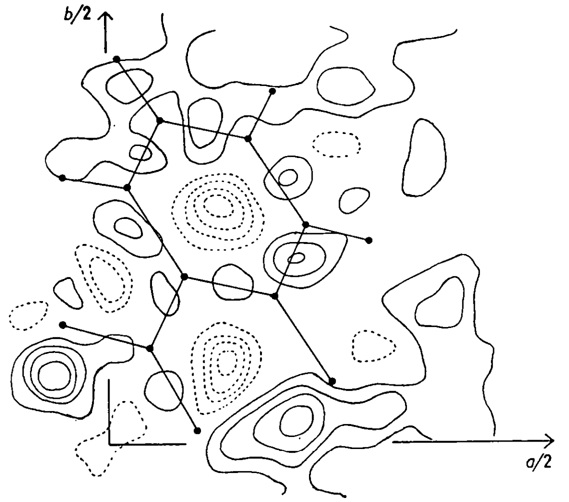

Fig. 6. The electron distribution in a single molecule from which carbon, oxygen and the four hydrogen atoms of the benzene ring have been subtracted. Contours as in Fig. 7.

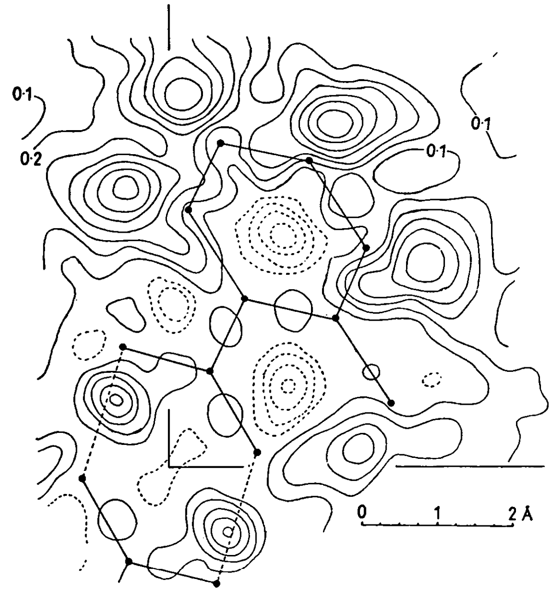

Fig. 7. The electron distribution in a single molecule from which carbon and oxygen atoms have been subtracted. Contours at every 0·1 e.Å^{-2}, zero contour omitted, negative contours broken.

of the atoms was not allowed for, but the value of γ was taken to correspond fairly closely to that of $\alpha+\frac{1}{2}\beta$ in Table 2.

If the molecule is planar, values of z should be given by $z = Ax+By+C$. Values of the constants determined from the experimental values of x, y and z by the method of least squares are $A = -1{\cdot}817$, $B = -1{\cdot}657$, $C = 0{\cdot}9770$. Values of z obtained from this linear relation are listed under z_c of Table 3. Calculated and observed z coordinates deviate by a mean of 0·008 Å, and a maximum of 0·017 Å. The assumption of molecular planarity is therefore justified, and in calculating bond lengths values of z_c were used.

Table 3. *Final atomic parameters*

Atom	z	z_c	γ
C_1	0·506	$0{\cdot}505_1$	1·5
C_2	0·361	$0{\cdot}360_2$	1·5
C_3	0·163	$0{\cdot}159_8$	1·8
C_4	0·105	$0{\cdot}108_4$	1·8
C_5	—	$0{\cdot}250_1$	1·8
C_6	0·446	$0{\cdot}445_9$	1·8
C_7	0·714	$0{\cdot}712_8$	1·5
O_1	—	$0{\cdot}843_4$	1·8
O_2	0·768	$0{\cdot}769_9$	1·8
O_3	0·404	$0{\cdot}405_4$	1·8
H_1	—	(0·962)	—
H_2	—	(0·557)	—
H_3	—	0·071	1·7
H_4	—	−0·026	1·7
H_5	—	0·232	1·7
H_6	—	0·532	1·7

Bond lengths and angles calculated from the coordinates given in Tables 2 and 3 are shown in Fig. 8(*a*). The difference (n_o-n_c) between the number of electrons in a particular area and the number subtracted from that area, was evaluated from the (F_o-F_c)-synthesis shown in Fig. 6, for each of the areas shown in Fig. 9. The results are given in Table 4.

