ately strong hydrogen bonds, two with the pyrrole nitrogen atoms of the imidazole rings and one with an oxygen atom O(4) (see Fig. 2 for distances). Variations in the N–O distances as a function of the strength of the hydrogen bonding in which the oxygen atom is involved have been observed in the study of other complexes. For example, in the structure of $Cu(NO_3)_2Pz$ (Pz = pyrazine, $C_4N_2H_4$) (Santoro, Mighell & Reimann, 1970), the three independent N–O distances range from 1·21 to 1·29 Å and in the structure of nitratobis(dipyridine)-cobalt(III) hydroxide nitrate tetrahydrate (Reimann, Zocchi, Mighell & Santoro, 1971), the four independent distances range from 1·19 to 1·31 Å.

The computer calculations were made with local programs, with the *Program System for X-ray Crystallography* (1967) developed at the University of Maryland in collaboration with the National Bureau of Standards and the Geological Survey, and with C.K. Johnson's *ORTEP* plotting program.

Thanks are due to Dr C. W. Reimann for suggesting the problem and for the preparation of the crystals.

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The Crystal and Molecular Structure of Portulal *p*-Bromophenylsulphonylhydrazone

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The crystal structure of portulal *p*-bromophenylsulphonylhydrazone has been determined by a three-dimensional X-ray analysis. The stereochemistry and absolute configuration of portulal, a naturally occurring diterpene isolated from *Portulaca grandiflora* as a plant growth regulator, has thus been established. The crystals are orthorhombic, space group $P2_12_12_1$, with four molecules of $C_{26}H_{37}O_5N_2SBr$ in a unit cell of dimensions, $a = 10{\cdot}68$, $b = 36{\cdot}98$ and $c = 6{\cdot}67$ Å. The structure has been refined by least-squares methods to a final R value of 0·123 for 2089 observed reflexions collected by the photographic method. Portulal belongs to a new type of bicyclic diterpene containing a perhydroazulene nucleus.

Introduction

Portulal, $C_{20}H_{32}O_4$, was first isolated by Mitsuhashi & Shibaoka (1965) from leaves of *Portulaca grandiflora Hook.* as a plant growth regulator. At the initial stage, it was thought to be an inhibitor of plant growth induced by indoleacetic acid. Subsequent studies, however, revealed that it specifically accelerates adventitious root formation of plant cuttings such as *Raphanus*, *Phaseolus* and *Azukia*.

In an attempt to establish the molecular structure and to extend the physiological studies of portulal, X-ray analysis of its *p*-bromophenylsulphonylhydrazone was carried out.

Experimental

Treatment of portulal (168 mg) with an equivalent amount of *p*-bromophenylsulphonylhydrazine (128 mg) in dry methanol at room temperature overnight gave the corresponding hydrazone. Recrystallization from methanol yielded well-formed transparent plates. Elementary analysis gave: C, 54·57; H, 6·51; N, 4·92%. $C_{26}H_{37}O_5N_2SBr$ requires C, 54·83; H, 6·55; N, 4·92%.

Oscillation and Weissenberg photographs were taken with crystals mounted along the c and a axes respectively with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å). The unit-cell dimensions were determined from the two zero-layer Weissenberg photographs, on which the powder pat-

