

2-Benzoylbenzoic Acid: Structures and Hydrogen-Bonding Patterns of the Anhydrous and Hydrated Forms

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Abstract. (I) $C_{14}H_{10}O_3$, $M_r = 226.231$, monoclinic, $P2_1/c$, $a = 14.129$ (7), $b = 7.313$ (3), $c = 11.390$ (4) Å, $\beta = 103.95$ (3)°, $V(236\text{ K}) = 1142.2$ (8) Å³, $Z = 4$, $D_m(295\text{ K}) = 1.29$ (1), $D_x[295\text{ K}; V = 1150$ (1) Å³] = 1.306 g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 0.995\text{ cm}^{-1}$, $F(000) = 472$, $T = 236$ (1) K, $R = 0.050$ for 1544 observed reflections. (II) $C_{14}H_{10}O_3 \cdot H_2O$, $M_r = 244.247$, triclinic, $P\bar{1}$, $a = 7.711$ (7), $b = 8.32$ (1), $c = 9.947$ (7) Å, $\alpha = 75.73$ (8), $\beta = 96.84$ (6), $\gamma = 93.58$ (8)°, $V(233\text{ K}) = 614$ (1) Å³, $Z = 2$, $D_m(295\text{ K}) = 1.29$ (1), $D_x[295\text{ K}; V = 621$ (1) Å³] = 1.306 g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 1.048\text{ cm}^{-1}$, $F(000) = 256$, $T = 233$ (1) K, $R = 0.047$ for 1966 observed reflections. In (I), pairs of molecules with opposite conformational chirality form centrosymmetric carboxyl dimers. In (II), these pairs, with generally minor changes in conformation, move apart by an additional 2.45 Å to accommodate insertion of a bridging water molecule into each H bond.

Introduction. Our exploration of the H-bonding modes of keto carboxylic acids (Leiserowitz, 1976; Vanderhoff, Thompson & Lalancette, 1986; Lalancette, Slifer & Thompson, 1989) has led us to examine the case of the title compound. This compound is of interest with respect not only to the possibility of internal H bonding, rarely observed in γ -keto acids (Griffe, Durant & Pieret, 1972; Sheldrick & Trowsch, 1983), but also to the investigation of both solution and solid-state ring-chain tautomerism (phthalide formation) in 2-acylbenzoic acids (Bhatt & Kamath, 1968; Bowden & Taylor, 1971; Tyman & Najam, 1977). Although no complete structure has been reported for the title compound, two apparently discrepant entries in the literature offer potential confusion. Kundu & Chakravorty (1967) cite a triclinic structure ($P1$ or $P\bar{1}$), while Delettre (1969) describes a monoclinic structure ($P2_1/c$). The former authors were apparently unaware that they were dealing with a hydrate,

although an anhydrous and a monohydrated crystalline form of this compound were recognized over a century ago (Plascuda & Zincke, 1873; Plaskuda, 1874). These forms may be differentiated by their melting points and obtained reproducibly by recrystallizing dehydrated material [(I), m.p. 400 K] from solvent either carefully dried (I) or doped with water (II).

Experimental. Commercial (Eastman Kodak) anhydrous material was recrystallized from dry benzene by evaporation at 295 K to give the monoclinic (I), space group $P2_1/c$; density was measured by flotation in methylene chloride-hexane. A rectangular rod $0.20 \times 0.65 \times 1.2$ mm was mounted on a glass fiber; attempts to cleave these crystals were unsuccessful. Data ($2\theta_{\text{max}} = 60^\circ$, $0 \leq h \leq 20$, $0 \leq k \leq 10$, $-16 \leq l \leq 16$) were collected on a Syntex $P2_1$ diffractometer with a graphite monochromator using Mo $K\alpha$ radiation; 15 high-angle reflections were used to calculate the orientation matrix and best cell dimensions. With three standard reflections recorded every 47 reflections ($\pm 5.9\%$), 3577 unique reflections were measured in the θ - 2θ scan mode. Of these, 2033 were unobserved and 1544 had $I \geq 3\sigma(I)$; the low percentage of reflections observed was due to the low power at which the diffractometer was run during this data cycle. Absorption corrections, made after accurately measuring the three pairs of parallel crystal faces normal to the principal crystal axes, were based on Howells' analytical expression for polyhedra, with $\text{min.} = 1.020$, $\text{max.} = 1.069$ (Hollander, 1975). The structure was solved using MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); all non-H atoms were found from the best E map (CFOM = 2.99) and all H atoms were calculated in their best geometrical positions except for the carboxyl H atom, which was found in a difference Fourier map. The H-atom positional parameters were held constant and their isotropic thermal parameters were fixed at $(B + 1) \text{ \AA}^2$, where B was the corresponding value for the atom to which the H is bound. All

