Table 2. *Selected bond lengths* (Å) *and angles* (°) *in* (−)-(6′*R*)-3′,6′-*epoxyaurapten*

C5–O1	1·347 (4)	C9–O1	1·440 (4)
C8–O2	1·447 (4)	C17–O2	1·438 (5)
C2–O3	1·378 (4)	C4–O3	1·390 (5)
C4–O4	1·210 (5)	C8–C1	1·549 (5)
C9–C1	1·501 (5)	C18–C1	1·567 (5)
C6–C2	1·380 (5)	C10–C2	1·385 (5)
C10–C3	1·427 (6)	C12–C3	1·334 (6)
C12–C4	1·438 (6)	C6–C5	1·387 (5)
C14–C5	1·399 (5)	C18–C7	1·521 (6)
C13–C8	1·531 (5)	C15–C8	1·519 (5)
C16–C10	1·403 (5)	C18–C11	1·531 (6)
C19–C13	1·538 (6)	C16–C14	1·364 (6)
C18–C17	1·530 (5)	C19–C17	1·534 (6)
C9–O1–C5	117·8 (3)	C17–O2–C8	96·6 (3)
C4–O3–C2	121·8 (3)	C9–C1–C8	114·9 (3)
C18–C1–C8	101·9 (3)	C18–C1–C9	116·4 (3)
C6–C2–O3	116·1 (4)	C10–C2–O3	120·8 (4)
C10–C2–C6	123·2 (4)	C12–C3–C10	120·9 (5)
O4–C4–O3	116·1 (4)	C12–C4–O3	116·7 (4)
C12–C4–O4	127·2 (5)	C6–C5–O1	125·4 (4)
C14–C5–O1	115·7 (4)	C14–C5–C6	118·9 (4)
C5–C6–C2	118·9 (4)	C1–C8–O2	102·0 (3)
C13–C8–O2	101·8 (3)	C13–C8–C1	108·1 (3)
C15–C8–O2	109·9 (3)	C15–C8–C1	118·1 (3)
C15–C8–C13	114·9 (4)	C1–C9–O1	106·7 (3)
C3–C10–C2	118·1 (4)	C16–C10–C2	116·9 (4)
C16–C10–C3	124·9 (4)	C4–C12–C3	121·5 (5)
C19–C13–C8	102·2 (4)	C16–C14–C5	121·3 (4)
C14–C16–C10	120·8 (4)	C18–C17–O2	102·3 (3)
C19–C17–O2	101·7 (4)	C19–C17–C18	113·7 (4)
C7–C18–C1	112·8 (4)	C11–C18–C1	113·2 (4)
C11–C18–C7	109·1 (4)	C17–C18–C1	99·9 (3)
C17–C18–C7	114·7 (4)	C17–C18–C11	106·9 (4)
C17–C19–C13	101·0 (4)		

rather than of an aryl ring. It can be seen also that the positive charge may migrate to C5 which explains the shortened length (π character) of the O1–C5 bond *versus* the O1–C9 bond.

Finally, there is evidence of the *syn* relationship between the O2 bridge and the coumarin chain bonded to C1, a problem incompletely resolved until now by the nuclear Overhauser effect difference in NMR analysis. This verifies that anterior assignments based upon biogenetic pathways by Van Tamelen & Coates (1982) were correct.

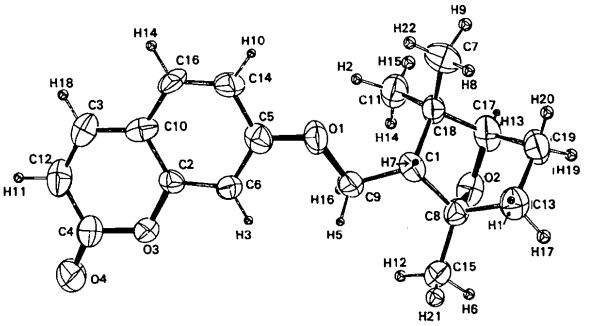

Fig. 1. *ORTEP* plot of the molecule of (−)-(6′*R*)-3′,6′-epoxyaurapten. For the sake of clarity, the isotropic thermal parameters of the H atoms were divided by ten.