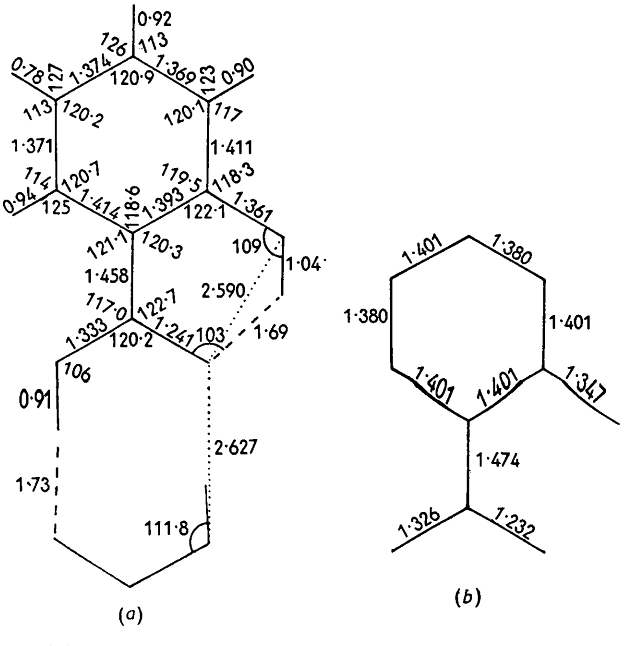

Fig. 8. (*a*) Measured bond lengths and bond angles. (*b*) Calculated bond lengths.

Table 4. *Numbers of electrons associated with particular atoms*

Area (see Fig. 9)	n_o-n_c	n_c	n_o
C_1	0	5·89	5·89
C_2	0	5·89	5·89
C_3H_3	+0·22	6·89	7·11
C_4H_4	+0·23	6·89	7·12
C_5H_5	+0·34	6·89	7·23
C_6H_6	+0·25	6·89	7·14
C_7	−0·02	5·89	5·87
O_1H_1	+0·31	8·26	8·57
O_2	0	8·26	8·26
O_3H_2	+0·55	8·26	8·81
Total	1·88	70·0	71·9

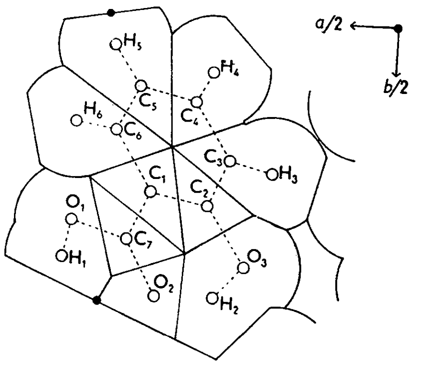

Fig. 9. Areas in which electron counts were made.

The standard deviation of the x-coordinate of the rth atom may be estimated from

$$\sigma(x_r) = \frac{2}{N_r}\left(\frac{\pi}{\lambda p}\right)^2\left(\frac{\pi}{A}\right)^{\frac{1}{2}}\sigma(F_o) \quad \text{(Booth, 1947).}$$

From a comparison of independent measurements, $\sigma(F_o) > 0{\cdot}20$, while from a comparison of values of F_o with values of F_c, $\sigma(F_o) < 0{\cdot}47$. The appropriate value of p is 4·15 Å^{-2}; taking $N_r = 6$, $\lambda = 1{\cdot}54$ Å, $A = 129$ Å^2 and $\sigma(F_o) = 0{\cdot}4$ (a safe overestimate), we find $\sigma(x_r) = 0{\cdot}005$ Å.

