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Structure of Calcium Tetrasulfinpyrazonate Dihydrate

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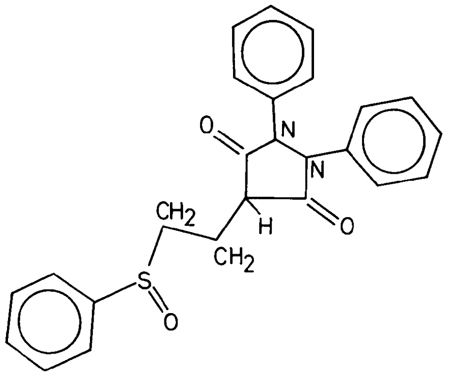
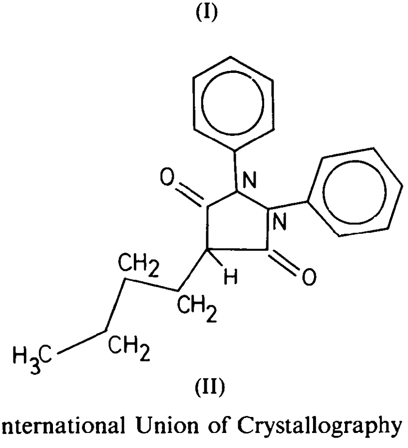
Abstract. Calcium tetrakis{1,2-diphenyl-4-[2-(phenylsulfinyl)ethyl]-3,5-pyrazolidinedionate} dihydrate, $Ca(C_{23}H_{19\cdot5}N_2O_3S)_4.2H_2O$, M_r = 1615·91, triclinic, $P\bar{1}$, a = 11·336 (2), b = 13·830 (4), c = 14·075 (11) Å, α = 76·00 (5), β = 85·82 (3), γ = 85·11 (2)°, V = 2130 (2) Å^3, Z = 1, D_m = 1·331 (5), D_x = 1·319 (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 0·27 mm^{-1}, μR = 0·03, F(000) = 886, T = 298 K, R = 0·085 for 4325 observed reflections with $I \geq 2\sigma(I)$. There are two partly deprotonated sulfinpyrazone molecules, one calcium and one water molecule in the asymmetric part of the unit cell. The conformations of the two crystallographically independent molecules are significantly different. The coordination geometry of the calcium cation is sixfold with octahedral symmetry. The distance of 2·450 (8) Å between the carbonyl O atoms of the crystallographically independent sulfinpyrazone molecules suggests strong hydrogen bonding between them. The crystal structure is stabilized by a network of intermolecular hydrogen bonds, van der Waals interactions and coordination bonds involving the calcium cation.

Introduction. Sulfinpyrazone (I) in which a phenylsulfinylethyl group replaces the butyl side chain of phenylbutazone (II) was synthesized by Pfister & Haflinger (1961). This compound increases the urinary uric acid excretion by inhibiting renal tubular reabsorption of uric acid and thereby reduces the plasma urate concentration and enhances the renal clearance of uric acid (Gutman, 1966). These properties of sulfinpyrazone have led to the intensive therapeutic applications of this compound as a uricosuric agent. The crystal structure of sulfinpyrazone has been reported earlier by Go & Kartha (1984). We have determined the structure of the calcium salt of sulfinpyrazone to elucidate its conformational and electronic properties so that its mechanism of action can be understood.



(I)



(II)