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Structure of the 1:1 Complex between 4-Amino-*N*-(4,6-dimethyl-2-pyrimidinyl)-benzenesulfonamide (Sulfadimidine) and 2-Hydroxybenzoic Acid (Salicylic Acid)

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Abstract. $C_{12}H_{14}N_4O_2S.C_7H_6O_3$, $M_r = 416{\cdot}46$, orthorhombic, *Pbca*, $a = 15{\cdot}7783\ (8)$, $b = 25{\cdot}3419\ (12)$, $c = 10{\cdot}2212\ (5)$ Å, $V = 4087{\cdot}0\ (4)$ Å^3, $Z = 8$, $D_m = 1{\cdot}360\ (5)$, $D_x = 1{\cdot}3535\ (2)$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}69$ mm^{-1}, $F(000) = 1744$, $T = 293$ K, final $R = 0{\cdot}053$ for 2733 observed reflections. The molecular complex between sulfadimidine and salicylic acid is obtained as a result of two hydrogen bonds

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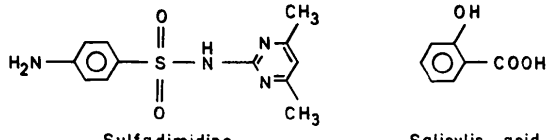
involving both the carboxyl group O atoms of salicylic acid and the imino and pyrimidine N atoms of sulfadimidine. The torsion angle C1–S8–N11–C12 of sulfadimidine is −66·4 (3)°. The two planar six-membered rings in sulfadimidine are rotated with respect to each other by 109·0 (4)°. The structure contains an extensive scheme of hydrogen bonding and a distinct environment of van der Waals interactions involving six-membered rings of sulfadimidine and salicylic acid.

Introduction. Sulfonamides are well known antibacterial agents. They produce antimicrobial effects by competitively inhibiting the enzyme dihydropteroate synthase (DHPS) to its substrate *p*-aminobenzoic acid (PABA) (Bock, Miller, Schaper & Seydel, 1974). As part of our programme of systematic studies on sulfonamides, their complexes with other biologically interesting molecules and the enzyme DHPS (Haridas & Singh, 1987), we report here the crystal structure of a 1:1 complex between sulfadimidine and salicylic acid (I). We have reported earlier the crystal structure of sulfadimidine (Tiwari, Haridas & Singh, 1984).



(I)

Experimental. Samples of sulfadimidine and salicylic acid obtained commercially, crystallized from solution in acetonitrile of sulfadimidine and salicylic acid in equimolar ratio at 293 K. Thin, transparent, platy hexagonal crystals; one 0·50 × 0·30 × 0·20 mm used for data collection. Unit-cell dimensions and space group from oscillation and Weissenberg photographs. Cell dimensions refined on an automatic computer-controlled diffractometer using 20 independent reflections (θ range: 4·0 to 25·0°). Density by flotation in benzene and carbon tetrachloride. Intensity data collected on Enraf–Nonius CAD-4 automatic four-circle diffractometer in ω–2θ scan mode using graphite-monochromated Cu $K\alpha$ radiation. Total number of reflections measured 3458, total number of independent reflections 27 $[I \geq 2{\cdot}5\sigma(I)]$ for $(\sin\theta)/\lambda \leq 0{\cdot}47$ Å^{-1} with $h = 0$ to 18, $k = 0$ to 30, $l = 0$ to 11. Corrections for Lorentz and polarization effects but not for absorption ($\mu R = 0{\cdot}51$). Intensity measurements of two standard reflections (240 and 042) repeated after every 50 reflections. Variations in intensity throughout the experiment ≤4·5%, R_{int} (for merged data) = 4·1%. Structure solved by *MULTAN*71 (Germain, Main & Woolfson, 1971) and refined by block-diagonal structure-factor least-squares procedure. Positions of H atoms from difference Fourier map. Non-H atoms refined anisotropically and H atoms isotropically. For 2733 observed reflections, final $R = 0{\cdot}053$, $wR = 0{\cdot}072$, $S = 4{\cdot}64$. Final $\Delta\rho$ fluctuations −0·15 to 0·14 e Å^{-3} and $(\Delta/\sigma)_{max} = 0{\cdot}18$. Weighting function $w = 1/(7{\cdot}62\,|F_{obs}| + 0{\cdot}0047\,|F_{obs}|^2)$ (Cruickshank, 1961) adjusted to make the average independent of F_{obs}. $\sum w(\Delta F)^2$ used in block-diagonal least-squares refinement. *SFLS* programs originally written by Shiono (1968/1971) and extensively modified by the authors. Atomic scattering factors for S atom from *International Tables for X-ray Crystallography* (1962), for C,N,O atoms from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965). All calculations on the HP computers at the All India Institute of Medical Sciences, New Delhi.