If the small error introduced by the uncertainty of the molecular orientation is ignored, the standard deviation of a C–C bond can be shown to be, in this case,

$$\sigma(b) = 0{\cdot}005\frac{\sqrt{2}.b}{d},$$

where b is the length of the bond and d its length in projection on (001). For the average C–C bond, $\sigma(b) = 0{\cdot}009$ Å.

The standard deviations $\sigma(\varrho_o-\varrho_c)$ and $\sigma(n_o-n_c)$, the latter for an area of about 2 Å^2, were similarly estimated using formulae given previously (Cochran, 1951*a*), and were found to be 0·08 e.Å^{-2} and 0·05 respectively. The value of $\sigma(n_o)$ is increased from 0·05 to about 0·1 by uncertainties caused by the use of semi-empirical f curves.

4. Discussion

The measured bond lengths are in good agreement with the assumption that the molecular structure can be described in terms of resonance between 'structures' I, II and III of Fig. 5. When these 'structures' are given weights of 0·66, 0·20 and 0·14 respectively, the bond lengths calculated from

$$R = R_1-(R_1-R_2)\{3x/(2x+1)\} \qquad \text{(Pauling, 1945)}$$

are as shown in Fig. 8(b). In this equation, x represents the double-bond character of a bond of length R, $R_1 = 1{\cdot}54$ for C–C and 1·42 for C–O, and $R_2 = 1{\cdot}34$ for C=C and 1·20 for C=O. The mean deviation between theoretical and observed bond lengths is 0·012 Å, the maximum is 0·027 Å. The agreement is therefore almost within the limits of experimental error, which is surprising in view of the very simple assumptions made in calculating the lengths. Although in the calculation no account has been taken of the fact that the molecules occur as dimers linked by hydrogen bonds, it is probable that 'structures' II and III are stabilised by the hydrogen bonds. The bond lengths in other associated carboxylic acids on which reasonably accurate measurements have been made, are in good agreement with those reported here (for a summary, see Vaughan & Donohue, 1952).

The C–H bonds shown in Fig. 8(a), whose standard deviation must be about 0·1 Å, have an average length of 0·89 Å. This is considerably smaller than the accepted value (1·07 Å), but there is no reason to suppose in this case that the point of maximum electron density coincides with the proton. The O–H bond lengths (0·91 and 1·03 Å) are also less than the covalent bond distance appropriate to a hydrogen which is at the same time forming a hydrogen bond. This distance has been estimated as 1·04 (Davies & Sutherland, 1938), 1·07 (Hofstadter, 1938) and 1·12 Å (Davies, 1946).

The electron distributions of Fig. 6 (benzene hydrogens, carbons and oxygens subtracted) and of Fig. 7 (carbons and oxygens subtracted) show some interesting and significant features. Both show quite clearly the departure from circular symmetry of the projected carbon and oxygen atoms. The value of $(\varrho_o-\varrho_c)$ at or near the centre of every bond is positive, varying from +0·10 to +0·31 e.Å^{-2}. At the same time the value of $(\varrho_o-\varrho_c)$ in regions between adjacent but not directly-bonded atoms, such as the centre of the benzene ring, is always negative. Similar features were in fact shown, although with a greater random error, in the map of the electron distribution in the adenine molecule (Cochran, 1951a, Fig. 6). The distribution shown in Figs. 6 and 7 is of course not independent of the temperature factors assumed for the various atoms of ϱ_c. The subtraction of an atom with a thermal vibration mainly in an 'east–west' direction results in a transfer of electrons in the difference map from points east and west of the atomic centre to points north and south of the centre. The temperature-factor parameters listed in Table 2 were in fact chosen so as to make the deviations of $(\varrho_o-\varrho_c)$ from zero, in either a positive or a negative direction, as small as possible. Furthermore, they can be given a reasonable physical interpretation, which is in agreement with general predictions made by Coulson, Higgs & March (1951) to the effect that translation and libration of the molecule as a whole probably occurs in the crystal. The value of α is nearly the same for all atoms, and corresponds to an isotropic thermal movement of r.m.s. amplitude 0·21 Å. Values of β are nearly the same for the three oxygen atoms, and in each case the direction of maximum thermal vibration is roughly perpendicular to the C–O bond. For the carbon atoms, values of β increase with increasing distance of the atom from the centre of the dimer. If we assume that the anisotropic movement consists of an oscillation of the molecule in its own plane, with the centre of the dimer remaining fixed, the variation of β and of ψ from one atom to another is satisfactorily explained. A value of 1·6° for the r.m.s. angular displacement of the molecule gives best agreement with the experimental results. Observed values of β and of ψ are compared with those calculated on the above assumptions in Table 5.