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Experimental. After repeated attempts crystals of the title compound were grown from a water–ethanol mixture (10/90 vol. %) and at a pH between 4·50 and 5·50. Very thin plate-like crystal of dimensions 0·25 × 0·19 × 0·06 mm was used for intensity data collection on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation in ω–2θ scan mode. Unit-cell parameters were refined with 25 reflections ($7 \leq \theta \leq 19°$). The density was measured by flotation. Standard reflections ($\bar{1}\bar{5}\bar{3}$; 420; $4\bar{1}\bar{1}$) showed intensity changes less than 4·6% during the data collection. All 7849 reflections (h: $-13 \rightarrow 13$, k: $-10 \rightarrow 16$, l: $0 \rightarrow 16$) with $2\theta \leq 50·3°$ were measured. 4325 reflections were considered observed [$I \geq 2\sigma(I)$]. Corrections for Lorentz and polarization effects were made but not for absorption ($\mu R = 0·03$). The structure was solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All the non-H atoms were refined anisotropically by full-matrix least-squares procedures by minimizing $\sum w|\Delta F|^2$ with *SHELX*76 (Sheldrick, 1976). The Ca atom was kept fixed at the special position (1·0, 0·0, 1·0). The H-atom positions were determined geometrically and were included in the final cycles of refinement as fixed parameters. The refinement converged at $R = 0·085$ for 4325 observed reflections with $wR = 0·085$ and $S = 3·02$. Weights $w = 1$ were used. Final max. and min. values of $\Delta\rho$ are $-0·14$ and $0·18$ e Å^{-3} respectively, and maximum shift/e.s.d. ratio 0·18. The scattering factors for the non-H atoms and the H atoms were taken from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) respectively. The atomic scattering factors for sulfur and calcium were taken from *International Tables for X-ray Crystallography* (1962). Final positional and equivalent isotropic thermal parameters for non-H atoms are listed in Table 1.*

Table 1. *Postional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$)

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

	x	y	z	U_{eq}
Ca	10000	0	10000	18 (1)
N(1)	11879 (6)	3471 (5)	6158 (4)	37 (4)
N(2)	11723 (6)	3510 (5)	5159 (4)	37 (4)
C(3)	11146 (7)	2646 (5)	5152 (5)	31 (5)
C(4)	10793 (7)	2172 (5)	6097 (5)	31 (5)
C(5)	11248 (7)	2667 (5)	6744 (5)	34 (5)
O(6)	11060 (5)	2440 (4)	4306 (4)	39 (4)
O(7)	11160 (6)	2514 (4)	7651 (4)	51 (4)
C(8)	10176 (7)	1220 (6)	6444 (6)	38 (5)
C(9)	8865 (7)	1354 (6)	6694 (5)	36 (5)
S(10)	8567 (2)	1696 (2)	7862 (1)	37 (1)
C(11)	6974 (7)	1755 (6)	7836 (6)	39 (5)
C(12)	6396 (9)	2689 (8)	7567 (9)	70 (9)
C(13)	5189 (10)	2782 (9)	7482 (10)	87 (11)
C(14)	4568 (9)	1934 (10)	7730 (9)	80 (10)
C(15)	5147 (9)	1020 (9)	8019 (8)	66 (8)
C(16)	6356 (8)	923 (8)	8079 (6)	53 (7)
O(17)	8922 (5)	763 (4)	8629 (4)	45 (4)
C(18)	11881 (7)	4432 (6)	6395 (6)	36 (5)
C(19)	12234 (8)	4425 (6)	7336 (6)	45 (6)
C(20)	12263 (9)	5364 (8)	7549 (7)	62 (8)
C(21)	11921 (9)	6246 (7)	6904 (8)	61 (8)
C(22)	11595 (9)	6218 (7)	5997 (8)	59 (7)
C(23)	11532 (8)	5312 (6)	5743 (7)	46 (6)
C(24)	12709 (7)	3829 (6)	4468 (6)	38 (5)
C(25)	13847 (8)	3760 (7)	4777 (7)	49 (6)
C(26)	14754 (9)	4084 (8)	4092 (9)	72 (9)
C(27)	14505 (10)	4450 (8)	3105 (8)	68 (8)
C(28)	13375 (10)	4535 (7)	2820 (7)	59 (7)
C(29)	12448 (8)	4233 (6)	3501 (6)	40 (6)
N(1′)	7981 (5)	985 (4)	12287 (4)	30 (4)
N(2′)	8037 (5)	1120 (4)	13243 (4)	29 (4)
C(3′)	9205 (7)	1294 (5)	13370 (5)	31 (5)
C(4′)	9865 (7)	1365 (7)	12480 (5)	30 (5)
C(5′)	9119 (6)	1155 (5)	11804 (5)	27 (5)
O(6′)	9520 (5)	1334 (4)	14204 (4)	38 (4)
O(7′)	9305 (5)	1137 (4)	10924 (4)	36 (4)
C(8′)	11163 (7)	1518 (5)	12320 (6)	34 (5)
C(9′)	11435 (8)	2636 (6)	12026 (6)	42 (6)
S(10′)	11024 (2)	3176 (2)	10788 (2)	46 (2)
C(11′)	11502 (9)	4418 (7)	10706 (6)	52 (6)
C(12′)	10716 (11)	5066 (7)	11120 (8)	69 (8)
C(13′)	11003 (14)	6054 (9)	11030 (10)	90 (11)
C(14′)	12056 (16)	6364 (10)	10505 (9)	98 (12)
C(15′)	12826 (14)	5700 (11)	10117 (8)	95 (11)
C(16′)	12556 (11)	4685 (8)	10208 (7)	70 (8)
O(17′)	11909 (6)	2721 (5)	10138 (4)	64 (5)
C(18′)	6914 (7)	1365 (6)	11804 (5)	35 (5)
C(19′)	6685 (8)	1072 (7)	10957 (6)	50 (6)
C(20′)	5642 (9)	1441 (8)	10486 (8)	64 (8)
C(21′)	4827 (8)	2052 (8)	10877 (8)	68 (8)
C(22′)	5035 (8)	2336 (8)	11731 (7)	58 (7)
C(23′)	6075 (7)	1993 (6)	12181 (6)	45 (6)
C(24′)	7355 (7)	465 (6)	14002 (5)	36 (5)
C(25′)	6956 (7)	−399 (6)	13854 (7)	50 (6)
C(26′)	6350 (10)	−1033 (9)	14587 (9)	70 (9)
C(27′)	6189 (10)	−844 (11)	15485 (10)	88 (10)
C(28′)	6527 (10)	57 (13)	15663 (7)	96 (11)
C(29′)	7125 (8)	753 (10)	14891 (6)	73 (8)
O*W*(30)	11463 (5)	1151 (4)	9353 (4)	41 (4)

