O1—C7—C6	90.7 (4)	F4—C18—C17	121.5 (5)
O1—C7—C14	115.1 (4)	F4—C18—C19	120.1 (6)
C6—C7—C14	114.9 (5)	C17—C18—C19	118.4 (6)
O2—C8—O3	123.6 (5)	F5—C19—C14	118.6 (5)
O2—C8—C9	110.3 (4)	F5—C19—C18	117.7 (6)
O3—C8—C9	126.1 (6)	C14—C19—C18	123.7 (6)
C3—C10—C11	111.4 (4)		

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Software*. Data reduction: local program (Brock). Structure solution, structure refinement, molecular graphics and software used to prepare material for publication: *SHELXTL/PC* (Sheldrick, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1119). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two *N*-Saccharin Peracids

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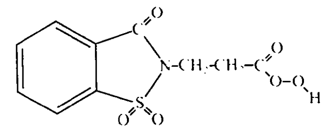
Abstract

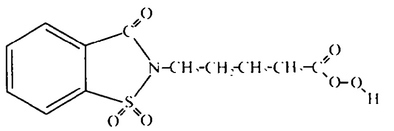
The crystal structures of *N*-saccharinperpropanoic acid [3-oxo-2*H*-1,2-benzisothiazole-2-peroxypropanoic acid 1,1-dioxide, $C_{10}H_9NO_6S$, (I)] and *N*-saccharinperpentanoic acid [3-oxo-2*H*-1,2-benzisothiazole-2-peroxypentanoic acid 1,1-dioxide, $C_{12}H_{13}NO_6S$, (II)] have been determined. Hydrogen bonding in (I) produces chains of molecules through the interaction of the peracid proton and keto O atom, while in (II) the result is ten-membered centrosymmetric peracid ring dimers. We believe this to be the first example of such a centrosymmetric motif in an organic peracid.

Comment

As part of a general study of the stability of organic peracids and peracid salts (Kariuki & Jones, 1990), and in particular of the role of hydrogen bonding in controlling the crystal structure of peracid and acid amides (Feeder & Jones, 1992), we report here the structures of *N*-saccharinperpropanoic acid, (I), and *N*-saccharinperpentanoic acid, (II).



(I)



(II)

In both compounds, the bond lengths and angles found for the saccharin moiety are similar to those reported for saccharin (Okaya, 1969), *N*-cyanomethylsaccharin (Junii, Guilan, Zhongyuan & Liu, 1989) and (*R*)-(+)-supidimide (Winter, Graudums & Frankus, 1983), and a series of saccharin derived carboxylic acids (Feeder & Jones, 1994*a*). The bond lengths and angles for the peracid function are not significantly different to those found for peroxypelargonic acid (Belitskus & Jeffrey, 1965), *o*-nitroperoxybenzoic acid (Sax, Beurskens & Chu, 1965) and *p*-nitroperoxybenzoic acid (Kim, Chu & Jeffrey, 1970), and for a series of *p*-amidoperbenzoic acids (Feeder & Jones, 1994*b*). The two sulfone O atoms in both structures lie approximately 1.2 Å out of the plane of the saccharin group.

The structure solution of (I) demonstrated that, except for the sulfone O atoms and the two methylene groups, the molecule is planar and lies on a crystallographic mirror plane. The two methylene groups are disordered across this mirror plane and the two C atoms were therefore refined with half occupancies. The methylene H atoms could not be located. The peroxycarboxylic acid proton was located in a reasonable position from the difference Fourier map, although it was found to refine with a very high isotropic displacement parameter. Hydrogen bonding within the structure of (I) generates chains of molecules through a motif which is commonly observed in short chain ω-phthalimido aliphatic acids (Feeder & Jones, 1994*c*). The interaction is between peracid protons and keto O atoms of molecules related by an *a* glide. These chains are stacked through C—H···O contacts into sheets along the *b* axis.

In (II) the peracid and saccharin groups are not coplanar and the peracid H atom was not located. Based upon short O···O distances, the hydrogen bonding observed in (II) appears to result in two motifs. The first is a ten-membered centrosymmetric cyclic peracid-dimer motif. This arrangement has an extremely common analogue in the crystal structures of carboxylic acids (Leiserowitz, 1976). However, we believe this to be the first example in a peracid crystal structure. Unlike the acid motif, the ring is not planar and appears to adopt a type of chair conformation, presumably to increase packing efficiency. The second type of motif involves a short O···O distance also from the terminal peroxy O atom, but in this case to a sulfone O atom, thereby linking molecules related by translation along the *b* axis into chains. As with (I), there are a number of short C—H···O contacts.