Table 5. *Comparison of observed and calculated temperature-factor parameters*

Atom	ψ_o	ψ_c	β_o	β_c
C_1	147°	143°	0·4	0·28
C_2	147	133	0·4	0·45
C_3	135	136	0·6	0·75
C_4	147	143	1·2	1·00
C_5	180	154	0·8	0·75
C_6	180	157	0·4	0·45
C_7	—	—	0·0	0·10

Another significant feature of the electron distribution shown in Fig. 7 is the markedly smaller number of electrons in H_1 and H_2 than in H_3, H_4, H_5 and H_6. The peak representing H_1 contains only 0·3 electrons, while H_2 contains 0·5. Apart from experimental error, these figures may be in error because of the necessarily somewhat arbitrary assignment of areas to particular atoms. For example, O_1, O_2 and O_3 are so close to H_1 and H_2 in projection that electrons which are in fact closely associated with the oxygen atoms may be counted as part of the hydrogens, and vice versa. Nevertheless, it is perfectly clear that the number of electrons associated with each of H_1 and H_2 is significantly less than one. This explains why it was found that the experimental atomic scattering factors of oxygen and carbon corresponded to atoms having numbers of electrons in the ratio 1·4:1. At the time this was taken to correspond to 8·26 electrons in an average oxygen atom, and 5·89 in an average carbon atom, since $8{\cdot}26 \div 5{\cdot}89 = 1{\cdot}4$, and $3\times 8{\cdot}26+7\times 5{\cdot}89 =$

Table 6. *Observed and calculated structure factors; values of* $2F(hk0)$

Values of F_{c1} include a contribution from all atoms, including hydrogens. Values of F_{c2} include an additional contribution from bonding electrons. The contribution of the latter was calculated only for structure factors having $\sin\theta < 0{\cdot}7$. Those terms outside this range having $F_o = 0$ were excluded from all $(F_o - F_c)$-syntheses.

