

The appreciable degree of conjugation between the alternating single and double bonds throughout the polyene chain is apparent with the single bonds (mean = 1.451 Å) slightly shorter and the double bonds (mean = 1.353 Å) slightly longer than for a non-resonating single-bond-double-bond system. This result is in good agreement with other conjugated-chain structures (Gilardi, Karle & Karle, 1972; Bart & MacGillavry, 1968). C(9)–C(10) does not enter into the resonance system as it has the expected single-bond value of 1.54 Å. The bond distances for C(1)–C(11) and C(1)–C(17) suggest that these bonds have less double-bond character than the other single bonds in the conjugated side chain. This results from the restricted resonance between the phenyl rings and the side chain caused by the non-planarity of the phenyl rings with the plane formed by the side chain. The short bond length of 1.287 Å between C(1) and N(2) is consistent with the unambiguous location of the double bond to the N. The carbonyl bond length, 1.232 Å, agrees with the accepted normal value.

The bond angles along the chain, with the exception of those around C(1), N(2) and C(9), show no significant deviation from the mean value of 124.4°. The decreased bond angles opposite the methyl group at C(9) and around C(1) may be due to the steric crowding which would be eased by the observed slight

distortion in bond angles. There are no intermolecular hydrogen bonds or short contact distances between molecules.

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2,3-Diphenyl-5-(α -D-lyxofuranosyl)tetrazolium Bromide

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Abstract. C₁₈H₁₉BrN₄O₄, $M_r = 435.27$, tetragonal, $P4_32_12$, $a = b = 8.4723$ (3), $c = 52.303$ (3) Å, $Z = 8$, $D_x = 1.54$ g cm⁻³. The X-ray analysis corroborates chemical and spectroscopic evidence about the molecular configuration.

Introduction. Pale-yellow crystals of the title compound were obtained by slow evaporation of its water solution under a thin benzene surface. Cell dimensions were obtained from a powder photograph at 20°C taken in a Guinier–Hägg focusing camera with highly monochromatized Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å) using

KCl as an internal standard [$a = 6.2919$ (4) Å]. Distances on the film were measured with a SAAB film scanner connected to an IBM 1800 computer and were evaluated using the program *PILT* (Malmros & Werner, 1973). A prismatic specimen (0.45 × 0.45 × 0.15 mm) was mounted on a goniometer head approximately along the c axis. Intensities were collected on a Philips PW 1100 four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The 2090 independent data available within $0 < \theta < 67^\circ$ were collected with θ – 2θ scans of 1° scan width. Lorentz-polarization and absorption corrections were applied. The crystal structure was solved by the heavy-atom

method. Successive cycles of anisotropic full-matrix least-squares refinement gave an R value of 0.09 for all data.* H atoms were placed geometrically but their positions were not refined. The hydroxyl H atoms were not found. Since the chemical problem was settled at this stage we decided to discontinue further refinement of the structure.

Atomic parameters are shown in Table 1. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) for non-hydrogen atoms and from Stewart, Davidson & Simpson (1965) for H atoms.

Discussion. Anhydrotalose formazans were obtained in an irregular deacetylation process of the N,O -peracetyl derivatives of D-galactose N,N' -diphenylformazans with sodium methoxide (Messmer, Pintér & Soliman, 1970; Zsoldos-Mády, Messmer, Pintér & Neszmélyi, 1977). Chemical and NMR spectroscopic investigations pointed to the formation of a five-membered ring between C(2) and C(5). Reaction of the corresponding formazan with N -bromosuccinimide gave the title compound (Zsoldos-Mády *et al.*, 1978).

* Lists of structure factors, thermal parameters, bond lengths, angles, torsion angles and an analysis of the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33802 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates for non-hydrogen atoms ($x \times 10^4$, $y \times 10^4$, $z \times 10^5$)