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Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors for compound (I)

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2acc\cos\alpha)\beta_{13} + (2bcc\cos\alpha)\beta_{23}].$$

	x	y	z	$B_{eq}/B_{iso}(\text{\AA}^2)$
O(1)	0.5906 (1)	0.1221 (2)	0.0812 (2)	3.67 (1)
O(2)	0.4991 (1)	0.1863 (3)	-0.1027 (2)	4.10 (1)
O(3)	0.7007 (2)	0.3846 (3)	0.2940 (2)	5.09 (1)
C(1)	0.6170 (2)	0.4017 (3)	-0.0104 (2)	2.96 (1)
C(2)	0.6894 (2)	0.4581 (3)	0.0898 (2)	3.17 (1)
C(3)	0.7317 (2)	0.6290 (4)	0.0863 (3)	4.14 (1)
C(4)	0.7038 (2)	0.7407 (4)	-0.0140 (3)	4.63 (1)
C(5)	0.6324 (2)	0.6846 (4)	-0.1125 (3)	4.23 (1)
C(6)	0.5888 (2)	0.5158 (4)	-0.1104 (2)	3.59 (1)
C(7)	0.5683 (2)	0.2235 (3)	-0.0065 (2)	3.03 (1)
C(8)	0.7248 (2)	0.3453 (3)	0.2024 (2)	3.24 (1)
C(9)	0.7994 (2)	0.2004 (4)	0.2024 (2)	3.28 (1)
C(10)	0.8282 (3)	0.0867 (4)	0.3014 (3)	5.04 (1)
C(11)	0.9012 (3)	-0.0404 (5)	0.3046 (4)	6.42 (2)
C(12)	0.9441 (2)	-0.0571 (6)	0.2103 (5)	6.83 (2)
C(13)	0.9130 (3)	0.0509 (7)	0.1109 (4)	7.34 (2)
C(14)	0.8407 (2)	0.1780 (5)	0.1062 (3)	5.35 (2)
HC(3)	0.7797	0.6572	0.1536	5.14
HC(4)	0.7331	0.8629	-0.0067	5.63
HC(5)	0.6220	0.7600	-0.1800	5.23
HC(6)	0.5372	0.4850	-0.1807	4.59
HC(10)	0.7993	0.1236	0.3709	6.04
HC(11)	0.9134	-0.1083	0.3772	7.42
HC(12)	0.9990	-0.1410	0.2180	7.83
HC(13)	0.9410	0.0320	0.0440	8.34
HC(14)	0.8290	0.2590	0.0370	6.35
H(O2)	0.4770	0.0680	-0.0920	5.10

Table 2. Fractional atomic coordinates and equivalent isotropic temperature factors for compound (II)