Table 1. *Fractional coordinates* (×10^4) *of the non*-H *atoms and equivalent isotropic thermal parameters* (Å^2×10^3)

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}
C1	−805 (2)	3213 (1)	1202 (3)	47 (2)
C2	−1410 (2)	3429 (1)	2044 (3)	58 (2)
C3	−2251 (2)	3293 (1)	1892 (4)	66 (2)
C4	−2502 (2)	2941 (1)	907 (4)	61 (2)
C5	−1881 (2)	2725 (1)	94 (3)	57 (2)
C6	−1041 (2)	2863 (1)	232 (3)	53 (2)
N7	−3333 (2)	2812 (1)	760 (4)	98 (3)
S8	255 (1)	3385 (1)	1435 (1)	48 (1)
O9	384 (1)	3525 (1)	2780 (2)	63 (1)
O10	778 (1)	2983 (1)	868 (3)	68 (1)
N11	427 (2)	3951 (1)	681 (2)	52 (1)
C12	402 (2)	4035 (1)	−651 (3)	48 (2)
N13	132 (2)	3651 (1)	−1419 (2)	52 (1)
C14	114 (2)	3754 (1)	−2701 (3)	57 (2)
C15	374 (2)	4241 (1)	−3200 (3)	82 (2)
C16	649 (2)	4621 (1)	−2313 (3)	54 (2)
N17	658 (2)	4515 (1)	−1037 (2)	36 (1)
C18	−194 (3)	3318 (2)	−3579 (4)	80 (3)
C19	944 (3)	5155 (1)	−2741 (4)	75 (2)
C20	1884 (2)	5571 (1)	2413 (3)	55 (2)
C21	2158 (2)	6043 (1)	1844 (4)	68 (2)
C22	2529 (3)	6425 (1)	2627 (5)	82 (3)
C23	2614 (2)	6348 (2)	3938 (4)	79 (2)
C24	2345 (2)	5888 (2)	4520 (4)	75 (2)
C25	1989 (2)	5489 (1)	3753 (3)	65 (2)
C26	1478 (2)	5162 (1)	1602 (3)	56 (2)
O27	1321 (2)	5277 (1)	394 (2)	64 (1)
O28	1286 (2)	4727 (1)	2081 (2)	75 (2)
O29	1755 (2)	5040 (1)	4353 (3)	91 (2)

Discussion. There are two molecules in the asymmetric unit, one each of sulfadimidine and salicylic acid. The final positional and equivalent isotropic temperature factors of non-H atoms are given in Table 1.* The bond lengths and valence angles involving non-H atoms are listed in Table 2. A perspective view with the numbering scheme is illustrated in Fig. 1. The crystal

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles, hydrogen-bond parameters, least-squares-planes data and intermolecular contact distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44895 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *involving non-*H *atoms*

C1–C2	1·397 (4)	C14–C18	1·504 (5)
C1–C6	1·381 (4)	C15–C16	1·392 (4)
C1–S8	1·744 (3)	C16–N17	1·332 (4)
C2–C3	1·380 (4)	C16–C19	1·496 (4)
C3–C4	1·402 (5)	C20–C21	1·399 (4)
C4–C5	1·397 (4)	C20–C25	1·400 (4)
C4–N7	1·359 (4)	C20–C26	1·474 (4)
C5–C6	1·378 (4)	C21–C22	1·386 (5)
S8–O9	1·435 (2)	C22–C23	1·361 (8)
S8–O10	1·433 (2)	C23–C24	1·376 (7)
S8–N11	1·651 (2)	C24–C25	1·397 (5)
N11–C12	1·379 (4)	C25–O29	1·344 (4)
C12–N13	1·322 (3)	C26–O27	1·293 (4)
C12–N17	1·341 (3)	C26–O28	1·245 (4)
N13–C14	1·336 (3)		
C14–C15	1·397 (4)		