Discussion. The asymmetric unit contains two molecules of sulfinpyrazone, one water molecule and a Ca atom at the symmetry centre (1,0,1). The numbering scheme for the molecules of sulfinpyrazone (hereafter referred to as molecules *A* and *B*) is given in Fig. 1. The bond lengths and angles of molecules *A* and *B*, as seen from Table 2, are very similar. The presence of Ca^{2+} in the structure deprotonates the C atoms C(4) and C(4′) in the sulfinpyrazone molecules. As a result of the deprotonation, the bond lengths in the pyrazolidinedione moiety have acquired a partial double-bond character due to delocalization of the extra electron at the C(4) and C(4′) atoms.

The short distance of 2·450 (8) Å between the O(6) and O(6′) atoms suggests that a strong symmetrical hydrogen bond is present between O atoms O(6) and O(6′) in the present structure (Pauling, 1960; Godychi, Rundle, Voter & Banks, 1951; Godychi & Rundle, 1953). Since there are two molecules of sulfinpyrazone in the asymmetric unit, it appears that one proton is symmetrically bonded to both O(6) and O(6′) atoms to produce a strong symmetric

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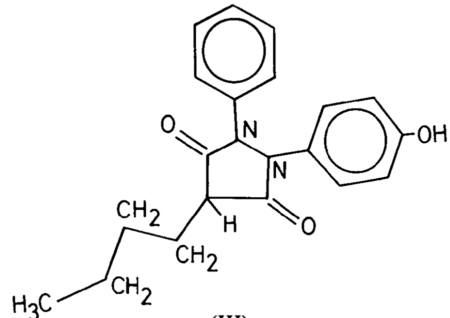
* Lists of observed and calculated structure factors, anisotropic thermal parameters of non-H atoms, fractional coordinates and isotropic temperature factors of H atoms and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52610 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