Table 1. *Atomic parameters and their e.s.d.'s*

Anisotropic temperature factors in the expression, $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})\}$, are multiplied by 10^5. The estimated standard deviations are given in parentheses.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	1·0071 (2)	0·1583 (1)	0·2406 (6)	705 (18)	56 (2)	3804 (103)	−123 (12)	−120 (99)	486 (24)
S	0·7552 (4)	0·0433 (1)	0·8321 (9)	359 (33)	28 (3)	1322 (198)	40 (18)	−344 (146)	90 (38)
O(1)	0·7236 (14)	0·0609 (4)	1·0185 (25)	938 (169)	61 (12)	573 (540)	−132 (77)	326 (510)	−86 (125)
O(2)	0·8327 (11)	0·0102 (3)	0·8372 (26)	374 (109)	14 (8)	3105 (629)	235 (52)	−532 (457)	125 (116)
O(3)	0·5846 (12)	0·2875 (3)	1·2451 (32)	481 (116)	42 (10)	3282 (662)	53 (57)	229 (568)	−261 (155)
O(4)	0·8443 (13)	0·2328 (4)	0·6744 (28)	562 (130)	47 (11)	2961 (722)	50 (63)	679 (514)	480 (142)
O(5)	0·2803 (12)	0·2004 (3)	0·4975 (26)	517 (130)	29 (9)	1704 (538)	112 (56)	412 (446)	28 (113)
N(1)	0·6263 (12)	0·0306 (3)	0·7224 (29)	295 (111)	17 (9)	1280 (614)	100 (52)	−429 (489)	214 (130)
N(2)	0·5492 (12)	0·0613 (4)	0·6778 (29)	265 (114)	16 (9)	2306 (743)	144 (56)	333 (491)	203 (136)
C(1′)	0·9339 (18)	0·1244 (5)	0·4281 (37)	395 (163)	25 (13)	1757 (875)	−131 (78)	−240 (612)	144 (164)
C(2′)	0·9147 (21)	0·1334 (5)	0·6133 (38)	842 (221)	29 (14)	1045 (834)	−187 (93)	841 (702)	−69 (165)
C(3′)	0·8579 (18)	0·1096 (5)	0·7473 (43)	588 (175)	39 (14)	1672 (842)	−53 (82)	−51 (750)	−283 (191)
C(4′)	0·8277 (17)	0·0740 (4)	0·6627 (33)	430 (158)	15 (11)	975 (782)	−69 (70)	−827 (576)	55 (140)
C(5′)	0·8505 (21)	0·0659 (5)	0·4701 (36)	954 (240)	34 (14)	183 (801)	−162 (98)	247 (716)	54 (159)
C(6′)	0·9054 (21)	0·0892 (6)	0·3451 (38)	886 (230)	61 (18)	1251 (914)	−272 (117)	89 (723)	−274 (210)
C(1)	0·2573 (17)	0·1267 (4)	0·6942 (32)	465 (154)	34 (12)	402 (734)	−107 (79)	447 (613)	13 (145)
C(2)	0·2128 (20)	0·0937 (5)	0·8233 (38)	820 (222)	45 (15)	1672 (944)	−158 (99)	388 (719)	71 (195)
C(3)	0·1686 (19)	0·0605 (5)	0·6950 (39)	720 (193)	32 (13)	1437 (932)	−47 (88)	−537 (718)	240 (174)
C(4)	0·1904 (18)	0·0527 (4)	0·5102 (39)	477 (174)	22 (13)	1477 (823)	−85 (77)	−482 (648)	−10 (154)
C(5)	0·2753 (18)	0·0739 (5)	0·3687 (39)	400 (175)	51 (16)	1777 (885)	2 (86)	−625 (642)	−76 (185)
C(6)	0·3990 (16)	0·0890 (5)	0·4532 (33)	448 (160)	20 (12)	793 (764)	132 (79)	−438 (544)	−69 (153)
C(7)	0·4772 (17)	0·1056 (4)	0·2805 (36)	492 (176)	29 (11)	1088 (753)	−6 (73)	−19 (657)	−155 (158)
C(8)	0·5535 (17)	0·1353 (5)	0·3815 (34)	403 (152)	33 (13)	342 (722)	34 (76)	537 (545)	210 (148)
C(9)	0·4501 (15)	0·1544 (4)	0·5147 (32)	273 (133)	26 (12)	268 (673)	−23 (70)	15 (486)	74 (144)
C(10)	0·3860 (16)	0·1205 (4)	0·6133 (34)	411 (153)	5 (10)	742 (703)	−93 (66)	−11 (539)	−116 (129)
C(11)	0·5079 (19)	0·1770 (4)	0·6840 (31)	578 (162)	20 (11)	828 (759)	−96 (83)	−325 (734)	−3 (133)
C(12)	0·5581 (19)	0·2156 (4)	0·6248 (40)	549 (177)	14 (12)	2479 (926)	−80 (77)	−236 (703)	−25 (165)
C(13)	0·6360 (16)	0·2300 (4)	0·8021 (35)	333 (138)	32 (13)	793 (811)	−6 (71)	290 (557)	127 (156)
C(14)	0·5914 (18)	0·2547 (5)	0·9333 (38)	386 (169)	31 (14)	1883 (973)	11 (79)	−435 (624)	−118 (175)
C(15)	0·6667 (20)	0·2718 (6)	1·0923 (45)	524 (200)	76 (20)	2647 (1058)	82 (111)	90 (768)	−451 (234)
C(16)	0·7677 (17)	0·2153 (6)	0·8237 (37)	340 (153)	47 (14)	1538 (867)	12 (80)	420 (602)	−34 (173)
C(17)	0·6283 (19)	0·1587 (6)	0·2172 (41)	754 (194)	64 (17)	1246 (874)	86 (106)	538 (739)	378 (221)
C(18)	0·4743 (16)	0·0570 (4)	0·5381 (37)	283 (160)	22 (12)	1831 (825)	61 (71)	551 (556)	205 (154)
C(19)	0·1369 (22)	0·0182 (5)	0·4131 (50)	753 (229)	33 (16)	4899 (1263)	−210 (102)	−375 (918)	−724 (229)
C(20)	0·3623 (17)	0·1774 (5)	0·3787 (37)	397 (155)	25 (12)	1178 (768)	182 (75)	−216 (574)	62 (152)

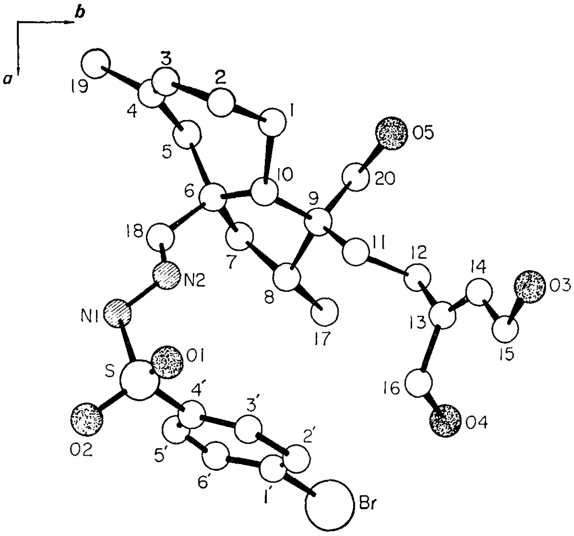


Fig. 1. The molecular structure of portulal *p*-bromophenylsulphonylhydrazone and the numbering scheme.

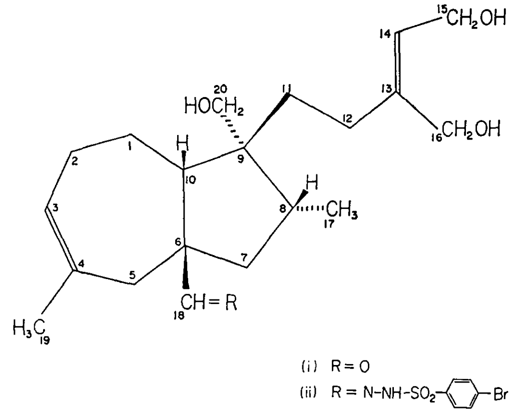


Fig. 2. The absolute stereochemistry of (i) portulal and (ii) portulal *p*-bromophenylsulphonylhydrazone.