hk	$2F_o$	$2F_{c1}$	$2F_{c2}$
00	—	576·0	576·0
20	45·9	47·1	46·8
40	51·9	50·2	52·3
60	−54·7	−54·2	−55·5
80	−24·0	−21·0	−23·4
10,0	−14·7	−13·9	−13·9
12,0	3·4	4·2	
14,0	− 7·3	− 7·4	
11	72·6	79·1	78·6
21	106·9	110·2	109·9
31	2·6	1·7	2·1
41	−18·6	−19·6	−19·4
51	−36·6	−38·8	−38·7
61	25·9	22·2	24·9
71	−30·4	−28·5	−29·6
81	− 3·9	− 3·0	− 3·3
91	0	1·5	1·0
10,1	− 1·4	− 1·4	− 1·5
11,1	3·4	4·4	
12,1	4·7	3·8	
13,1	− 6·4	− 6·7	
14,1	5·7	5·4	
02	−37·7	−38·2	−38·0
12	33·5	34·2	33·9
22	− 6·1	− 5·8	− 4·9
32	−63·8	−60·8	−61·4
42	−25·1	−23·9	−24·5
52	5·5	4·9	5·6
62	−35·2	−34·4	−34·4
72	−36·4	−35·7	−35·6
82	20·7	20·1	21·1
92	− 8·0	− 7·3	− 7·9
10,2	− 3·2	− 2·7	− 2·4
11,2	1·4	1·8	1·3
12,2	2·7	2·4	
13,2	8·5	8·7	
14,2	− 5·4	− 6·0	
13	11·8	11·3	12·0
23	11·6	11·4	11·6
33	−15·2	−15·6	−14·3
43	9·7	8·7	9·4
53	−15·0	−15·4	−14·5
63	−14·5	−13·7	−14·4
73	20·0	19·3	19·5
83	10·5	11·6	11·1
93	18·8	17·9	18·0
10,3	− 4·3	− 4·3	− 4·1
11,3	2·4	1·3	2·0
12,3	0	0·3	
13,3	3·9	4·5	
14,3	− 4·5	− 5·6	
04	−49·6	−48·2	−49·2
14	28·8	31·3	30·2
24	−44·1	−40·4	−40·7
34	−16·7	−15·9	−16·7
44	−12·9	−13·8	−13·1
54	32·7	32·3	34·0
64	−13·6	−13·1	−12·8
74	− 7·6	− 8·3	− 7·2
84	27·6	28·1	27·5
94	29·3	30·7	29·6
10,4	31·3	31·2	30·9
11,4	0	0·2	
12,4	6·2	6·3	
13,4	2·1	2·1	
14,4	3·2	2·9	
15	8·1	6·8	7·4
25	− 5·4	− 3·0	− 4·6
35	−47·6	−44·6	−47·2
45	24·6	24·0	24·2
55	−35·5	−33·7	−35·7
65	10·0	8·8	10·2
75	−13·7	−15·6	−14·8
85	−13·6	−14·9	−14·9
95	9·3	8·8	9·0
10,5	13·5	14·2	13·3
11,5	13·7	15·0	
12,5	− 3·8	− 3·0	
13,5	5·4	5·9	
06	25·1	23·1	24·7
16	47·4	44·5	45·7
26	35·0	36·3	35·4
36	30·6	31·0	32·4
46	−51·3	−46·2	−48·6
56	14·5	14·8	14·2
66	15·1	14·4	14·3
76	−14·9	−14·7	−15·3
86	−16·5	−17·0	−16·3
96	− 8·5	− 8·6	− 7·9
10,6	12·9	13·2	
11,6	−11·6	−12·5	
12,6	4·1	6·0	
13,6	0	0·6	
17	25·9	27·2	26·7
27	21·6	20·8	22·2
37	17·7	17·1	17·4
47	− 4·3	− 4·3	− 4·5
57	7·2	6·8	7·4
67	−13·4	−12·5	−13·3
77	− 5·0	− 6·7	− 6·5
87	− 8·5	− 7·9	− 7·6
97	5·2	5·5	5·4
10,7	−10·3	−10·0	
11,7	0	0·8	
12,7	9·0	10·8	
08	15·6	17·1	17·3
18	0	− 2·2	− 2·3
28	20·5	20·8	21·8
38	− 1·7	− 0·5	− 0·5
48	− 8·4	− 8·5	− 7·4
58	−12·5	−12·5	−12·8
68	− 6·1	− 7·6	− 7·0
78	− 5·6	− 5·8	− 5·8
88	−10·3	−12·0	−11·4
98	−10·5	− 9·5	
10,8	− 6·2	− 7·3	
11,8	9·3	10·4	
12,8	− 9·8	−10·6	
19	3·9	3·3	3·9
29	4·5	4·2	4·5
39	4·8	5·5	5·7
49	−16·0	−17·4	−16·8
59	−10·7	−11·9	−11·3
69	− 9·9	− 9·2	− 9·5