C2–C1–C6	120·6 (3)	N13–C14–C15	121·7 (3)
C2–C1–S8	118·3 (2)	N13–C14–C18	116·6 (3)
C6–C1–S8	121·1 (2)	C15–C14–C18	121·7 (3)
C1–C2–C3	119·3 (3)	C14–C15–C16	117·7 (3)
C2–C3–C4	120·8 (3)	C15–C16–N17	120·1 (3)
C3–C4–C5	118·6 (3)	C15–C16–C19	122·2 (3)
C3–C4–N7	120·3 (3)	N17–C16–C19	117·8 (3)
C5–C4–N7	121·1 (3)	C12–N17–C16	117·9 (3)
C4–C5–C6	121·0 (3)	C21–C20–C25	119·9 (3)
C1–C6–C5	119·7 (3)	C21–C20–C26	120·1 (3)
C1–S8–O9	109·2 (1)	C25–C20–C26	120·0 (3)
C1–S8–O10	108·7 (1)	C20–C21–C22	119·2 (3)
C1–S8–N11	108·1 (1)	C21–C22–C23	120·7 (3)
O9–S8–O10	118·8 (1)	C22–C23–C24	121·1 (4)
O9–S8–N11	102·0 (1)	C23–C24–C25	119·8 (4)
O18–S8–N11	109·6 (1)	C20–C25–C24	119·2 (3)
S8–N11–C12	126·2 (2)	C20–C25–O29	122·8 (3)
N11–C12–N13	118·8 (2)	C24–C25–O29	117·8 (3)
N11–C12–N17	115·0 (2)	C20–C26–O27	117·5 (2)
N13–C12–N17	126·2 (2)	C20–C26–O28	120·5 (3)
C12–N13–C14	116·4 (2)	O27–C26–O28	122·0 (3)

structure and the hydrogen-bonding scheme are shown in Fig. 2. The average C–H and N–H distances are 0·96 (3) and 1·03 (4) Å, respectively. The bond lengths and angles of sulfadimidine in the complex with salicylic acid are very similar to those observed in the free molecule of sulfadimidine (Basak, Mazumdar & Chaudhuri, 1983; Tiwari, Haridas & Singh, 1984; Rambaud, Maury, Pauvert, Audran, Lasserre & Berge, 1985). This is in agreement with the molecular dimensions in sulfonamides found by Haridas & Singh (1987).

The two planar rings of sulfadimidine in the structure of the complex are inclined with respect to each other at 109·0 (4)°, whereas the corresponding value in free sulfadimidine is 102 (1)°. The plane of the benzene ring of salicylic acid is rotated with respect to the planes of the benzene and pyrimidine rings of sulfadimidine by 5·7 (3) and 108·7 (4)° respectively. The torsion angle about the S8–N11 bond is −66·4 (3)°, while in free sulfadimidine it is −84·9 (9)°. The other torsion angles (with the values for the free molecule in square brackets) are O9–S8–N11–C12 = 178·6 (3) [160·4 (9)], O10–S8–N11–C12 = 51·8 (3) [33·5 (10)], N11–S8–Cl–C6 = 97·6 (3) [130·6 (9)], N11–S8–Cl–C2 = −84·0 (3) [−55·0 (10)], O10–S8–Cl–C6 = −21·2 (3) [−11·0 (9)] and O10–S8–Cl–C2 = 157·2 (2)° [174·7 (9)°]. These values of torsion angles show that the conformation of sulfadimidine is different in its free state and in the complexed state with salicylic acid. The above observations on sulfadimidine suggest that the conformation of sulfonamides changes upon interaction with other molecules but its molecular dimensions remain constant. These results are in good agreement with the conclusions drawn on sulfonamides by Haridas & Singh (1987).

The molecular dimensions of salicylic acid in the complex are similar to those observed in free salicylic acid (Cochran, 1953; Sundaralingam & Jensen, 1965), many of its derivatives (Bertinotti, Giacomello & Liquori, 1954; Sasada, Takano & Kakudo, 1964; Wheatley, 1964; Mootz & Fayos, 1970) and its hydrogen-bonded complexes with caffeine (Shefter, 1968), with theophylline (Shefter, 1969) and with antipyrine (Singh & Vijayan, 1974). The hydroxyl group (O29) in salicylic acid is internally hydrogen-bonded to one of the O atoms (O28) of the carboxyl group; the length of this hydrogen bond is 2·537 (4) Å. The plane of the carboxyl group is inclined to the plane of the benzene ring by 6·5 (4)°, which is only slightly different from those observed in free salicylic acid, its derivatives and other hydrogen-bonded complexes.