terns of copper were superposed for calibration. The space group was uniquely determined from the systematic absences ($h00$ for $h=2n+1$, $0k0$ for $k=2n+1$ and $00l$ for $l=2n+1$). The crystal data are: $C_{26}H_{37}O_5N_2SBr$, M.W. 569·5, m.p. 170°C. Orthorhombic, $a=10·68\pm0·01$, $b=36·98\pm0·01$ and $c=6·67\pm0·01$ Å. $U=2634$ Å^3. $D_m=1·439$ g.cm^{-3} (by flotation in n-hexane-chloroform), $Z=4$, $D_x=1·435$ g.cm^{-3}. F(000) = 1044. Space group $P2_12_12_1$ (D_2^4-No. 19). Linear absorption coefficient for Cu $K\alpha$ ($\lambda=1·452$ Å), $\mu=39·0$ cm^{-1}. Two specimens used for the c- and a-axis photographs were cut to almost the same size, having a cross section of 0·2 × 0·3 mm. Three-dimensional intensity data were collected around the c and a axes with an equi-inclination Weissenberg goniometer, using the multiple film technique. Layers from $hk0$ to $hk4$ and $0kl$ were recorded. The data were put on a relative scale by using 200 $0kl$ reflexions, common to both axes. The absolute scale of each layer was obtained at the final stage by correlation with the calculated values. The data were converted to $|F|$ by applying the Lorentz and polarization corrections. No absorption corrections were made. With a calibrated intensity scale a total of 2089 independent reflexions were measured visually. The reflexions that were too weak to be measured were not included in any of the calculations.

Structure determination

The structure was solved by the heavy-atom method. A three-dimensional sharpened Patterson synthesis was evaluated and three prominent peaks on Harker sections were easily interpreted as Br–Br vectors. However, two of them existed quite near the axis ($a/2$, $c/2$) on the Patterson maps. This means that the x and z coordinates of the bromine atoms are close to 0 and $\frac{1}{4}$, respectively. This situation made it difficult to fix the y coordinate of the Br–Br peaks, with two alternative positions, $(\frac{1}{2}-2x, 2y, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}-2y, 2z)$. Therefore, two possible sets of coordinates for the bromine atom were obtained:

	x/a	y/b	z/c
(A)	0·0140	0·1582	0·2237
(B)	0·0140	0·0192	0·2237 .

The R values from the structure factor calculations with Br alone gave no evidence which could be used to distinguish between A and B ($R(A)=0·45$ and $R(B)=0·46$). The chemical structure of portulal was unknown. However, introduction of the *p*-bromophenylsulphonylhydrazono group, Br–Ph–SO$_2$NHN=CH–, provided a clue to the positions of the S atoms from the Patterson maps, because the intramolecular Br···S distance of 6·4 Å is known. Thus, the possible positions for the S atoms could be deduced for the two cases, A and B. Comparison of Fourier syntheses of electron density phased on the positions of the Br and S atoms for each case lead us to conclude that A was the more plausible position because A gave electron density maps with fewer false details than those based on B. At this stage the R value based on the Br and S atom positions was 0·43 and from the electron density maps the positions of 26 of the 33 lighter atoms in the empirical formula were located. Successive least-squares refinements with isotropic thermal factors, Fourier and difference Fourier syntheses revealed the locations of 35 non-hydrogen atoms. At this early stage all the lighter atoms were assumed to be carbon atoms and the R value was 0·195.

Refinement

Anisotropic temperature factors were then introduced for 35 non-hydrogen atoms. Discrimination of oxygen atoms, O(3), O(4) and O(5), from carbon atoms was also achieved at this stage by the examination of the temperature factors, peak heights of Fourier syntheses and bond lengths. The positions of the double bonds C(3)–C(4), C(13)–C(14) and C(18)–N(2), were also confirmed by calculations of bond lengths and angles.

The absolute configuration was determined using the anomalous dispersion effects of the Br and S atoms (Br: $\Delta f'=-0{\cdot}9$, $\Delta f''=1{\cdot}5$; S: $\Delta f'=0{\cdot}3$, $\Delta f''=0{\cdot}6$) for Cu $K\alpha$ radiation (Bijvoet, Peerdeman & van Bommel, 1951). It was further confirmed by taking an equi-inclination Weissenberg photograph, with Cr $K\alpha$ radiation, of the first layer around the *c* axis. When the *R* value became 0·133 the calculated and observed intensities of more than 300 Bijvoet pairs, *hkl* and $h\bar{k}l$, were compared. The absolute molecular structure is shown in Fig. 1. Hence, the absolute configuration of portulal itself was also established unambigously as illustrated in Fig. 2 (i).