hydrogen bond whereas the other proton is lost to leave a partial (−0·5) charge on the molecules. There are four sulfinpyrazone molecules in the unit cell and one calcium ion thus balancing the charges in the structure. The distances C(3)—O(6) and C(3′)—O(6′) involving the protonated carbonyl O atoms are 1·302 (10) and 1·267 (10) Å in molecules *A* and *B* respectively. The other C(5)—O(7) and C(5′)—O(7′) distances are 1·241 (9) and 1·247 (9) Å respectively. The corresponding distances in free sulfinpyrazone are 1·209 (2) and 1·211 (3) Å (Go & Kartha, 1984). The exocyclic angles about the C(3) and C(5) atoms of the pyrazolidinedione moiety of molecule *A* are 132·8 (8), 117·3 (7)° and 131·4 (8), 121·4 (7)° respectively and the corresponding exocyclic angles about C(3′) and C(5′) in molecule *B* are 130·4 (7), 120·5 (7)° and 131·1 (7), 121·1 (7)° respectively while the corresponding values in the molecular compound are 128·5 (3), 123·6 (3)° and 127·6 (3), 124·2 (3)°. The values of the corresponding exocyclic angles in the deprotonated form of phenylbutazone when it is complexed with piperazine (Singh & Vijayan, 1977) are 130·9 (6), 120·1 (6)° and 132·3 (6), 120·0 (6)° respectively. However, in the protonated form of phenylbutazone (Singh & Vijayan, 1977) and oxyphenbutazone (III) (Krishna Murthy & Vijayan, 1981), the values of such exocyclic angles are 127 (2), 123 (2)° and 128 (2), 125 (2)° respectively.



(III)

It might be mentioned here that the deprotonation changes the states of C(4) and C(4′) from sp^3 to sp^2 hybridization thus resulting in the increased planarity of the pyrazolidinedione moiety. This enhances the steric hindrance due to the bulky phenylsulfinylethyl group at the C(4) and C(4′) atoms. As a result, the values of the exocyclic C—C—O angles facing the phenylsulfinylethyl group are significantly larger than their counterparts.

The N atoms in the pyrazolidine ring exist in the pyramidal configuration. The N(1), N(2), N(1′) and N(2′) atoms deviate from the planes of the three respective surrounding atoms by −0·312 (9), 0·331 (9), −0·325 (9) and 0·310 (9) Å respectively. The sums of the angles about N(1), N(2), N(1′) and N(2′) are 346·4 (6), 344·1 (6), 345·4 (6) and 345·2 (6)° respectively which also indicate the pyramidal nature of these N atoms.

Table 2. *Bond lengths* (Å) *and angles* (°) *in calcium tetrasulfinpyrazonate dihydrate*