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2acc\cos\alpha)\beta_{13} + (2bcc\cos\alpha)\beta_{23}].$$

	x	y	z	$B_{eq}/B_{iso}(\text{\AA}^2)$
O(1)	0.1440 (2)	0.2199 (2)	0.1358 (2)	3.21 (1)
O(2)	0.3572 (2)	0.0694 (2)	0.1021 (2)	4.54 (1)
O(3)	0.1365 (2)	0.5480 (2)	0.2595 (2)	3.74 (1)
O(W)	-0.1268 (3)	0.1551 (2)	-0.0595 (2)	3.93 (1)
C(1)	0.4382 (3)	0.3165 (2)	0.1682 (2)	2.42 (1)
C(2)	0.4016 (3)	0.4331 (2)	0.2393 (2)	2.47 (1)
C(3)	0.5291 (3)	0.5530 (3)	0.2591 (2)	3.36 (1)
C(4)	0.6916 (3)	0.5546 (3)	0.2124 (3)	3.81 (1)
C(5)	0.7281 (3)	0.4378 (3)	0.1444 (3)	3.56 (1)
C(6)	0.6014 (3)	0.3192 (3)	0.1211 (2)	3.01 (1)
C(7)	0.2973 (3)	0.1975 (2)	0.1344 (2)	2.55 (1)
C(8)	0.2341 (3)	0.4325 (2)	0.3019 (2)	2.69 (1)
C(9)	0.1989 (3)	0.2970 (2)	0.4246 (2)	2.71 (1)
C(10)	0.0375 (3)	0.2874 (3)	0.4766 (3)	3.49 (1)
C(11)	0.0042 (4)	0.1653 (3)	0.5935 (3)	4.35 (1)
C(12)	0.1318 (5)	0.0560 (4)	0.6602 (3)	4.64 (1)
C(13)	0.2929 (4)	0.0662 (3)	0.6113 (3)	4.33 (1)
C(14)	0.3270 (4)	0.1865 (3)	0.4925 (2)	3.37 (1)
H(C3)	0.4983 (48)	0.6341 (48)	0.3077 (42)	4.36
H(C4)	0.7757 (51)	0.6427 (50)	0.2289 (42)	4.81
H(C5)	0.8399 (54)	0.4349 (48)	0.1176 (43)	4.56
H(C6)	0.6233 (46)	0.2365 (48)	0.0741 (40)	4.01
H(C10)	-0.0491 (49)	0.3705 (49)	0.4306 (41)	4.49
H(C11)	-0.1042 (56)	0.1594 (54)	0.6304 (47)	5.35
H(C12)	0.1075 (55)	-0.0253 (56)	0.7411 (46)	5.64
H(C13)	0.3940 (53)	-0.0035 (54)	0.6618 (46)	5.33
H(C14)	0.4406 (51)	0.1985 (47)	0.4578 (42)	4.37
H1 (W)	-0.1384 (52)	0.2462 (58)	-0.1158 (48)	4.93
H2 (W)	-0.0383 (57)	0.1588 (50)	0.0066 (48)	4.93
H(O2)	0.2604 (52)	0.0007 (53)	0.0864 (43)	5.54

non-H atoms were refined with anisotropic thermal parameters; $\sum||F_o| - |F_c||^2$ was minimized; $R = 0.050$, $wR = 0.064$, $S = 1.10$, $w = 1/\sigma^2$ with $\sigma = 0.005F_o + 3.454$ for $F_o \leq 90.0$, $\sigma = 0.033F_o + 0.721$ for $F_o > 90.0$, last cycle max. $\Delta/\sigma = 0.004$, average = 0.001, final difference Fourier map: max. = 0.28, min. = 0.08 e \AA^{-3} . The empirical weighting function was derived from a smoothed plot of the average values of $|\Delta F|/|F_o|$ for various ranges of $|F_o|$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and no anomalous-dispersion corrections were used.

Crystals of the triclinic modification (II) were grown at 295 K by slow evaporation from benzene to which a very small quantity of H₂O had been added. An emerald-cut tablet 0.20 × 0.53 × 0.70 mm was used to collect the data ($0 \leq h \leq 11$, $-12 \leq k \leq 12$, $-14 \leq l \leq 14$), as described for (I). The transformation (1,0,0/0,-1,0/0,0,-1) applied to the working unit-cell translations gives the reduced cell with all angles acute, i.e. $\alpha = 75.73$, $\beta = 83.16$, $\gamma = 86.42^\circ$. The choice of space group $P\bar{1}$ was later confirmed by the structure determination. With three standard reflections recorded every 47 reflections ($\pm 2.0\%$), 3607 unique reflections were collected; 1641 were unobserved and 1966 had $I \geq 3\sigma(I)$. Absorption corrections, made after accurately meas-