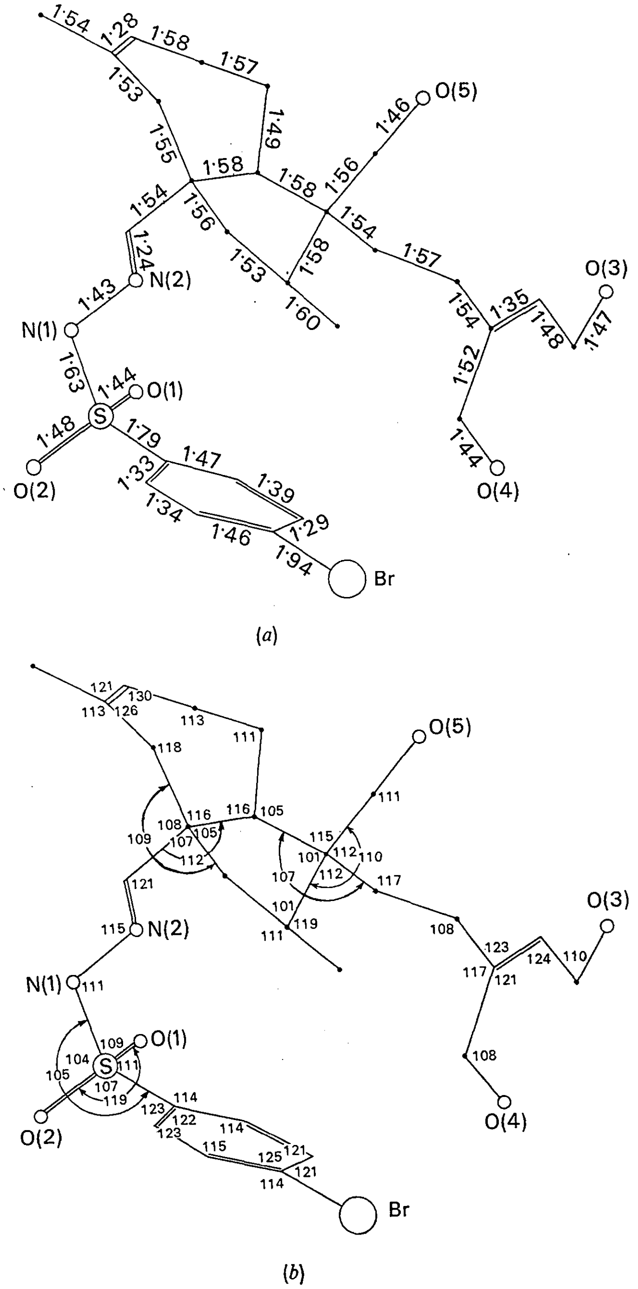
Atomic form factors and the real and imaginary parts of the anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (1962). At the final stage of the refinement, a difference Fourier synthesis was evaluated; some diffuse maxima occurred in positions stereochemically acceptable for hydrogen atoms but it was not possible to determine their coordinates. At a final stage of the least-squares refinement, the coordinates of 28 hydrogen atoms, calculated by assuming the C–H distance to be 1·08 Å, were included, but their coordinates were not varied. The temperature factors were assumed to be isotropic and given the value 2·0 Å^2. The final *R* value was 0·123. The final fractional coordinates and anisotropic temperature factors and their standard deviations are listed in Table 1; The proposed coordinates of the hydrogen atoms are given in Table 2, and the observed and calculated structure factors are compared in Table 3.

Table 2. *Proposed coordinates of hydrogen atoms*

	x/a	*y/b*	*z/c*
H(2′)	0·944	0·160	0·667
H(3′)	0·837	0·117	0·902
H(5′)	0·823	0·040	0·414
H(6′)	0·927	0·082	0·190
H(1*a*)	0·257	0·151	0·785
H(1*b*)	0·193	0·130	0·570
H(2*a*)	0·136	0·102	0·917
H(2*b*)	0·289	0·085	0·919
H(3)	0·112	0·041	0·772
H(5*a*)	0·222	0·097	0·312
H(5*b*)	0·299	0·056	0·245
H(7*a*)	0·417	0·117	0·166
H(7*b*)	0·538	0·086	0·214
H(8)	0·631	0·128	0·477
H(10)	0·433	0·113	0·752
H(11*a*)	0·585	0·162	0·745
H(11*b*)	0·438	0·181	0·798
H(12*a*)	0·481	0·234	0·595
H(12*b*)	0·616	0·214	0·492
H(14)	0·494	0·262	0·920
H(15*a*)	0·724	0·293	1·026
H(15*b*)	0·727	0·252	1·159
H(16*a*)	0·768	0·186	0·799
H(16*b*)	0·803	0·221	0·971
H(18)	0·462	0·031	0·473
H(20*a*)	0·306	0·160	0·287
H(20*b*)	0·419	0·194	0·281
H(N1)	0·641	0·016	0·584

Discussion

The bond lengths and valency angles are shown in Fig. 3(*a*) and (*b*) respectively. The mean value of the estimated standard deviations for the bond lengths between all the non-hydrogen atoms except Br and S is 0·026 Å and that for the angles is 1·5°. Most of the bond lengths agree, within experimental error, with the accepted values. However, the Br–C(1′) bond (1·94 ± 0·02 Å) is slightly longer than the value, 1·85 ± 0·01 Å, reported by Sutton (1965) and rather nearer to the Br–



(*a*)

(*b*)

Fig. 3. (*a*) Bond lengths. (*b*) Bond angles.

non-aromatic carbon distance of 1·948 Å (Ohrt, Cooper & Norton, 1969). The lengths of S–C(4′), 1·79, S–O(1), 1·44 and S–O(2), 1·48 Å may be compared with the values reported in 3*β*,6*β*-dimethoxy-5*β*,19-cycloandrostan-17-one *N*-acetyl-*p*-bromophenylsulphonylhydrazone; S–C, 1·77 Å, and the average value of S–O 1·45 Å, respectively (Tamura & Sim, 1968). The S–N(1) bond (1·63 Å) is somewhat shorter than the reported value of 1·71 Å (Tamura & Sim, 1968). The N(1)–N(2) single bond (1·43 Å) is in close agreement with the nitrogen–nitrogen single bond length of 1·46 Å in hydrazine (Giguère & Schomaker, 1943). The N(2)–C(18) double bond (1·24 Å) also agrees with the value of 1·27 Å in 2-(2-hydroxyethylamino)-2-thiazoline (Miller, Robertson, Sim, Clapp, Long & Hasselstrom, 1964) and a mean value of 1·269 Å in a number of oximes and amine oxides (Folting, Lipscomb & Jerslev, 1964). The average sp^3-carbon–sp^3-carbon single bond length (1·549 Å) and the average length in the benzene ring, (1·38 Å) do not differ significantly from the known values of 1·545 and 1·397 Å. Non-aromatic C–C double bonds C(3)–C(4) and C(13)–C(14) have the average value of 1·32 Å, corresponding to the value (1·34 Å) of Sutton (1965). The average value of the three C–O single bonds, C(15)–O(3), C(16)–O(4) and C(20)–O(5), is 1·46 Å, which, within experimental errors, is in agreement with 1·426 Å, reported by Sutton (1965) and with 1·44 Å reported by Ohrt, Cooper & Norton (1969). The average valency angle of the five-membered ring (103·2°) agrees well with the value 103·8° observed in the *D* ring of steroids (Ohrt, Cooper & Norton, 1969; Gopalakrishna, Cooper & Norton, 1969). The five-membered ring has an envelope conformation, C(9) and C(8) being out of plane V, at distances 0·1 and −0·65 Å respectively (see Table 5). The angles of the seven-membered ring containing one sp^2-carbon–sp^2-carbon double bond are consistently greater than the normal values of sp^2 and sp^3-carbon atoms. The angles of C(2)–C(3)–C(4) and C(3)–C(4)–C(5) are 130 and 126° respectively, the average angle at five sp^3-carbon atoms being 115°. The increase in bond angles may be compared with that observed in isoclovene hydrochloride (Clunie & Robertson, 1961), cyclononylamine hydrobromide (Bryan & Dunitz, 1960) and 1,6-*trans*-diaminocyclodecane dihydrochloride (Huber-Buser & Dunitz, 1960). In these com-

