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A Refinement of the Benzoic Acid Structure at Room Temperature

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Abstract. $C_7H_6O_2$, monoclinic, $P2_1/c$, $a = 5·510\ (5)$, $b = 5·157\ (6)$, $c = 21·973\ (8)$ Å, $\beta = 97·41\ (8)°$, $Z = 4$, $D_c = 1·31$ Mg m^{-3}. The cyclic hydrogen-bonded dimers, arranged around the symmetry centres, are nearly planar, the torsion angle around the C—CO_2H bond being 1·5°. The benzene C atoms are coplanar within ±0·004 Å and the C—C bond lengths average 1·388 (6) Å. The internal benzene angles deviate very slightly from the ideal value of 120°, ranging from 119·7 (4) to 120·5 (4)° (mean 120·1°). The two C—O bond lengths are nearly equal, their values being 1·263 (3) and 1·275 (4) Å. Correspondingly, the C—C—O angles are 118·8 (3) and 118·0 (4)°. The O···O bridge distance is 2·633 (3) Å. The C—O bond lengths and the difference Fourier map indicate that there is a mixture of the two possible orientations of the dimer at the same crystal site.

Introduction. After many attempts suitable single crystals were obtained from an alcohol–water mixture by slow evaporation. Cell parameters were determined by refinement of 21 reflexions on an automated single-crystal Siemens AED diffractometer. Intensity data were collected using a crystal of approximate dimensions 0·1 × 0·1 × 0·3 mm, mounted along **b**.

Three-dimensional data were collected at 293 K using Mo $K\alpha$ radiation by the θ–2θ scan technique, within the limiting sphere of $\theta = 27°$. A total of 469 independent reflexions having $I \geq 2\sigma(I)$ were collected and used in the calculations; Lorentz and polarization factors were applied but no correction was made for absorption. The structure was refined anisotropically starting from the parameters of the non-hydrogen atoms from the two-dimensional determination (Sim, Robertson & Goodwin, 1955). The benzene H atoms were placed in chemically reasonable positions (C—H, 1·00 Å) and all occurred in regions of positive electron charge density on the difference Fourier map. On this map, an electron density peak of 0·2 e Å^{-3} appeared just in the middle of the O(1)—O(2′) line (no other peak >0·1 e Å^{-3} was detected). This peak was assumed (see below) to be due to the overlap of two H atoms, with occupancy factors of one half (O—H, 0·90 Å, and ∠C—O—H, 119°). The final block-diagonal-matrix anisotropic refinement, including the contribution of the H atoms held constant (B = 6 Å^2), gave a final R of 0·038.† The final weighting scheme was $W = 1/(A + |F_o| + B|F_o|^2)$, where $A = 3·5$ and $B = 0·012$ were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $\sin \theta/\lambda$. Atomic scattering factors were those of Moore (1963) and calculations were carried out with programs written by Albano, Domenicano & Vaciago (1966).

The final atomic coordinates are given in Table 1 and the numbering scheme is shown in Fig. 1 together with bond lengths and angles.

Table 1. *Fractional atomic coordinates* (×10^4, *for* H ×10^3) *with estimated standard deviations in parentheses*

	x	*y*	*z*
O(1)	2213 (4)	2372 (5)	132 (1)
O(2)	−908 (4)	1410 (5)	647 (1)
C(1)	1001 (5)	2713 (7)	576 (1)
C(2)	1816 (6)	4740 (7)	1037 (1)
C(3)	3849 (6)	6265 (8)	970 (2)
C(4)	4596 (7)	8182 (8)	1406 (2)
C(5)	3317 (7)	8534 (8)	1902 (2)
C(6)	1299 (7)	7024 (8)	1965 (2)
C(7)	533 (7)	5133 (7)	1534 (2)
H(C3)	473	599	61
H(C4)	606	924	136
H(C5)	382	991	221
H(C6)	41	730	232
H(C7)	−91	405	158
H(1)	176	107	−14
H(1*)	136	−13	−38