uring the five pairs of parallel crystal faces, two of which were normal to principal crystal axes, were based on Howells' analytical expression for polyhedra, with min. = 1.019, max. = 1.049 (Hollander, 1975). All non-H atoms were found from the best E map (CFOM = 2.70) and all H atoms were found in subsequent difference Fourier maps. H-atom positional parameters were refined in this structure, but their isotropic temperature factors were set as described above. The isotropic extinction parameter refined to 1.3 (2); $R = 0.047$, $wR = 0.070$, $S = 1.04$, $w = 1/\sigma^2$ with $\sigma = 0.015F_o + 2.784$ for $F_o \leq 90.0$, $\sigma = 0.081F_o - 3.583$ for $F_o > 90.0$, last cycle max. $\Delta/\sigma = 0.0003$, average = 0.00005, final difference Fourier map: max. = 0.22, min. = -0.05 e \AA^{-3} . The empirical weighting function was derived as described above.

Computer programs used: data reduction - local adaptation of Glick's (1975) Lp correction SYNCOR and Hollander's (1975) ABSOR [from Templeton & Templeton's (1973) AGNOST]; direct methods - MULTAN80 (Main *et al.*, 1980); refinement and Fourier synthesis analysis - FLINUS [Andrews (1974) from ORFLS (Busing, Martin & Levy, 1962)]; Fourier analysis and difference maps - FORDAP (Zalkin,

Table 3. Interatomic distances (Å) for compounds (I) and (II)

Parentheses contain e.s.d.'s for the least significant digit.

	(I)	(II)
C(1)—C(2)	1.399 (3)	1.393 (3)
C(1)—C(6)	1.390 (4)	1.391 (3)
C(1)—C(7)	1.480 (3)	1.489 (3)
C(2)—C(3)	1.390 (4)	1.389 (3)
C(2)—C(8)	1.505 (4)	1.499 (3)
C(3)—C(4)	1.382 (4)	1.386 (4)
C(4)—C(5)	1.378 (4)	1.372 (4)
C(5)—C(6)	1.382 (4)	1.386 (4)
C(8)—C(9)	1.495 (4)	1.482 (3)
C(9)—C(10)	1.382 (4)	1.394 (4)
C(9)—C(14)	1.370 (4)	1.388 (3)
C(10)—C(11)	1.383 (5)	1.381 (4)
C(11)—C(12)	1.360 (6)	1.376 (5)
C(12)—C(13)	1.363 (6)	1.377 (4)
C(13)—C(14)	1.373 (5)	1.388 (3)
O(1)—C(7)	1.223 (3)	1.210 (3)
O(2)—C(7)	1.309 (3)	1.310 (3)
O(3)—C(8)	1.208 (3)	1.218 (3)
O(2)—H(O2)	0.937	0.93 (4)
O(2)···O(1 ^a)	2.627 (2)	
H(O2)···O(1 ^a)	1.708	
O(1)···O(W)		2.799 (3)
O(2)···O(W ^b)		2.573 (4)
O(W)···O(W ^b)		3.234 (4)
O(2)···O(1 ^b)		5.079 (5)
O(1)···H1(W)		1.92 (5)
O(W)···H1(W)		0.89 (5)
O(W)···H2(W)		0.83 (5)
O(W ^b)···H(O2)		1.66 (4)

Symmetry code: (i) 1 - x, - y, - z; (ii) - x, - y, - z.

Table 4. Bond and interatomic angles (°) for (I) and (II)

Parentheses contain e.s.d.'s for the least significant digit.