Table 3. *Observed and calculated structure factors* (×3)

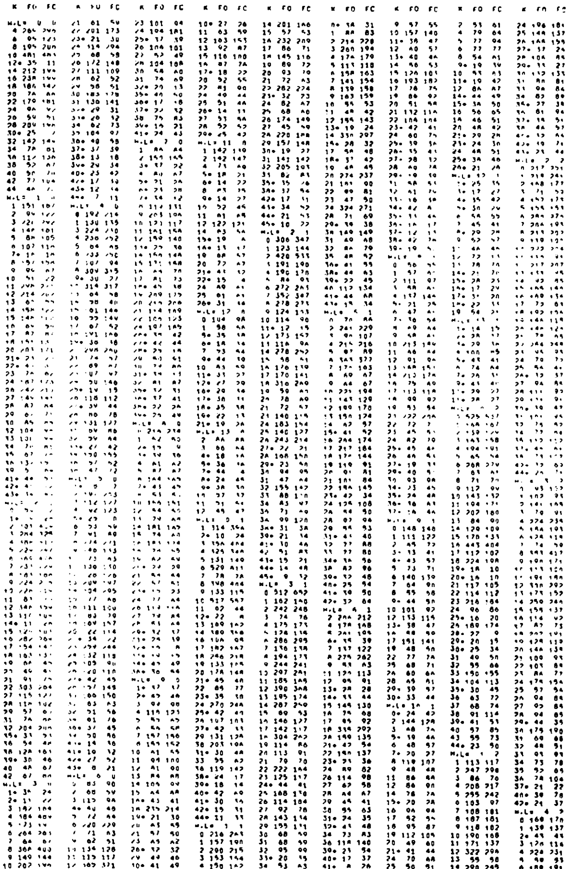
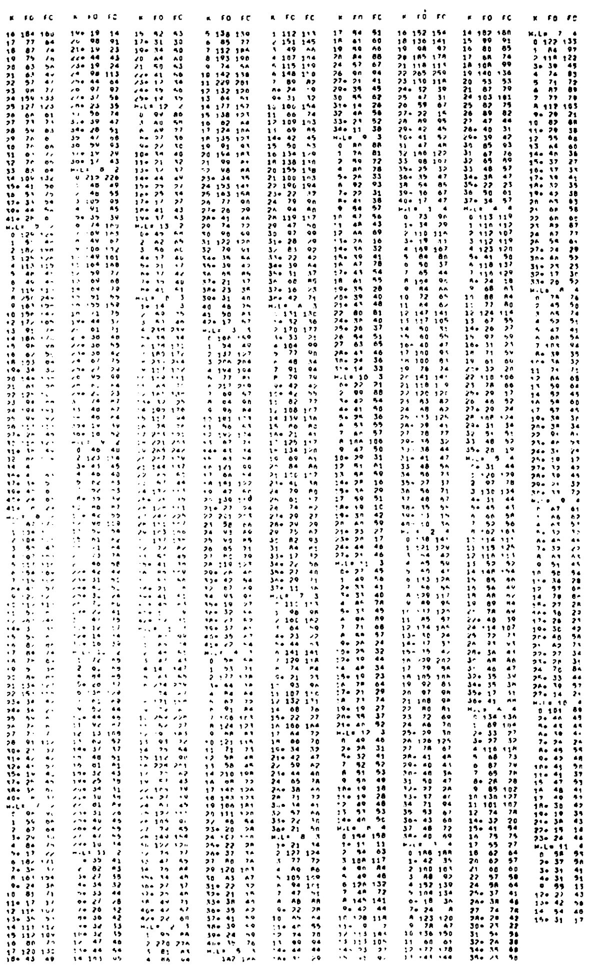


Table 3 (*cont.*)



pounds similar large values for the ring angles have been reported. Some least-squares planes are listed in Table 5. The C(1) atom deviates from plane I by 0·53 Å, and C(6) and C(10) are also out of the plane, by −0·94 and −0·53 Å respectively.

Table 4(*a*). *Some intramolecular contacts less than* 4·0 Å

C(1)····C(3)	2·63 Å	C(11)···C(13)	2·52 Å
C(1)····C(4)	3·08	C(12)···C(14)	2·54
C(1)····C(5)	2·92	C(13)···C(15)	2·49
C(1)····C(6)	2·60	C(13)···O(4)	2·38
C(1)····C(9)	2·59	C(14)···C(16)	2·49
C(2)····C(4)	2·60	C(14)···O(3)	2·41
C(2)····C(5)	3·20	C(14)···O(4)	3·31
C(2)····C(6)	3·17	C(15)···C(16)	2·96
C(3)····C(5)	2·50	C(18)···N(1)	2·26
C(3)····C(19)	2·47	C(1′) ···C(3′)	2·34
C(4)····C(6)	2·63	C(1′) ···C(5′)	2·36
C(5)····C(7)	2·52	C(2′) ···C(4′)	2·40
C(5)····C(10)	2·65	C(2′) ···C(6′)	2·44
C(5)····C(18)	2·49	C(3′) ···C(5′)	2·46
C(6)····C(8)	2·43	C(4′) ···C(6′)	2·34
C(6)····C(9)	2·51	N(1)····O(1)	2·50
C(6)····N(2)	2·42	N(1)····O(2)	2·45
C(7)····C(9)	2·40	N(2)····S	2·52
C(7)····C(18)	2·48	O(1)····O(2)	2·52
C(8)····C(10)	2·43	S·······C(3′)	2·74
C(9)····C(12)	2·65	S·······C(5′)	2·76
C(10)···C(18)	2·58	Br······C(2′)	2·84
		Br······C(6′)	2·86