Table 6 (*cont.*)

hk	$2F_o$	$2F_{c1}$	$2F_{c2}$
79	0	0	0·4
89	− 8·5	− 8·4	
99	− 1·8	− 2·8	
10,9	3·9	4·4	
11,9	− 3·1	− 3·3	
0,10	3·2	1·9	1·0
1,10	−13·7	−14·9	−14·2
2,10	22·4	24·2	22·9
3,10	3·3	3·3	3·5
4,10	− 3·2	− 3·1	− 3·1
5,10	− 9·0	−10·1	−10·4
6,10	− 6·5	− 6·0	
7,10	− 5·9	− 5·9	
8,10	0	− 0·7	
9,10	0	0·4	
10,10	3·8	3·8	
1,11	7·6	8·5	
2,11	9·9	8·9	
3,11	− 9·3	− 8·6	
4,11	26·3	27·5	
5,11	− 4·5	− 4·1	
6,11	2·5	2·1	
7,11	0	− 2·4	
8,11	0	2·6	
9,11	0	− 2·0	
0,12	− 2·6	− 2·5	
1,12	8·0	9·3	
2,12	−19·6	−22·2	
3,12	18·4	18·8	
4,12	0	− 0·6	
5,12	0	0·8	
6,12	0	1·9	
7,12	3·6	3·9	
8,12	0	1·7	
1,13	0	− 2·2	
2,13	6·9	7·2	
3,13	3·6	4·3	
4,13	0	− 1·4	
5,13	2·5	3·0	
6,13	2·9	3·3	
0,14	0	− 1·0	
1,14	2·7	2·8	
2,14	0	1·4	
3,14	3·2	3·5	

Table 7. *Observed and calculated structure factors; values of* $2F(h0l)$

hl	$2F_o$	$2F_c$
20	48·0	49·3
40	51·2	48·7
60	−54·2	−53·1
80	−23·6	−22·0
10,0	−14·4	−16·6
$\overline{10}$,1	− 4·9	− 9·2
$\bar{8}$1	8·7	8·0
$\bar{6}$1	73·9	68·8
$\bar{4}$1	−64·3	−59·8
$\bar{2}$1	23·8	22·5
01	−57·8	−55·7
21	−40·8	−35·3
41	−10·2	−15·1
61	−26·9	−26·3
81	−24·1	−29·5
10,1	0	− 1·3
$\overline{10}$,2	8·7	10·2
$\bar{8}$2	22·7	24·2
$\bar{6}$2	33·5	30·5
$\bar{4}$2	32·2	34·5
22	− 9·7	−13·8
02	−43·4	−42·1
22	−46·5	−52·4
42	− 4·2	− 3·9
62	0	− 0·4
82	8·2	10·4
10,2	0	1·0
$\bar{8}$3	5·8	5·6
$\bar{6}$3	16·5	17·4
$\bar{4}$3	8·5	5·3
$\bar{2}$3	6·4	7·9
03	−42·0	−43·7
23	−53·4	−56·6
43	0	− 0·3
63	12·6	15·0
83	− 8·3	− 6·1
$\bar{6}$4	−37·4	−34·3
$\bar{4}$4	−28·0	−26·5
$\bar{2}$4	32·1	30·3
04	0	− 2·7
24	35·1	34·5
44	0	− 0·4
64	0	4·4

66, the number of electrons in three oxygen atoms (24) and seven carbons (42). The required transfer of electrons from carbon to oxygen does not appear plausible. A more satisfactory explanation is that the average oxygen atom contains 8·40 electrons, and the average carbon contains 6·00. This gives a ratio of 1·4:1, and a total of 67·2 electrons, and therefore requires a transfer of 1·2 electrons from hydrogen to oxygen. The effects of this assumption have been considered. Values of F_c are slightly increased in scale, and values of F_o must be increased (by about 2%) to correspond. The maximum change in the electron densities shown in Figs. 6 and 7 is $-0{\cdot}03$ e.Å^{-2}, so that all significant features of these maps are quite unaffected. Values of n_o-n_c (Table 4) are decreased by amounts varying from 0·07 to 0·14. Since, however, values of n_c are increased from 8·26 to 8·40, and from 5·89 to 6·00, the final values of n_o are the *same* as those given in Table 4, within 0·03 electrons. This establishes a point made earlier, that, within limits, the use of an incorrect 'model' electron distribution, ϱ_c, does not affect the final results in many respects.