N(1)—N(2)	1·417 (9)	N(1′)—N(2′)	1·409 (9)
N(1)—C(5)	1·427 (9)	N(1′)—C(5′)	1·424 (9)
N(1)—C(18)	1·447 (11)	N(1′)—C(18′)	1·428 (10)
N(2)—C(3)	1·414 (11)	N(2′)—C(3′)	1·397 (10)
N(2)—C(24)	1·452 (10)	N(2′)—C(24′)	1·446 (9)
C(3)—C(4)	1·379 (10)	C(3′)—C(4′)	1·398 (10)
C(3)—O(6)	1·302 (10)	C(3′)—O(6′)	1·267 (10)
C(4)—C(5)	1·412 (12)	C(4′)—C(5′)	1·414 (11)
C(4)—C(8)	1·502 (11)	C(4′)—C(8′)	1·497 (11)
C(5)—O(7)	1·241 (9)	C(5′)—O(7′)	1·247 (9)
C(8)—C(9)	1·508 (11)	C(8′)—C(9′)	1·553 (11)
C(9)—S(10)	1·819 (8)	C(9′)—S(10′)	1·801 (8)
S(10)—C(11)	1·803 (8)	S(10′)—C(11′)	1·819 (10)
S(10)—O(17)	1·514 (5)	S(10′)—O(17′)	1·508 (7)
C(11)—C(12)	1·377 (13)	C(11′)—C(12′)	1·407 (15)
C(11)—C(16)	1·358 (13)	C(11′)—C(16′)	1·372 (15)
C(12)—C(13)	1·375 (16)	C(12′)—C(13′)	1·404 (17)
C(13)—C(14)	1·378 (18)	C(13′)—C(14′)	1·400 (22)
C(14)—C(15)	1·358 (16)	C(14′)—C(15′)	1·393 (21)
C(15)—C(16)	1·372 (14)	C(15′)—C(16′)	1·435 (19)
C(18)—C(19)	1·409 (13)	C(18′)—C(19′)	1·397 (13)
C(18)—C(23)	1·382 (10)	C(18′)—C(23′)	1·396 (12)
C(19)—C(20)	1·405 (15)	C(19′)—C(20′)	1·395 (13)
C(20)—C(21)	1·377 (13)	C(20′)—C(21′)	1·374 (16)
C(21)—C(22)	1·365 (17)	C(21′)—C(22′)	1·392 (17)
C(22)—C(23)	1·392 (14)	C(22′)—C(23′)	1·374 (12)
C(24)—C(25)	1·379 (12)	C(24′)—C(25′)	1·380 (13)
C(24)—C(29)	1·384 (11)	C(24′)—C(29′)	1·401 (14)
C(25)—C(26)	1·384 (13)	C(25′)—C(26′)	1·366 (14)
C(26)—C(27)	1·399 (16)	C(26′)—C(27′)	1·348 (19)
C(27)—C(28)	1·357 (16)	C(27′)—C(28′)	1·418 (24)
C(28)—C(29)	1·389 (13)	C(28′)—C(29′)	1·437 (16)
Ca—O(17)	2·339 (5)	Ca—O(7′)	2·326 (6)
Ca—O*W*(30)	2·375 (5)		
C(5)—N(1)—C(18)	123·2 (7)	C(5′)—N(1′)—C(18′)	121·7 (6)
N(2)—N(1)—C(18)	115·1 (6)	N(2′)—N(1′)—C(18′)	116·3 (6)
N(2)—N(1)—C(5)	108·1 (6)	N(2′)—N(1′)—C(5′)	107·4 (6)
N(1)—N(2)—C(24)	116·8 (6)	N(1′)—N(2′)—C(24′)	115·8 (6)
N(1)—N(2)—C(3)	106·1 (6)	N(1′)—N(2′)—C(3′)	108·0 (6)
C(3)—N(2)—C(24)	121·2 (7)	C(3′)—N(2′)—C(24′)	121·4 (6)
N(2)—C(3)—O(6)	117·3 (7)	N(2′)—C(3′)—O(6′)	120·5 (7)
N(2)—C(3)—C(4)	109·9 (7)	N(2′)—C(3′)—C(4′)	109·0 (7)
C(4)—C(3)—O(6)	132·8 (8)	C(4′)—C(3′)—O(6′)	130·4 (7)
C(3)—C(4)—C(8)	128·6 (7)	C(3′)—C(4′)—C(8′)	125·5 (7)
C(3)—C(4)—C(5)	108·0 (7)	C(3′)—C(4′)—C(5′)	107·5 (7)
C(5)—C(4)—C(8)	122·9 (7)	C(5′)—C(4′)—C(8′)	126·7 (7)
N(1)—C(5)—C(4)	107·2 (7)	N(1′)—C(5′)—C(4′)	107·8 (6)
C(4)—C(5)—O(7)	131·4 (8)	C(4′)—C(5′)—O(7′)	131·1 (7)
N(1)—C(5)—O(7)	121·4 (7)	N(1′)—C(5′)—O(7′)	121·1 (7)
C(4)—C(8)—C(9)	115·2 (7)	C(4′)—C(8′)—C(9′)	113·2 (7)
C(8)—C(9)—S(10)	112·1 (6)	C(8′)—C(9′)—S(10′)	109·6 (6)
C(9)—S(10)—O(17)	105·0 (4)	C(9′)—S(10′)—O(17′)	106·1 (4)
C(9)—S(10)—C(11)	95·7 (4)	C(9′)—S(10′)—C(11′)	96·8 (4)
C(11)—S(10)—O(17)	106·6 (4)	C(11′)—S(10′)—O(17′)	105·3 (5)
S(10)—C(11)—C(16)	122·2 (7)	S(10′)—C(11′)—C(16′)	119·2 (8)
S(10)—C(11)—C(12)	117·2 (7)	S(10′)—C(11′)—C(12′)	116·7 (8)
C(12)—C(11)—C(16)	120·7 (9)	C(12′)—C(11′)—C(16′)	124·1 (10)
C(11)—C(12)—C(13)	120·0 (11)	C(11′)—C(12′)—C(13′)	119·4 (11)
C(12)—C(13)—C(14)	118·9 (11)	C(12′)—C(13′)—C(14′)	118·3 (12)
C(13)—C(14)—C(15)	120·4 (11)	C(13′)—C(14′)—C(15′)	121·0 (14)
C(14)—C(15)—C(16)	120·8 (11)	C(14′)—C(15′)—C(16′)	121·7 (13)
C(11)—C(16)—C(15)	119·2 (10)	C(11′)—C(16′)—C(15′)	115·6 (11)
N(1)—C(18)—C(23)	122·0 (8)	N(1′)—C(18′)—C(23′)	121·4 (7)
N(1)—C(18)—C(19)	116·5 (7)	N(1′)—C(18′)—C(19′)	119·3 (8)
C(19)—C(18)—C(23)	121·5 (8)	C(19′)—C(18′)—C(23′)	119·3 (8)
C(18)—C(19)—C(20)	116·0 (8)	C(18′)—C(19′)—C(20′)	119·3 (9)
C(19)—C(20)—C(21)	123·0 (10)	C(19′)—C(20′)—C(21′)	121·1 (9)
C(20)—C(21)—C(22)	119·0 (10)	C(20′)—C(21′)—C(22′)	121·1 (10)
C(21)—C(22)—C(23)	120·9 (10)	C(21′)—C(22′)—C(23′)	118·8 (10)
C(18)—C(23)—C(22)	119·4 (9)	C(18′)—C(23′)—C(22′)	121·3 (9)
N(2)—C(24)—C(29)	117·1 (7)	N(2′)—C(24′)—C(29′)	116·7 (8)
N(2)—C(24)—C(25)	120·9 (7)	N(2)—C(24′)—C(25′)	121·3 (7)
C(25)—C(24)—C(29)	122·0 (9)	C(25′)—C(24′)—C(29′)	122·0 (8)
C(24)—C(25)—C(26)	118·7 (9)	C(24′)—C(25′)—C(26′)	121·0 (9)
C(25)—C(26)—C(27)	119·6 (10)	C(25′)—C(26′)—C(27′)	119·9 (11)
C(26)—C(27)—C(28)	120·7 (10)	C(26′)—C(27′)—C(28′)	121·3 (12)
C(27)—C(28)—C(29)	120·5 (10)	C(27′)—C(28′)—C(29′)	119·5 (11)
C(24)—C(29)—C(28)	118·4 (8)	C(24′)—C(29′)—C(28′)	116·0 (11)
O*W*(30)—Ca—O(17)	87·3 (2)	O(17)—Ca—O(7′)	95·6 (2)
		O*W*(30)—Ca—O(7′)	84·9 (2)