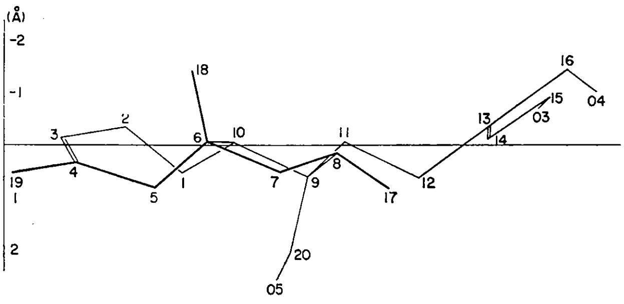


Fig. 4. The deviations of the atoms from the least-squares plane X.

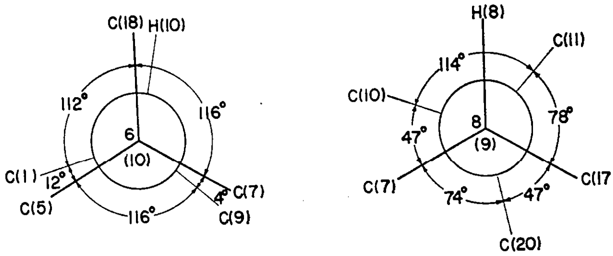


Fig. 5. Newman projections down the C(6)–C(10) and C(8)–C(9) bonds with the relevant dihedral angles.

Table 4(*b*). *Intermolecular contacts less than* 4·0 Å

i	(x,y,z)	ii	$(\frac{1}{2}-x,-y,\frac{1}{2}+z)$
iii	$(x,y,1+z)$	iv	$(\frac{3}{2}-x,-y,\frac{1}{2}+z)$
v	$(-1+x,y,z)$	vi	$(-\frac{1}{2}+x,\frac{1}{2}-y,1-z)$
vii	$(-\frac{1}{2}+x,\frac{1}{2}-y,2-z)$	viii	$(\frac{3}{2}-x,-y,-\frac{1}{2}+z)$

Atom A	Atom B		Distance	Atom A	Atom B		Distance
N(1) ···	C(19)	ii	3·57 Å	C(3)····	C(3′)	v	3·80 Å
N(2) ···	C(19)	ii	3·88	C(3)····	C(4′)	v	3·68
C(18)···	C(19)	ii	3·92	C(3)····	C(5′)	v	3·72
C(3)····	C(19)	ii	3·86	C(3)····	C(6′)	v	3·81
O(1)····	C(5′)	iii	3·31	C(4)····	C(1′)	v	3·85
O(1)····	C(6′)	iii	3·09	C(4)····	C(5′)	v	3·67
O(1)····	C(7)	iii	3·57	C(4)····	C(6′)	v	3·51
O(1)····	C(17)	iii	3·98	C(5)····	C(6′)	v	3·99
O(3)····	C(12)	iii	3·68	C(19)···	C(5)	v	3·55
C(2)····	C(5)	iii	3·76	C(19)···	C(6′)	v	3·63
C(11)···	C(17)	iii	3·85	C(20)···	Br	v	3·72
C(13)···	C(17)	iii	3·83	O(3)····	Br	vi	3·90
C(16)···	C(17)	iii	3·68	O(5)····	O(4)	vi	2·81
S ······	N(1)	iv	3·98	O(5)····	C(12)	vi	3·99
O(1)····	O(2)	iv	3·44	O(5)····	C(13)	vi	3·60
O(1)····	N(1)	iv	3·98	O(5)····	C(14)	vi	3·88
O(2)····	S	iv	3·96	O(5)····	C(16)	vi	3·78
O(2)····	O(2)	iv	3·85	C(12)···	O(4)	vi	3·58
O(2)····	N(1)	iv	3·01	C(14)···	Br	vi	3·54
O(2)····	N(2)	iv	3·70	C(15)···	Br	vi	3·80
O(2)····	C(5′)	iv	3·54	C(20)···	O(4)	vi	3·34
O(2)····	C(18)	iv	3·49	O(3)····	O(4)	vii	2·73
N(1)····	C(5′)	iv	3·94	O(3)····	C(2′)	vii	3·57
O(5)····	Br	v	3·72	O(3)····	C(16)	vii	3·42
C(1)····	C(1′)	v	3·88	O(5)····	O(3)	vii	2·74
C(1)····	C(2′)	v	3·70	O(5)····	C(15)	vii	3·18
C(2)····	C(2′)	v	3·77	C(1)····	O(3)	vii	3·69
C(2)····	C(3′)	v	3·87	C(14)···	O(4)	vii	3·75
C(3)····	C(1′)	v	3·88	C(14)···	C(16)	vii	3·98
C(3)····	C(2′)	v	3·86	C(15)···	O(4)	vii	3·79
				N(1)····	O(2)	viii	3·01

The conformations of four asymmetric carbon atoms C(6), C(8), C(9) and C(10) are shown in Fig. 5 with the relevant dihedral angles. The torsional angles of C(5)–C(6)–C(10)–C(1) and C(7)–C(6)–C(10)–C(9) are 12 and 4° respectively, showing that the five and seven-membered rings, *cis*-fused to each other, are twisted slightly around the C(6)–C(10) bond. The C(1) atom deviates from plane III by 0·28 Å. This situation may be due to steric repulsion of hydrogen atoms attached to the C(1) and C(5) atoms (2·16 Å as calculated value) as well as to ring strain. The carbon atoms attached to the C(8) and C(9) atoms are in an almost staggered relationship to one another with the relevant off-set angles shown in Fig. 5. The C(11) and C(20) atoms linked with the C(9) atom are displaced from plane VI by −1·31 and 1·25Å respectively. Both Fig. 5 and Fig. 2 (ii) show the absolute configuration of the asymmetric carbon atoms. They have 6(*S*), 8(*R*), 9(*R*) and 10(*R*) configurations respectively (Cahn, Ingold & Prelog, 1956).