	(I)	(II)
C(2)—C(1)—C(6)	120.1 (2)	120.0 (2)
C(2)—C(1)—C(7)	119.2 (2)	119.4 (2)
C(6)—C(1)—C(7)	120.7 (2)	120.5 (2)
C(1)—C(2)—C(3)	118.4 (2)	118.8 (2)
C(1)—C(2)—C(8)	124.2 (2)	123.6 (2)
C(3)—C(2)—C(8)	117.4 (2)	117.5 (2)
C(2)—C(3)—C(4)	121.1 (2)	120.8 (2)
C(3)—C(4)—C(5)	120.2 (3)	120.2 (2)
C(4)—C(5)—C(6)	119.6 (3)	119.9 (2)
C(1)—C(6)—C(5)	120.6 (2)	120.3 (2)
C(1)—C(7)—O(1)	121.9 (2)	122.6 (2)
C(1)—C(7)—O(2)	114.6 (2)	113.0 (2)
O(1)—C(7)—O(2)	123.4 (2)	124.5 (2)
C(2)—C(8)—O(3)	120.1 (2)	120.3 (2)
C(2)—C(8)—C(9)	118.5 (2)	118.5 (2)
O(3)—C(8)—C(9)	120.9 (2)	121.0 (2)
C(8)—C(9)—C(10)	119.7 (3)	118.9 (2)
C(8)—C(9)—C(14)	121.4 (3)	121.0 (2)
C(10)—C(9)—C(14)	118.9 (3)	119.9 (2)
C(9)—C(10)—C(11)	119.8 (3)	119.8 (2)
C(10)—C(11)—C(12)	120.8 (4)	119.9 (3)
C(11)—C(12)—C(13)	119.2 (3)	120.8 (2)
C(12)—C(13)—C(14)	120.8 (4)	119.9 (3)
C(9)—C(14)—C(13)	120.4 (3)	119.6 (2)
C(7)—O(2)—H(O2)	106.8	107.0 (20)
C(7)—O(2)···O(1 ^a)	112.4 (2)	
O(2)—H(O2)···O(1 ^a)	165.9	
C(7)—O(1)···H1(W)		124.0 (10)
O(1)···O(W)···O(2 ^b)		141.9 (1)
H1(W)—O(W)—H2(W)		111.0 (40)
H1(W ^b)—O(W ^b)···H(O2)		131.0 (30)
O(2)—H(O2)···O(W ^b)		166.0 (40)
O(1)···H1(W)—O(W)		167.0 (40)

Symmetry code: (i) 1 - x, - y, - z; (ii) - x, - y, - z.

1962); geometric atom position calculation - *GEOM* (Shiono, 1971); analysis of variance - *NANOVA* (Lalancette, Cefola, Hamilton & La Placa, 1967); bond-distance and bond-angle error analysis - *ORFFE* (Busing, Martin & Levy, 1964); graphics - *ORTEPII* (Johnson, 1970).

Discussion. Tables 1 and 2 list positional and isotropic thermal parameters* for the anhydrous monoclinic (I) and the triclinic monohydrate (II) forms, respectively. Table 3 lists interatomic distances and Table 4 interatomic and bond angles for both (I) and (II); these values are comparable with those commonly observed in related molecules (Leiserowitz, 1976).

Fig. 1 shows a view of molecule (II) and the numbering scheme, which also applies to (I). Fig. 2 is a view of (I) showing that the molecules form a pair of H bonds, yielding a centrosymmetric acid dimer. Fig. 3 is a view of (II) which shows the expansion of the acid dimer to include the two water molecules. The total separation of the carboxyl groups has

increased by 2.45 Å relative to (I), but Fig. 4 shows that the carboxyl groups in (II) no longer lie in the same plane, as they do in (I), but in parallel planes 1.30 Å apart. The water molecules do not lie in these planes, but 0.18 Å outside, away from the center of symmetry. Only one of the water hydrogens [H1(W)] is involved in this H-bonding scheme; the second water hydrogen [H2(W)] has O(1) as its closest neighbor at 3.09 (4) Å.