The six phenyl rings in the structure are all essentially planar. The interplanar and torsion angles which define the conformations of the molecules *A* and *B* are listed in Table 3. As seen from Table 3, the conformations of the two crystallographically independent molecules are substantially different. The phenyl rings attached to the pyrazolidine ring in the calcium salt of sulfinpyrazone are inclined with respect to the five-membered pyrazolidine ring at 40·8 and 52·1° in molecule *A* and at 44·7 and 49·3° in molecule *B* while the corresponding values in free sulfinpyrazone are 46·3 and 69·6° respectively. The corresponding angles in free phenylbutazone are 40 and 66° in molecule *A* and 42 and 61° in molecule *B* while in the deprotonated form of phenylbutazone, these values are 41·4 and 42·0° respectively. The corresponding values in oxyphenbutazone are 53 (2) and 64 (2)° respectively.

Calcium coordination. Calcium is octahedrally coordinated by atoms O(17), O(7′) and O*W*(30) and their centrosymmetrical counterparts. The Ca—O distances in the present structure vary from 2·326 (6) to 2·375 (5) Å. The Ca—O distances in coordination with sterically unhindered small molecules vary from 2·30 to 2·50 Å whereas most contact distances in systems involving interaction of calcium with large molecules and various complexes of sugars and sugar-related molecules approach 2·70 Å (Cook & Bugg, 1976; Singh, Reinhardt & Poonia, 1984; Brown, 1988). It seems that the Ca—O distances in the present case are very short and indicate that the binding molecules are flexible.