Plane I makes dihedral angles of 158 and 123° with planes II and III, respectively. The maximum deviations from planes VII and VIII are 0·052 and 0·078 Å respectively and these are coplanar with the aromatic ring. The average plane X calculated through the atoms of the perhydroazulene skeleton and the side chains is illustrated in Fig. 4. Some intramolecular

Table 5. *Least-squares planes*

Deviations

Plane I		Plane II		Plane III		Plane IV		Plane V	
C(2)	0·003 Å	C(1)	0 Å	C(5)	0 Å	C(6)	0 Å	C(6)	0 Å
C(3)	−0·013	C(2)	0	C(6)	0	C(10)	0	C(7)	0
C(4)	0·022	C(5)	0	C(10)	0	C(18)	0	C(10)	0
C(5)	−0·007								
C(19)	−0·004								
				Atoms out of plane					
C(1)	0·527	C(3)	0·434	C(1)	0·283	C(1)	1·245	C(1)	0·991
C(6)	−0·936	C(4)	0·475	C(4)	1·256	C(5)	1·147	C(5)	1·198
C(10)	−0·530	C(6)	−1·293	C(7)	−1·297	C(7)	−1·354	C(8)	−0·650
		C(10)	−1·212	C(9)	−1·363	C(9)	−1·323	C(9)	0·105

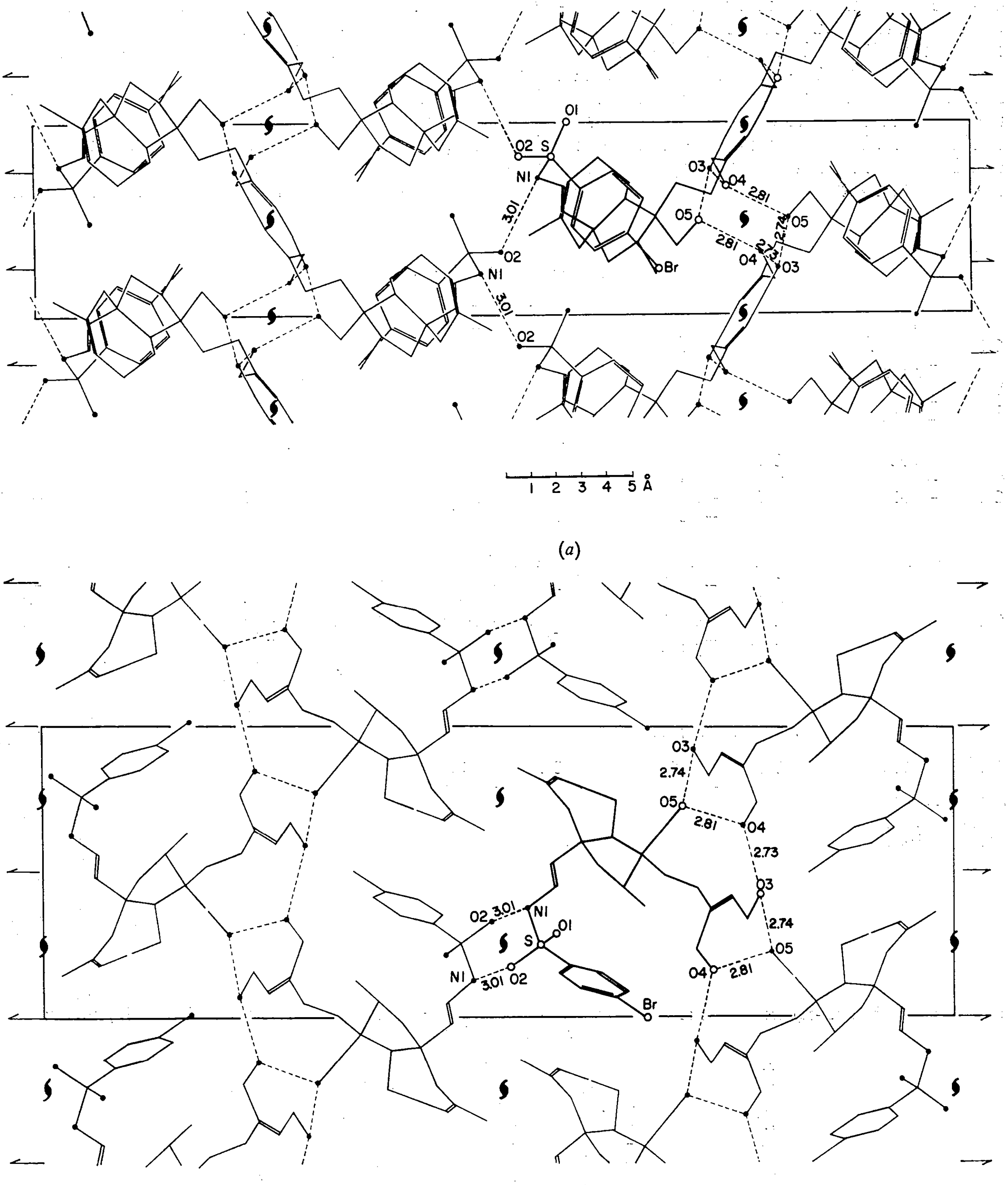
Plane VI		Plane VII		Plane VIII		Plane IX		Plane X	
C(8)	0	C(12)	−0·028	N(1)	−0·044	Br	0·032	O(3)	−0·788
C(9)	0	C(13)	0·015	N(2)	0·016	S	0·022	O(4)	−1·046
C(10)	0	C(14)	0·052	C(6)	−0·046	C(1′)	−0·003	O(5)	2·618
		C(15)	−0·044	C(18)	0·078	C(2′)	−0·026	C(1)	0·549
		C(16)	0·006			C(3′)	0·002	C(2)	−0·343
						C(4′)	−0·005	C(3)	−0·148
						C(5′)	0·003	C(4)	0·348
						C(6′)	−0·025	C(5)	0·808
		Atoms out of plane						C(6)	−0·045
C(5)	0·786	O(3)	0·461	C(5)	0·740			C(7)	0·508
C(6)	1·101	O(4)	−1·340	C(7)	−1·553			C(8)	0·166
C(11)	−1·310	C(11)	1·419	C(10)	0·334			C(9)	0·618
C(17)	0·273							C(10)	−0·040
C(20)	1·245							C(11)	−0·031
								C(12)	0·628
								C(13)	−0·331
								C(14)	−0·138
								C(15)	−0·950
								C(16)	−1·521
								C(17)	0·827
								C(18)	−1·467
								C(19)	0·440
								C(20)	2·171