Of the relatively minor angular differences between (I) and (II), the most easily seen in Figs. 2-4 is the change in dihedral angle between the plane of the carboxyl group and its aromatic ring. In (I), these two planes meet at an angle of 2.3 (1)°, in the rotational sense which gives the two carbonyl O atoms within the same molecule greater separation. In (II), this angle is 20.0 (1)° in the opposite sense, *i.e.* a rotational change of 22.3°. The dihedral angles formed by the benzoyl ring and the plane defined by the ketone plus its two attached C atoms are virtually unchanged in (I) [9.8 (1)°] versus (II) [10.4 (1)°]; both twists are in the sense giving greater separation of the two carbonyl oxygens in the molecule. The dihedral angles formed by the disubstituted ring and the plane of the ketone are 11.1 (1) and 21.9 (1)°, respectively,

* Lists of structure factors, anisotropic thermal parameters, and bond distances and angles involving H atoms for (II) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52731 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

from orthogonal in (I) and (II), both in the sense allowing greater separation of the two carbonyl O atoms; the change in angle is thus 10.8° . The planes of the two aromatic rings in (I) meet at a dihedral angle $2.4(2)^\circ$ from orthogonal in (I), compared with one $14.3(1)^\circ$ from orthogonal in the same sense in (II). This change of 11.9° moves the benzoyl ring closer to (and the ketone O atom thus farther from) the carboxyl group in (II). Finally, the dihedral angle formed by the carboxyl and the ketone in (I) is $8.9(1)^\circ$ from orthogonal, while in (II) this angle is $24.2(1)^\circ$ from orthogonal in the opposite sense, a 33.1° change.

The largest of the changes in dihedral angle for (I) versus (II) (33.1°) involves the relationship of the two carbonyl groups. This change comprises the individual rotations of the ketone and of the carboxyl relative to their common ring. In (I) versus (II) these changes so nearly compensate for each other that this non-bonded O...O distance [(I), $3.188(3)$; (II), $3.266(4)$ Å] changes by only about 0.078 Å, or less than 2.5%.

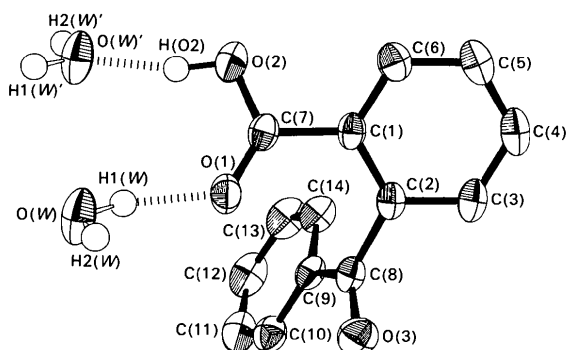


Fig. 1. The atom-numbering scheme, shown here for compound (II), also applies to compound (I).

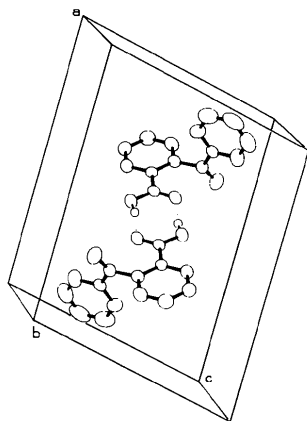


Fig. 2. A view of compound (I), showing the intermolecular hydrogen bonding in the acid dimer. For clarity only half of the unit-cell contents are displayed.

The solid-state (KBr) infrared spectra of (I) and (II), as expected, each have two carbonyl bands of similar strength. The ketone carbonyl groups, which are not involved in H bonding in either compound, have their absorptions at 1676 and 1663 cm^{-1} , respectively. The carboxyls, whose carbonyl groups both participate in H bonding, have their C=O absorptions at 1690 and 1684 cm^{-1} , respectively, for (I) and (II), very close to the solid-state value of *ca* 1687 cm^{-1} for benzoic acid. Thus the substitution of a water molecule for a second carboxyl in this H bond produces only a very slight difference in the position of the infrared absorption for carboxyl carbonyl.