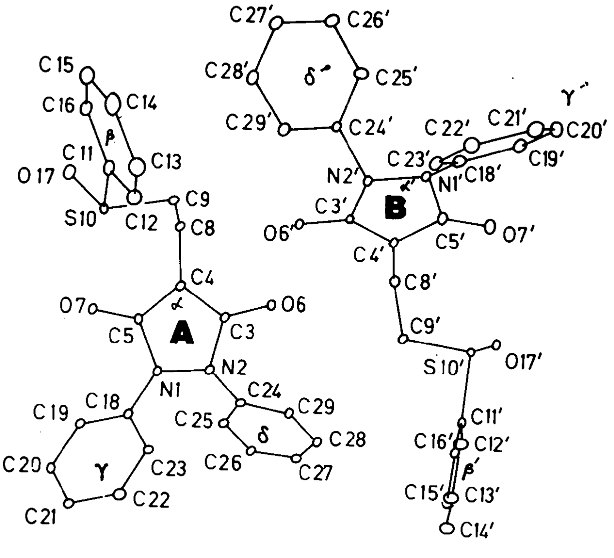


Fig. 1. Numbering scheme and conformations of molecules *A* and *B*.

Table 3. *Angles (°) between the planes of various rings and some torsion angles (°)*

Ring 1	Ring 2	Molecule *A*	Molecule *B*	Sulfinpyrazone*
α	β	100·8	64·4	158·2
α	γ	139·2	44·7	46·1
α	δ	127·9	49·3	110·4
β	γ	67·3	73·9	112·5
β	δ	62·7	43·3	65·6
γ	δ	82·8	87·6	86·4
O(17)—S(10)—C(11)—C(16)		−28·2 (9)	−6·6 (10)	0·3 (4)
C(8)—C(9)—S(10)—C(11)		−179·6 (6)	−178·2 (6)	54·5 (3)
C(4)—C(8)—C(9)—S(10)		−75·5 (8)	−72·2 (8)	155·1 (2)
C(5)—C(4)—C(8)—C(9)		86·1 (10)	98·6 (9)	51·6 (3)
C(3)—C(4)—C(8)—C(9)		−102·3 (10)	−89·1 (10)	−68·4 (3)
N(1)—N(2)—C(24)—C(29)		−159·0 (7)	−162·8 (8)	−164·8 (3)
N(2)—N(1)—C(18)—C(19)		−169·5 (9)	−166·0 (7)	−135·6 (3)
C(18)—N(1)—N(2)—C(24)		71·3 (9)	75·5 (8)	68·2 (3)
N(1)—N(2)—C(3)—C(4)		8·8 (9)	5·5 (8)	6·9 (3)
N(2)—C(3)—C(4)—C(5)		−6·0 (9)	−4·5 (9)	−4·4 (3)
C(3)—C(4)—C(5)—N(1)		0·8 (9)	1·8 (9)	0·3 (3)
C(4)—C(5)—N(1)—N(2)		4·7 (9)	1·6 (8)	3·8 (3)
C(5)—N(1)—N(2)—C(3)		−8·1 (8)	−4·3 (8)	−6·8 (3)

* Go & Khartha (1984).

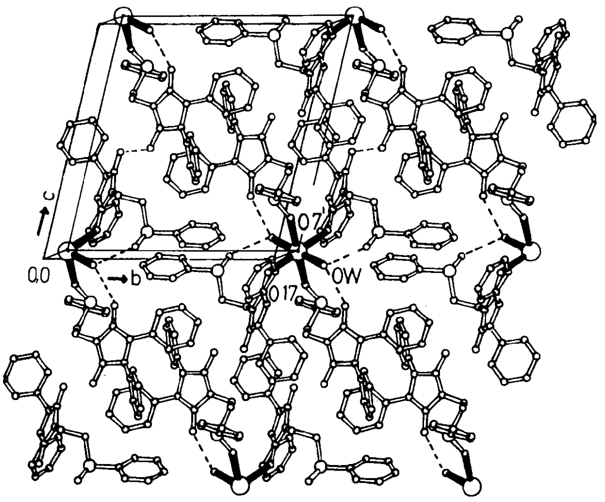


Fig. 2. Molecular packing and coordination geometry as seen down the *a* axis. The hydrogen bonds are indicated by dashed lines.