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35192 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Discussion. On the whole, the molecular structure and the crystal packing are similar to those resulting from the two-dimensional refinement (Sim, Robertson & Goodwin, 1955), but the accuracy of the present results allows some details of the molecular geometry to be clarified. Thus, it is possible to obtain additional information about the deformations of the benzene ring due to the substitution of a H atom (Domenicano & Murray-Rust, 1979; Domenicano, Mazzeo & Vaciago, 1976), and the hydrogen-bond characteristics in benzoic acid and its ring-substituted derivatives (Hayashi & Unemura, 1974).

The phenyl-ring atoms are coplanar within ±0·004 Å with C—C bond lengths varying from 1·379 (6) to 1·401 (6) Å and endocyclic C—C—C bond angles from 119·7 (4) to 120·5 (4)° (mean 120·1°). The bond-angle pattern, shown in Fig. 1, is in fair agreement with the values expected for the angular deviations from the ideal value of 120° given by Domenicano & Murray-Rust (1979), although the deviations foreseen are small and fall within the experimental errors. The CO_2 group is slightly rotated by 1·5° with respect to the benzene ring, the displacement of C(1), O(1) and O(2) from the benzene plane being −0·001, −0·23 and +0·033 Å, respectively. Thus, the displacement of C(1) and O(2), out of the phenyl plane, reported by Sim *et al.* (1955), is not confirmed by this refinement. The two C—O bond lengths are nearly equal, being 1·275 (4) and 1·263 (3) Å; the corresponding C—C—O angles are 118·0 (4)and 118·8 (3)° (*cf.* Fig. 1).

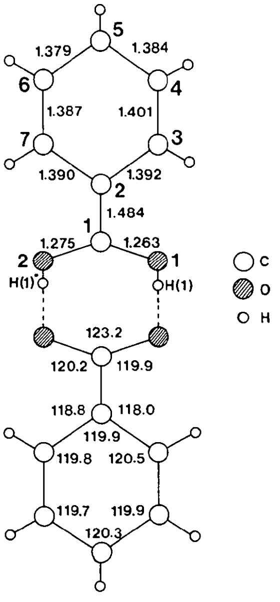
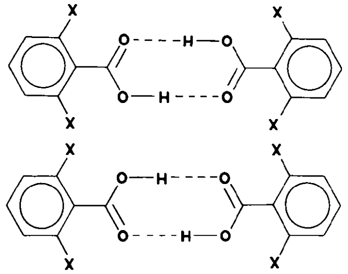


Fig. 1. The numbering scheme for the atoms together with bond lengths (Å) and angles (°). The benzene H atoms are labelled with the symbol of the C atoms to which they are attached. E.s.d.'s are in the range 0·003–0·004 and 0·005–0·006 Å for C–O and C—C distances, respectively, and 0·3–0·4° for bond angles.

The O(1)···O(2′) hydrogen-bond distance is 2·633 (3) Å. The correlation between O—H and O···O distances, reported in *The Hydrogen Bond* (Schuster, Zundel & Sandorfy, 1976) and based on precise neutron diffraction analyses, should give a value for the O—H distance of about 1·0 Å. On the other hand, the two C—O bond lengths of the carboxyl group are nearly equal and a peak of 0·2 e $Å^{-3}$ is found on the Fourier difference map along the O(1)···O(2′) line at 1·35 and 1·29 Å, respectively, from the two O atoms.

These data may be interpreted on the assumption of an occupancy of about 50% at the same crystal site by the two equivalent configurations of the dimeric unit, as already suggested for other dimers of ring-substituted benzoic acid derivatives (Benghiat & Leiserowitz, 1972). This interpretation is in agreement with the suggestion of Hayashi & Unemura (1974), based on spectroscopic data, although it is still unclear how the two configurations can interchange in the solid state when the temperature is changed.



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