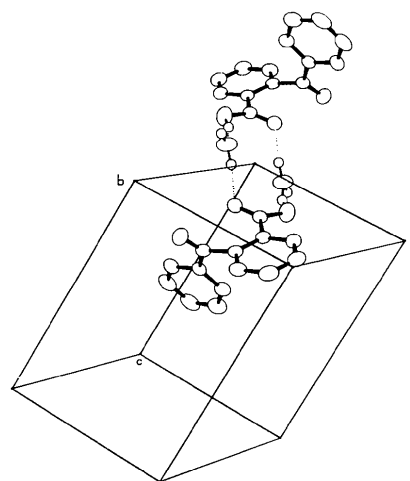


Fig. 3. A view of compound (II); two asymmetric units centrosymmetrically related about the origin are displayed to show the H bonding which generates the hydrated acid dimer.

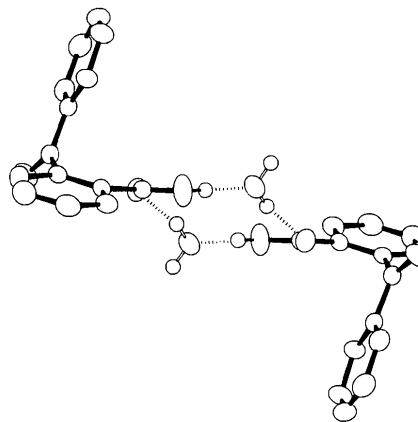


Fig. 4. A side view of the hydrated carboxyl dimer (II), showing the separation of the carboxyl planes by 1.30 Å.

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6 α - and 6 β -Trifluoromethyl-Substituted Androstenedione

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Abstract. 6 β -Trifluoromethyl-4-androstene-3,17-dione (I), C₂₀H₂₅F₃O₂, $M_r = 354.42$, orthorhombic, $P2_12_12_1$, $a = 8.123$ (3), $b = 10.348$ (3), $c = 21.725$ (11) Å, $V = 1826.1$ (15) Å³, $Z = 4$, $D_x = 1.289$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.0964$ mm⁻¹, $F(000) = 752$, $T = 293$ K, $R = 0.052$, $wR = 0.061$ for 930 observations. 6 α -Trifluoromethyl-4-androstene-3,17-dione (II), C₂₀H₂₅F₃O₂, $M_r = 354.42$, tetragonal, $P4_12_12$, $a = 10.896$ (2), $c = 29.569$ (6) Å, $V = 3510.7$ (6) Å³, $Z = 8$, $D_x = 1.341$ Mg m⁻³, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 0.8647$ mm⁻¹, $F(000) = 1504$, $T = 293$ K, $R = 0.065$, $wR = 0.093$ for 1576 observations. The novel 6 β steroid (I) was prepared from a photochemical rearrangement of a dienoltriflate; its α epimer (II) was prepared from acid treatment of (I). The overall conformation of (I) is nearly identical to that of the parent molecule, androst-4-ene-3,17-dione, to which

the structures of both (I) and (II) are conveniently compared. The *A*-ring conformation of (I) may be described either as a (1 α -2 β) half-chair or as a 1 α -sofa; *A*-ring asymmetry parameters are $\Delta C_2^{1,2} = 14.2$, $\Delta C_s^1 = 12.5$ with an average internal ring torsion angle of 26.9°. The *D*-ring conformation is a 14 α -envelope; $\Delta C_s(14) = 15.6$. The *A*-ring bowing angle is 19.2°. For (II) a disordered *A* ring with two half-occupancy positions for C(2) is found. The *A*-ring conformation thus may be described both as a 2 α - and a 2 β -sofa; *A*-ring asymmetry parameters are $\Delta C_s(2\alpha) = 6.5$, $\Delta C_s(2\beta) = 2.4$; average torsion angle within the ring = 24.4 (2 α) or 24.2° (2 β). The *B* and *C* rings adopt normal chair conformations; the *D* ring is a 14 α -envelope with $\Delta C_s(14) = 9.2$. The steroid bowing angle is 43.9° with inclusion of all *A*-ring atoms.

Introduction. In conjunction with an interest in the design of inhibitors for the enzyme steroid 5 α -reductase, the 6 β -trifluoromethyl-substituted andro-

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