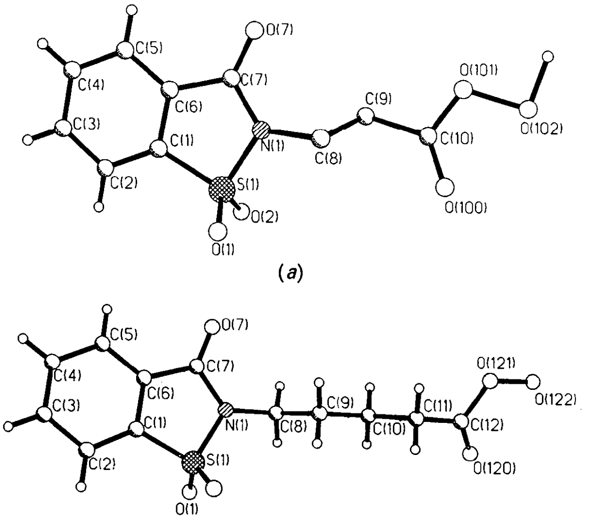


Fig. 1. (*a*) Atomic numbering scheme for (I) and (*b*) atomic numbering scheme for (II).

Experimental

Compound (I)

Crystal data

$C_{10}H_9NO_6S$
$M_r = 271.24$
Orthorhombic
Pnma
$a = 13.659$ (3) Å
$b = 6.9360$ (10) Å
$c = 11.980$ (2) Å
$V = 1135.0$ (4) Å^3
$Z = 4$
$D_x = 1.587$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8–14°$
$\mu = 0.306$ mm^{-1}
$T = 293$ (2) K
Plate
0.50 × 0.30 × 0.30 mm
White transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/2θ scans
Absorption correction: none
1089 measured reflections
1089 independent reflections
677 observed reflections $[I > 2\sigma(I)]$

$\theta_{\max} = 24.97°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 14$
2 standard reflections monitored every 100 reflections intensity variation: 5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0683$
$wR(F^2) = 0.2208$
$S = 1.343$
1089 reflections
119 parameters
Only H-atom *U*'s refined
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.1458P)^2 + 0.4118P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.741$

$\Delta\rho_{\max} = 0.578$ e Å^{-3}
$\Delta\rho_{\min} = -0.566$ e Å^{-3}
Extinction correction: *SHELXL* (Sheldrick, 1994)
Extinction coefficient: 0.0069 (45)
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* (Å^2) *for* (I)

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

	x	y	z	$U_{\rm eq}$
S1	0.16184 (12)	1/4	0.84732 (13)	0.0627 (7)
C7	0.1380 (5)	1/4	1.0599 (5)	0.060 (2)
C5	−0.0487 (4)	1/4	1.0658 (5)	0.051 (2)
C6	0.0397 (4)	1/4	1.0116 (4)	0.0440 (14)
C1	0.0413 (4)	1/4	0.8952 (5)	0.0482 (15)
C2	−0.0426 (5)	1/4	0.8329 (6)	0.069 (2)
C3	−0.1295 (6)	1/4	0.8893 (7)	0.081 (2)
C4	−0.1334 (5)	1/4	1.0051 (6)	0.067 (2)
O1	0.1868 (3)	0.0635	0.7928 (3)	0.0868 (14)
N1	0.2062 (4)	1/4	0.9766 (5)	0.082 (2)
O7	0.1602 (4)	1/4	1.1575 (4)	0.094 (2)
C8	0.3099 (7)	0.1560 (16)	0.9946 (10)	0.072 (3)
C9	0.3657 (9)	0.3344 (18)	1.0432 (10)	0.083 (4)
C10	0.4742 (7)	1/4	1.0386 (8)	0.097 (3)
O101	0.5115 (4)	1/4	1.1380 (5)	0.132 (3)
O100	0.5194 (5)	1/4	0.9540 (5)	0.101 (2)
O102	0.6188 (4)	1/4	1.1291 (5)	0.113 (3)

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

S1—O1	1.488 (2)	C10—O100	1.186 (10)
S1—N1	1.662 (6)	C10—O101	1.295 (10)
C7—O7	1.208 (8)	O101—O102	1.470 (8)
C7—N1	1.366 (8)		
O(7)···O(102$^{\rm i}$)	2.618 (10)		
O1—S1—O1$^{\rm ii}$	120.7 (2)	O100—C10—O101	125.5 (8)
O1—S1—N1	109.0 (2)	O100—C10—C9	120.9 (7)
O1$^{\rm ii}$—S1—N1	109.0 (2)	O101—C10—C9	109.5 (8)
O7—C7—N1	122.4 (7)	C10—O101—O102	109.0 (6)
C7—N1—S1	115.6 (5)		
O7—C7—N1—C8	28.9 (5)	N1—C8—C9—C10	−169.6 (7)
C6—C7—N1—C8	−151.1 (5)	C8—C9—C10—O100	80.4 (8)

C1—S1—N1—C8	152.3 (5)	C8—C9—C10—O101	−121.3 (7)
C7—N1—C8—C9	−88.5 (8)	C9—C10—O101—O102	157.1 (5)
S1—N1—C8—C9	120.8 (6)		

Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{5}{2} - z$; (ii) $x, \frac{1}{2} - y, z$.