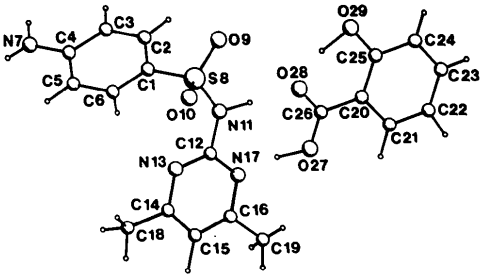


Fig. 1. A perspective view of the molecules with the numbering scheme.

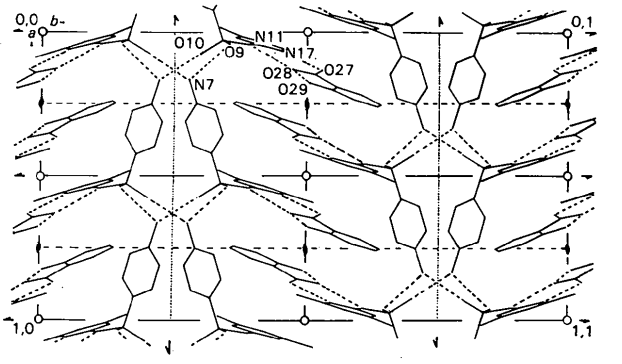


Fig. 2. The crystal structure as viewed along the *c* axis. The dashed lines indicate hydrogen bonds.

Molecular packing. The molecular association between sulfadimidine and salicylic acid is achieved through two intermolecular hydrogen bonds: (1) the imino N11 atom and the carboxyl O28 atom of length 2·719 (4) Å; and (2) the carboxyl O27 atom and the pyrimidine N17 atom of length 2·603 (3) Å. In addition to these, the amino N7 atom forms two hydrogen bonds with atoms O9 ($x-\frac{1}{2}$, y, $\frac{1}{2}-z$) and O10 ($x-\frac{1}{2}$, $\frac{1}{2}-y$, $-z$) of the symmetry-related molecules which are of lengths 2·945 (4) and 2·899 (4) Å, respectively. The structure contains a pattern of strong hydrogen bonds interlinking groups of four molecules of sulfadimidine and pairs of sulfadimidine and salicylic acid. It also contains distinct environments of van der Waals interactions involving six-membered rings of sulfadimidine and salicylic acid.

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Structure Cristalline de la Dihydroxyméthyl-3,6 Pyridazine

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Abstract. $C_6H_8N_2O_2$, 3,6-pyridazinedimethanol, $M_r = 140·1$, orthorhombic, $Pca2_1$, $a = 13·059$ (6), $b = 4·224$ (1), $c = 12·046$ (4) Å, $V = 664$ (1) Å^3, $Z = 4$, $D_m = 1·37$ (3), $D_x = 1·40$ g cm^{-3}, λ(Mo $K\bar{\alpha}$) = 0·7107 Å, $\mu = 1·16$ cm^{-1}, $F(000) = 296$, $T = 298$ K, $R = 0·030$, $wR = 0·029$ ($w = 1$) for 536 independent reflexions. The most characteristic feature of the molecular structure is the absence of symmetry, essentially at the hydroxyl group level; the distances of these groups to the ring plane are significantly different. This molecular distortion is at least partially due to the hydrogen-bond scheme.

Introduction. La préparation et l'étude structurale de la dihydroxyméthyl-3,6 pyridazine s'inscrit dans le cadre général de la synthèse et de la caractérisation de ligands polydentates azotés pouvant conduire à des complexes polymétalliques (Sueur, Lagrenee, Abraham & Brémard, 1987; Mernari, 1987). La rigidité de la liaison N—N nécessaire au positionnement futur des atomes métalliques est assurée par la structure du cycle pyridazine. La substitution de cet hétérocycle en position 3,6 par le groupement hydroxyméthyle permet sa transformation en dérivés carbonyles, précurseurs de nombreux dérivés azotés tétrachélatants tels que les oximes et les hydrazones. Nous avons modifié la synthèse de ce diol réalisée précédemment par Novitskii, Sadovaya & Baskina (1970) de façon à obtenir des quantités plus importantes de produit.

Partie expérimentale. Le diacétoxyméthyl-2,5 furanne, obtenu par acétylation du dihydroxyméthyl-2,5 furanne

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