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2-Bromoacetoxybenzoic Acid, a Brominated Aspirin Analog

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Abstract

The crystal structure of 2-bromoacetoxybenzoic acid, $C_9H_7BrO_4$, shows it to be a close structural analog of aspirin. The carboxylic acid moiety is twisted by 7.7 (4)° out of the plane of the aromatic ring. The acetyl group, like that of aspirin, shows bond-angle distortions from ideal values while remaining essentially planar. The Br atom is rotationally disordered and has been modeled as occupying two sites related by a 13 (1)° rotation about the C8—C9 bond.

Comment

Aspirin exerts its anti-inflammatory and antipyretic effects through inactivation, *via* specific covalent modification, of the cyclooxygenase enzyme. In the course of our studies of this enzyme, we synthesized the title compound, (I), which covalently modifies and inactivates the cyclooxygenase in a manner analogous to aspirin. In addition, (I) carries the heavy Br atom, enabling us to employ it as a crystallographic probe of the enzyme's active site (Loll, Picot & Garavito, 1995).
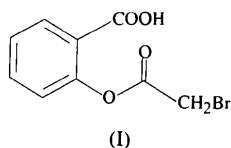

(I)

Fig. 1 shows a perspective view of the title compound. Three distinct planar groups are seen in the molecule. The six members of the benzene ring show an r.m.s. deviation from the least-squares plane of 0.005 Å, while atoms O3, O4, C8 and C9 of the acetyl group show an r.m.s. deviation of 0.006 Å from their least-squares plane. The plane of the acetyl group makes an angle of 84.5 (1)° with that of the ring. As is the case for aspirin (Wheatley, 1964), the three atoms of the carboxylic acid moiety are not coplanar with the ring; in this case, however, the angle is more pronounced, being 7.7 (4)°. This large twist may be required to accommodate the packing of the bulky Br atom in the lattice, while maintaining the intermolecular hydrogen bonding between carboxylic acid groups across the center of symmetry.
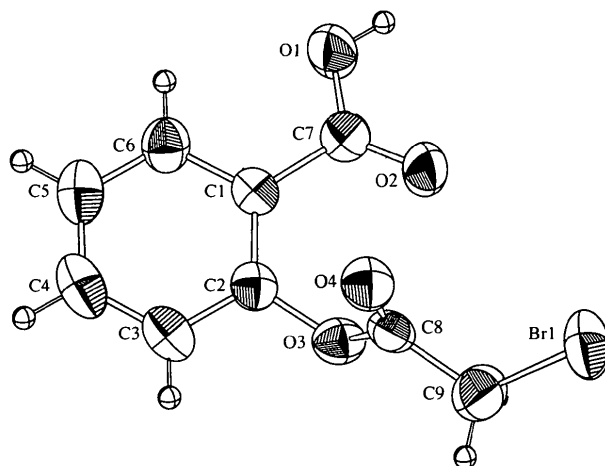

Fig. 1. View of the title compound showing the atomic labeling scheme (*ORTEP*II; Johnson, 1976). Displacement ellipsoids for non-H atoms are plotted at the 50% probability level and H atoms are drawn as spheres of arbitrary radii. Only one of the two rotameric positions of the Br atom is shown for clarity.

All bond lengths within the title molecule are normal. Slight distortions in the ring angles are observed around the C1 atom, suggesting that even with the large twist of the carboxylate group, repulsion between that group and the ring tends to pull C1 outward slightly from the ring center. Pronounced deviations from the ideal bond-angle value of 120° are found in the acetyl group, with the C9—C8—O3 angle being only 107.9 (3)°. Similar non-ideal angles are seen in the acetyl group of aspirin.

The C8—C9 bond has been modeled as existing in two rotameric states with O4—C8—C9—Br torsion angles of −31.2 (6) and −44.0 (9)°, and refined occupancies of 0.60 (2) and 0.40 (2), respectively (see Fig. 2). In each case, the Br atom is in van der Waals contact with the aromatic H3, H4 and H5 atoms from neighboring molecules. Details of the packing may be seen in Fig. 3.
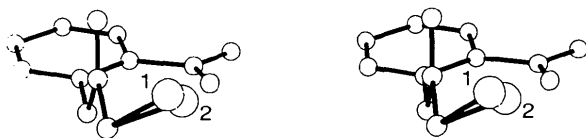
Fig. 2. Stereodrawing of the title compound showing the disorder associated with the Br atom. Numbers 1 and 2 refer to the major and minor rotameric populations, respectively.
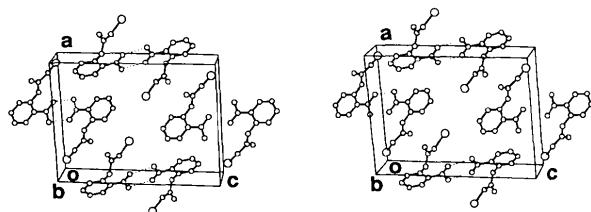

Fig. 3. Stereoview of the crystal packing of 2-bromoacetoxybenzoic acid. Hydrogen bonds are drawn as dashed lines.