Crystal packing and hydrogen bonding. The crystal structure of sulfinpyrazone as seen down the *a* axis is illustrated in Fig. 2. As discussed above, molecules *A* and *B* are linked through a very strong hydrogen bond of distance 2·45 (8) Å between the protonated O(6) and O(6′) atoms. The water molecule O*W*(30) participates as a donor in two hydrogen bonds with the carbonyl O atoms O(7) and sulfoxide O atom O(17′) at a distance of 2·690 (9) and 2·761 (10) Å respectively. The carbonyl O atom O(7′), the sulfoxide O atom O(17) and the water O atom O*W*(30) are involved in the strong coordination linkages with the calcium ion. There are significant van der Waals intermolecular interactions thus leading to very stable packing in the crystal.

In summary, the results of this analysis suggest the possible mode of action of sulfinpyrazone. The presence of Ca^{2+} deprotonates sulfinpyrazone at the C(4) and C(4′) positions providing the capability of forming strong hydrogen bonds between O(6) and O(6′). In addition to this, the coordination with calcium through sulfinyl O atoms converts this compound into an active species. The two crystallographically independent molecules exist in two significantly different molecular conformations, indicating that the molecules are flexible and can easily undergo a conformational change as a result of the variation of the intermolecular interactions. The inherent conformational flexibility and cation-induced deprotonated state of sulfinpyrazone make this molecule a suitable species for ligand action. This property of sulfinpyrazone may be responsible for its uricosuric effect.

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The Structure of Cyclonebularine Derivatives

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Abstract. (I) 7,8-Dihydro-2′,3′-*O*-isopropylidene-N^7-(*p*-toluenesulfonyl)-8(*R*),5′-*O*-cyclonebularine, $C_{20}H_{22}N_4O_6S$, $M_r = 446{\cdot}5$, triclinic, $P1$, $a = 11{\cdot}069\ (1)$, $b = 13{\cdot}087\ (1)$, $c = 8{\cdot}741\ (5)$ Å, $\alpha = 99{\cdot}31\ (1)$, $\beta = 102{\cdot}16\ (2)$, $\gamma = 109{\cdot}81\ (1)°$, $U = 1126{\cdot}6\ (7)$ Å^3, $Z = 2$, $D_x = 1{\cdot}316$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}5405$ Å, $\mu = 1{\cdot}619$ mm^{-1}, $F(000) = 468$, $T = 293$ K, final $R = 0{\cdot}035$ for 3673 reflexions. (II) N^7-Benzoyl-7,8-dihydro-2′,3′-*O*-isopropylidene-8(*R*),5′-*O*-cyclonebularine, $C_{20}H_{20}N_4O_5$, $M_r = 396{\cdot}4$, monoclinic, $P2_1$, $a = 11{\cdot}880\ (1)$, $b = 7{\cdot}603\ (1)$, $c = 10{\cdot}626\ (1)$ Å, $\beta = 102{\cdot}16\ (2)°$, $U = 958{\cdot}9\ (2)$ Å^3, $Z = 2$, $D_x = 1{\cdot}373$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}5405$ Å, $\mu = 0{\cdot}850$ mm^{-1}, $F(000) = 416$, $T = 293$ K, final $R = 0{\cdot}058$ for 1498 reflexions. (III) N^7-Acetyl-7,8-dihydro-2′,3′-*O*-isopropylidene-8(*R*),5′-*O*-cyclonebularine, $C_{15}H_{18}N_4O_5$, $M_r = 334{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 10{\cdot}194\ (1)$, $b = 18{\cdot}389\ (1)$, $c = 8{\cdot}400\ (4)$ Å, $U = 1574{\cdot}6\ (9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}410$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}5405$ Å, $\mu = 0{\cdot}918$ mm^{-1}, $F(000) = 704$, $T = 293$ K, final $R = 0{\cdot}043$ for 1337 reflexions. There is substantial difference in the conformations of the *p*-toluoyl groups in the two independent molecules of (I). The 8(*R*)-configuration is observed in all three compounds.

Introduction. In the course of our work on the synthetic chemistry of nucleosides, we obtained a novel type of nebularine (9-β-D-ribofuranosylpurine): N(7)-substituted [*p*-toluoyl (I), benzoyl (II) and acetyl (III)] 7,8-dihydro-8,5′-cyclonebularines