Equations for the least-squares planes are in the form $lX+mY+nZ+p=0$, where X, Y, Z and p are in Å units, referred to the crystallographic axes.

Plane	l	m	n	p
I	−0·796	0·527	−0·298	1·626
II	−0·949	0·189	−0·254	2·899
III	−0·036	−0·676	0·736	0·149
IV	−0·844	−0·414	0·342	3·920
V	−0·842	0·305	−0·445	3·931
VI	−0·643	−0·057	−0·764	6·030
VII	−0·344	−0·719	0·604	5·239
VIII	−0·728	−0·316	0·609	2·251
IX	−0·906	0·338	−0·256	8·206
X	—0·586	0·509	—0·630	2·686

contacts less than 4·0 Å are given in Table 4(*a*). All approach distances appear to be attributable to normal van der Waals interactions.

Intermolecular contacts less than 4·0 Å are summarized in Table 4(*b*). The closest contacts occur between $O(2^{viii})$ and $N(1^{i})$ and between $O(2^{i})$ and $N(1^{iv})$



(*a*)

(*b*)

Fig. 6. The packing of the molecules viewed along (*a*) the *a* axis and (*b*) the *c* axis. The dotted lines show the possible hydrogen bonds with their respective lengths.

both distances being 3·01 Å. The values represent normal NH$\cdots$O hydrogen bonded contacts. These hydrogen bonds construct a helical column, –O(2^{viii})$\cdots$N(1)–S–O(2^{i})$\cdots$N(1)–S–O(2^{iv})$\cdots$, around a twofold screw axis parallel to the *c* axis (Fig. 6). The atoms O(3), O(4) and O(5) are also linked by intermolecular hydrogen bonds of the type O–H$\cdots$O, the distances of O(3^{i})$\cdots$O(4^{vii}), O(5^{i})$\cdots$O(3^{vii}) and O(5^{i})$\cdots$O(4^{vi}) being 2·73, 2·74 and 2·81 Å, respectively. Thus, each oxygen atom is involved in forming a bifurcated hydrogen bond to the other two oxygen atoms of different molecules and O(3^{i})$\cdots$Br$^{\mathrm{vi}}$ and O(5^{i})$\cdots$Br$^{\mathrm{v}}$ are 3·90 and 3·72 Å. There are no other unusually short intermolecular distances, and the molecules retain the normal van der Waals contacts. The packing of the molecules in the crystal, viewed along the *a* and *c* axes, is illustrated in Fig. 6 and the suggested hydrogen bonds are marked with dotted lines.

Calculations were carried out on the HITAC 5020E computer at the Computer Centre of this University.

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Kristall- und Molekülstruktur von 3′-*O*-Acetyl-4-thiothymidin*

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(*Eingegangen am* 25. *September* 1970 *und wiedereingereicht am* 23. *Oktober* 1970)

Evaporation of an aqueous solution of 3′-*O*-acetyl-4-thiothymidine yielded yellow prismatic crystals of the orthorhombic space group $P2_12_12_1$ with $a = 13{\cdot}578$, $b = 5{\cdot}175$, $c = 19{\cdot}667$ Å. The crystal structure was determined by three-dimensional X-ray diffraction methods from 1213 independent reflexions measured with an automatic four-circle diffractometer. Using the heavy atom technique the structure was solved from a series of Patterson and Fourier syntheses and refined by least-squares methods to a final *R* value of 5·4%. 3′-*O*-Acetyl-4-thiothymidine displays the usual *anti* conformation, the dihedral angle C(2′)–C(1′)–N(1)–C(6) being −63·7°. The bonds C(4)–S and C(2)–O(2) of 1·673 and 1·211 Å length have double bond character indicating that the heterocycle is in the diketo form. The conformation of the deoxyribose is C(2′)-*endo*. The atoms comprising the acetyl group and the ribose atoms H(9), C(3′) and O(3′) are essentially coplanar. The structure exhibits only one intermolecular hydrogen bond between the sulphur atom and atom O(5′) of the sugar residue (3·227 Å). The heterocycles form a stack along and inclined by 45° towards the *b* axis with an interplanar spacing of 3·68 Å.

Einleitung

Lezius & Scheit (1969) gelang die enzymatische Synthese des alternierenden Copolymers poly d(A-s^{4}T) mit DNA-Polymerase, indem sie 4-Thiothymidin-5′-triphosphat anstelle von Thymidin-5′-triphosphat als Substrat einsetzten. Die analogen Copolymere poly d(A-T) und poly d(A-s^{4}T) zeigen ein unterschiedliches Verhalten gegenüber DNA-Polymerase und haben deutlich voneinander verschiedene physikalische Eigenschaften. Daraufhin wurden die chemischen und physikalischen Eigenschaften verschiedener 4-thiosubstituierter Pyrimidinnucleoside und der entsprechenden Oligo- und Polynucleotide genauer untersucht. So ergab die Röntgenstrukturanalyse des 4-Thiouridins (Saenger & Scheit, 1970), dass diese Substanz in der bisher

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