Experimental

Salicylic acid was acylated using bromoacetyl bromide, pyridine and dimethylaminopyridine (DMAP) in ethyl ether at 273 K (molar ratio salicylic acid/bromoacetyl bromide/pyridine/DMAP 1:1.2:1:0.006). This yielded the title compound, which was recrystallized twice from ethanol/water solution. Analysis for $C_9H_7BrO_4$: calculated C 41.73, H 2.72, Br 30.84, O 24.70%; found C 41.80, H 2.68, Br 30.90, O 24.76%. Crystals for diffraction studies were grown from acetone/benzene solution.

Crystal data

$C_9H_7BrO_4$	Mo $K\alpha$ radiation
$M_r = 259.06$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 250
$P2_1/n$	reflections
$a = 12.438\,(6)$ Å	$\theta = 5.8–18.8°$
$b = 4.726\,(3)$ Å	$\mu = 4.175$ mm^{-1}
$c = 16.703\,(6)$ Å	$T = 296$ K
$\beta = 92.50\,(2)°$	Block
$V = 980.9\,(9)$ Å^3	$0.43 \times 0.22 \times 0.18$ mm
$Z = 4$	Colorless
$D_x = 1.754$ Mg m^{-3}	

Data collection

Enraf–Nonius FAST area-detector diffractometer	963 observed reflections $[I > 2\sigma(I)]$
Rotation method, on-line box integration scans	$R_{int} = 0.084$
	$\theta_{max} = 23.28°$
Absorption correction:	$h = 0 \rightarrow 13$
none	$k = 0 \rightarrow 5$
8147 measured reflections	$l = -18 \rightarrow 18$
1404 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.001$
$R(F) = 0.0413$	$\Delta\rho_{max} = 0.408$ e Å^{-3}
$wR(F^2) = 0.1114$	$\Delta\rho_{min} = -0.490$ e Å^{-3}

$S = 0.961$
1404 reflections
147 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Br1†	0.1360 (4)	0.5171 (9)	0.0393 (2)	0.0690 (9)
Br2‡	0.1610 (14)	0.5006 (16)	0.0260 (7)	0.099 (2)
O1	0.5964 (2)	−0.0175 (6)	0.0830 (2)	0.0652 (9)
O2	0.4487 (2)	0.2386 (6)	0.06007 (15)	0.0597 (8)
O3	0.4053 (2)	0.6366 (5)	0.1702 (2)	0.0493 (7)
O4	0.2780 (2)	0.3106 (6)	0.1891 (2)	0.0555 (7)
C1	0.5426 (3)	0.2725 (7)	0.1872 (2)	0.0407 (8)
C2	0.4804 (3)	0.4849 (7)	0.2186 (2)	0.0427 (9)
C3	0.4951 (3)	0.5720 (9)	0.2969 (3)	0.0566 (11)
C4	0.5739 (4)	0.4461 (9)	0.3455 (3)	0.0644 (12)
C5	0.6383 (3)	0.2379 (9)	0.3155 (2)	0.0610 (11)
C6	0.6226 (3)	0.1511 (9)	0.2377 (2)	0.0514 (10)
C7	0.5252 (3)	0.1640 (8)	0.1041 (2)	0.0471 (9)
C8	0.3064 (3)	0.5212 (8)	0.1583 (2)	0.0457 (10)
C9	0.2421 (3)	0.7108 (8)	0.1030 (3)	0.0692 (13)

† Occupancy = 0.60 (2).   ‡ Occupancy = 0.40 (2).

Table 2. *Selected geometric parameters (Å, °)*

Br1—C9	1.894 (4)	C1—C6	1.399 (5)
Br2—C9	1.882 (5)	C1—C7	1.487 (5)
O1—C7	1.293 (4)	C2—C3	1.376 (6)
O2—C7	1.229 (4)	C3—C4	1.380 (6)
O3—C8	1.353 (4)	C4—C5	1.376 (6)
O3—C2	1.405 (4)	C5—C6	1.370 (6)
O4—C8	1.182 (4)	C8—C9	1.494 (5)
C1—C2	1.385 (5)		
C8—O3—C2	117.1 (3)	C5—C6—C1	121.2 (4)
C2—C1—C6	117.6 (3)	O2—C7—O1	123.4 (3)
C2—C1—C7	122.9 (3)	O2—C7—C1	122.5 (3)
C6—C1—C7	119.5 (3)	O1—C7—C1	114.1 (3)
C3—C2—C1	121.6 (4)	O4—C8—O3	124.3 (4)
C3—C2—O3	116.9 (3)	O4—C8—C9	127.8 (4)
C1—C2—O3	121.3 (3)	O3—C8—C9	107.9 (3)
C2—C3—C4	119.4 (4)	C8—C9—Br2	111.2 (4)
C5—C4—C3	120.3 (4)	C8—C9—Br1	113.5 (3)
C6—C5—C4	119.8 (4)		