Compound (II)

Crystal data

$C_{12}H_{13}NO_6S$
$M_r = 299.29$
Triclinic
$P\bar{1}$
$a = 8.449$ (2) Å
$b = 8.569$ (3) Å
$c = 11.100$ (4) Å
$\alpha = 66.78$ (3)°
$\beta = 70.70$ (3)°
$\gamma = 66.22$ (2)°
$V = 661.7$ (4) Å^3
$Z = 2$
$D_x = 1.502$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 8$–15°
$\mu = 0.270$ mm^{-1}
$T = 295$ (2) K
Cuboid
0.40 × 0.40 × 0.30 mm
White transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2444 measured reflections
2311 independent reflections
1553 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0143$
$\theta_{\rm max} = 24.97°$
$h = -9 \rightarrow 10$
$k = -9 \rightarrow 10$
$l = 0 \rightarrow 13$
2 standard reflections monitored every 100 reflections intensity variation: 6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0475$
$wR(F^2) = 0.1311$
$S = 1.283$
2311 reflections
186 parameters
Only H-atom U's refined
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0772P)^2 + 0.0703P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.631$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.276$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

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

	x	y	z	$U_{\rm eq}$
C1	0.3030 (3)	0.4782 (4)	0.7022 (3)	0.0470 (7)
C2	0.2598 (4)	0.6473 (4)	0.7109 (4)	0.0598 (8)
C3	0.2062 (5)	0.7888 (5)	0.6015 (4)	0.0711 (10)
C4	0.1945 (4)	0.7623 (5)	0.4918 (4)	0.0708 (10)
C5	0.2347 (4)	0.5934 (5)	0.4860 (3)	0.0618 (9)
C6	0.2910 (3)	0.4489 (4)	0.5930 (3)	0.0468 (7)
C7	0.3380 (4)	0.2571 (4)	0.6075 (3)	0.0542 (8)
C8	0.4309 (4)	−0.0381 (4)	0.7821 (4)	0.0683 (10)
C9	0.6234 (4)	−0.1430 (4)	0.7676 (3)	0.0513 (7)
C10	0.6493 (4)	−0.3416 (4)	0.8237 (3)	0.0521 (7)
C11	0.8414 (4)	−0.4513 (4)	0.8168 (4)	0.0616 (9)
C12	0.8654 (4)	−0.6469 (4)	0.8745 (3)	0.0559 (8)
S1	0.37383 (10)	0.27427 (11)	0.82262 (8)	0.0536 (3)
N1	0.3951 (3)	0.1567 (3)	0.7274 (3)	0.0545 (7)
O1	0.2368 (3)	0.2476 (4)	0.9376 (2)	0.0763 (7)
O2	0.5413 (3)	0.2450 (3)	0.8449 (2)	0.0741 (7)
O7	0.3300 (3)	0.1949 (3)	0.5311 (3)	0.0788 (7)
O120	0.8161 (3)	−0.7257 (4)	0.9873 (2)	0.0805 (7)
O121	0.9504 (3)	−0.7277 (3)	0.7790 (2)	0.0693 (6)
O122	0.9702 (4)	−0.9255 (4)	0.8312 (4)	0.1158 (11)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

C7—O7	1.197 (4)	S1—O2	1.422 (2)
C7—N1	1.390 (4)	S1—O1	1.424 (2)
C12—O120	1.189 (4)	S1—N1	1.653 (3)
C12—O121	1.339 (4)	O121—O122	1.516 (4)
O(122)···O(120$^{\rm i}$)	3.092 (6)	O(120)···O(122$^{\rm i}$)	3.092 (6)
O7—C7—N1	124.5 (3)	O2—S1—N1	110.42 (15)
O120—C12—O121	122.5 (3)	O1—S1—N1	110.00 (15)
O120—C12—C11	127.2 (3)	C7—N1—S1	115.0 (2)
O121—C12—C11	110.3 (3)	C12—O121—O122	112.3 (2)
O2—S1—O1	117.16 (15)		
C10—C11—C12—O120	−63.7 (4)	O120—C12—O121—O122	1.5 (4)
C10—C11—C12—O121	114.9 (3)	C11—C12—O121—O122	−177.2 (2)

Symmetry code: (i) $2 - x, 2 - y, 2 - z$.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL* (Sheldrick, 1994). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL*.

We acknowledge support from the SERC (studentship for NF). We are grateful to Solvay Interox, and in particular Dr A. James, for the provision of samples and numerous discussions.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1093). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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