Values of n_o are in good agreement with the charge distribution required from the weights assigned to 'structures' I, II and III. Taking the electronic charge with reversed sign as the unit, the predicted charge distribution is $-0{\cdot}34$ on O_2, $+0{\cdot}20$ on O_1H_1 and $+0{\cdot}14$ on O_3H_2. The corresponding experimental values are $-0{\cdot}26$, $+0{\cdot}43$ and $+0{\cdot}19$. The decrease in the electron density of H_1 and H_2 indicates that 'structures' such as IV and possibly V contribute to the state of the molecule. The dipole moment of the normal O–H bond indicates a transfer of about 0·2 electrons to the oxygen atom. The larger transfer observed in this case is tentatively ascribed to the stabilisation of IV and V by hydrogen bonding. The explanation of the high acid strength of salicylic acid, as compared with *p*- or *m*-hydroxybenzoic acid, is possibly to be sought along similar lines. The explanation given by Branch & Yabroff (1934) involves a resonance 'structure' which requires a covalent bond between O_2 and H_2. This is now known to be an unimportant contribution to the hydrogen bond (see Coulson, 1952, p. 304). Furthermore, the C–O bond lengths reported here are not consistent with Branch & Yabroff's explanation. Stabilisation of 'structure' V by the chelate hydrogen bond provides a simple explanation, which is in agreement with measured bond lengths and charge distribution.

In the final calculation of structure factors, the scattering factors for H_1 and H_2 were reduced by a factor of two. The value of R then fell from 0·065 to 0·058. Structure factors were also calculated in which the effects of bonding were approximately allowed for. Electron counts on Fig. 6 showed that the average peak in a bond contained 0·05 electrons. This number of electrons, distributed as shown in Fig. 10, was therefore placed at the centre of each bond, except for C_7O_1, C_1C_7 and C_3O_3 which, being nearly single bonds, were given only one half this number. This was probably an unnecessary refinement! Similarly, 0·17 electrons were subtracted from the centre of the benzene ring, 0·14 from the mid-point of the group $O_3C_2C_1C_7O_2$, and 0·11 from the mid-point of the group $C_6C_1C_7O_1$. These three figures are in the ratio 6:5:4, the ratio of the numbers of overlapping atoms at the points concerned. When the contribution of this idealized redistribution of electrons was included in F_c, the value of R fell from 0·058 to 0·041.

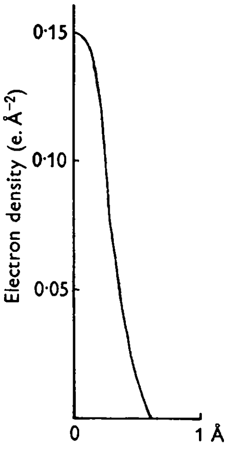

Fig. 10. Assumed electron distribution about the centre of a bond.

The extent of the departure from spherical symmetry agrees quite well with the results obtained by Bacon (1952), who estimated the number of electrons associated with the bonds in graphite as 0·12. The electron distribution in benzene has been calculated by March (1952), using the Thomas–Fermi and molecular-orbital methods. His results cannot be directly compared with those given here, since it is the electron densities in a section through the benzene ring, and in a parallel plane at a distance of 0·35 Å, that have been calculated. Certain points are worth noting however. March's approximate solution of the Thomas–Fermi equation gives the electron density as an *exact* superposition of six spherically-symmetric distributions centred on the carbon nuclei, when the influence of the hydrogen atoms is neglected. The molecular-orbital results appear to require a slight concentration of electrons in the bonds; inspection of March's results suggests that it is of the same order of magnitude as that reported here, which consists in a transfer of about 0·05 electrons per atom, or an average deviation from circular symmetry of less than 0·1 e.Å^{-2}. The π-electron density, which has hitherto been thought of as being spread fairly uniformly around the benzene ring, is shown by March's calculations to be almost entirely concentrated above the carbon atoms. This again agrees with our result that the departure from circular symmetry in projection is very slight.

I should like to conclude by thanking Prof. Sir Lawrence Bragg and Dr W. H. Taylor for their continued interest in, and support of this work. I am grateful to Mrs M. Remnant and Mrs A. E. Gill for their help with some very tedious computing.

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