The coordinates of the Br-atom position were located from a sharpened Patterson synthesis. The remaining non-H atoms were found in successive difference Fourier maps. After anisotropic refinement, the difference Fourier map revealed all the H-atom positions and disorder in the bromine site. The Br-atom position was modeled using two sites with occupancies summing to 1.0 and C9—Br distances restrained to be equal (target standard deviation 0.005 Å). H atoms were positioned using a riding model and given displacement parameters equal to $1.5U_{eq}$ of their respective carrier atoms.

Data collection: *MADNES* (Messerschmidt & Pflugrath, 1987). Cell refinement: *MADNES*. Data reduction: *MADNES*. Program(s) used to solve structure: *CCP4 Suite* (Collaborative Computational Project, Number 4, 1994). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *FRODO* (Jones, 1982), *ORTEPII* (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraphenylphosphonium Triiodide

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Abstract

The crystals of the title compound, $C_{24}H_{20}P^+.I_3^-$, are composed of slightly bent I_3^- anions and Ph_4P^+ cations separated by normal van der Waals distances; both ions lie on twofold axes. The I—I distances in the anion are 2.9180 (4) Å, with an I—I—I angle of 175.27 (3)°. In the cation, the P—C distances are identical [1.790 (4) Å] and the C—P—C angles are in the range 105.5 (3)–111.6 (2)°.

Comment

The alkylation of tetrathiotungstate ions is known to lead to a variety of polynuclear thiotungstates (Dhar & Chandrasekaran, 1989; Boorman, Wang & Parvez,

1995). During a study of the reaction between ethyl iodide and $(PPh_4)_2[WS_4]$, a red crystalline product was obtained from MeCN solution which had different spectroscopic properties from any known thiotungstate. Believing it to contain a new $[W_xS_y]^{n-}$ ion, we undertook an X-ray structural study. This product is shown here to be $PPh_4^+.I_3^-$, (I), which was formed as an unexpected by-product of this alkylation reaction.
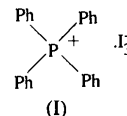

(I)

Fig. 1 shows the anion and the cation, together with the numbering scheme used. There are no short interactions of any significance between the anions and the cations. The I—I distances [2.9180 (4) Å] and I—I—I angle [175.27 (3)°] in the anion, which lies on a twofold axis, agree well with the corresponding distances and angles reported for $(C_2H_5)_4N^+.I_3^-$, form I [2.928 (3), 2.943 (3) Å and 180.0° in two anions in the asymmetric unit (Migchelsen & Vos, 1967)], and $(C_6H_5)_4As^+.I_3^-$ [2.920 (2) Å and 175.61 (5)° (Runsink, Swen-Walstra & Migchelsen, 1972)]. Several structures have been reported with unequal I—I distances in the anion, *e.g.* $(C_2H_5)_4N^+.I_3^-$, form II [2.981 (4), 2.892 (4) and 2.912 (4), 2.961 (4) Å in the two anions in the asymmetric unit (Migchelsen & Vos, 1967)], $(n-C_4H_9)_4N^+.I_3^-$ [2.887 (4), 2.951 (4) and 2.911 (4), 2.940 (4) Å (Herbstein, Kaftory, Kapon & Saenger, 1981)] and $(Ph_3P)_2N^+.I_3^-$ [2.896 (1) and 2.928 (1) Å (Tebbe & Krauss, 1990)]. The molecular dimensions in the cation, which also lies on a twofold axis, are as ex-
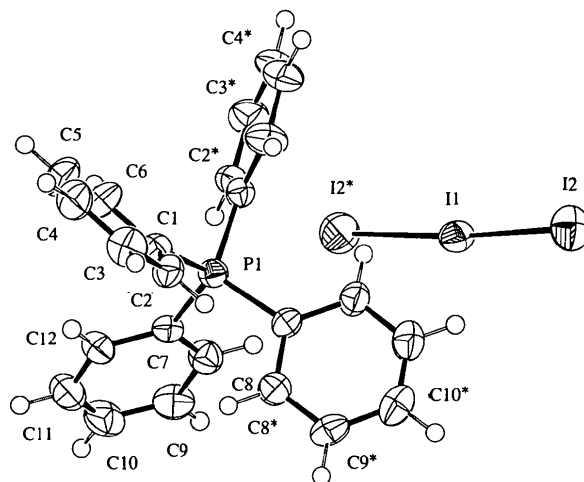

Fig. 1. An *ORTEPII* drawing (Johnson, 1976) of the title compound. The non-H atoms have been plotted as 50% probability displacement ellipsoids and H atoms have been assigned arbitrary radii. Starred atoms are symmetry generated.