	x	y	z
Br(1)	13373 (2)	4741 (2)	-06200 (3)
N(1)	12118 (13)	8143 (13)	-09701 (18)
N(2)	11839 (12)	8449 (13)	-07313 (18)
N(3)	13168 (14)	8911 (11)	-06117 (20)
N(4)	14292 (13)	8971 (13)	-07877 (23)
C(11)	10283 (15)	8255 (16)	-05990 (22)
C(12)	9440 (18)	6893 (18)	-06509 (28)
C(13)	7954 (17)	6770 (20)	-05411 (29)
C(14)	7449 (18)	7841 (22)	-03734 (28)
C(15)	8312 (18)	9163 (18)	-03276 (29)
C(16)	9753 (17)	9406 (17)	-04273 (26)
C(21)	13365 (16)	9305 (17)	-03313 (24)
C(22)	13086 (17)	8115 (18)	-01560 (24)
C(23)	13289 (20)	8434 (20)	00887 (23)
C(24)	13764 (19)	9891 (23)	01613 (24)
C(25)	14035 (18)	11039 (18)	-00175 (32)
C(26)	13862 (17)	10834 (17)	-02704 (26)
C(1)	13589 (16)	8476 (16)	-09985 (22)
C(2)	14430 (16)	8381 (19)	-12408 (26)
C(3)	14238 (15)	6741 (16)	-13786 (23)
C(4)	15847 (16)	6652 (16)	-15145 (22)
C(5)	16962 (17)	7208 (16)	-13110 (24)
C(6)	18571 (16)	7752 (17)	-13918 (25)
O(3)	12944 (11)	6728 (12)	-15427 (16)
O(4)	15823 (11)	7569 (11)	-17348 (15)
O(5)	16119 (10)	8599 (12)	-12108 (16)
O(6)	18506 (10)	8866 (12)	-15825 (16)

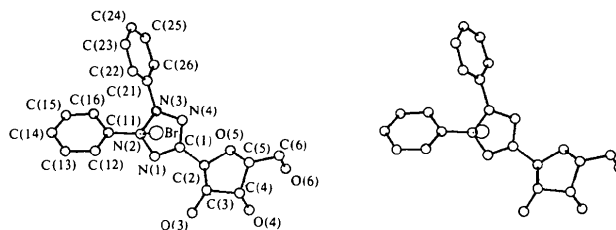


Fig. 1. Stereoscopic drawing of the title compound showing atomic numbering. The Br(1)···N(2) connection is marked by a dotted line.

Chemical and spectroscopic investigations suggested an inversion of the configuration at C(2). This assumption has been corroborated by X-ray analysis (*cf.* Fig. 1.). The relative displacements of the substituents of the D-talose moiety are (+)synclinal [O(3)—C(3)—C(4)—O(4) = +39.7°] and (–)synclinal [O(4)—C(4)—C(5)—C(6) = –42.5°]. The position of the C(6)—O(6) bond with respect to the sugar skeleton is synclinal both to the C(5)—C(4) and C(5)—O(5) bonds (–52.0 and 61.5°). Atoms C(2), C(3), C(5) and O(5) are coplanar within 0.01 Å (*cf.* data of least-squares planes)* while atom C(4) is out of this plane (–0.68 Å) forming a V_4 envelope conformation (Hall, Steiner & Pedersen, 1970) and bends to the same side as C(6).

On the basis of bond lengths and the analysis of planarity, a resonance structure can be attributed to the tetrazolium ring as was reviewed by Schiele (1967). The phenyl groups are nearly symmetrically arranged about the plane of the hetero-ring as shown by the dihedral angles formed by planes I and IV, respectively. The Br(1)···N(2) distance of 3.45 Å which is just the sum of van der Waals radii for Br and N (Pauling, 1960) seems to indicate that there is a partial positive charge on N(2).

Intermolecular contacts are determined by the Br anion which participates in two hydrogen bonds, Br(1)···O(3) ($\frac{3}{2} - x, y - \frac{1}{2}, z - \frac{1}{4}$) = 3.30 Å, and Br(1)···O(6) ($\frac{5}{2} - x, y - \frac{1}{2}, -z - \frac{1}{4}$) = 3.16 Å. The Br anion is situated at the top of a distorted trigonal pyramid maintaining the angles N(2)—Br(1)—O(3) = 119, N(2)—Br(1)—O(6) = 117 and O(3)—Br(1)—O(6) = 81°.

Atom O(6) which acts as a donor towards the Br ion also takes part in an intramolecular hydrogen bond forming a quasi six-membered ring with the O(4)—H moiety [O(4)···O(6) = 2.65 Å].

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* See previous footnote.

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The Structure of 4-Methyl-5-sulphosalicylic Acid Tetrahydrate

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Abstract. $C_8H_8O_6S \cdot 4H_2O$, monoclinic, space group $P2_1/c$, $a = 7.60$ (1), $b = 25.30$ (2), $c = 8.48$ (1) Å, $\beta = 119.0$ (1)°. $D_m = 1.43$, $D_x = 1.41$ g cm⁻³, $Z = 4$; $\mu(Cu K\alpha) = 23$ cm⁻¹. The three-dimensional crystal structure analysis revealed that the compound, in the crystalline state, exists in an ionized form as $H_7O_3^+H_3O^+ \cdot C_6H_2(COO^-)OHSO_3^-CH_3$, diaqua-oxonium oxonium 4-methyl-5-sulphonatosalicylate. A short intramolecular contact of 3.04 Å between the methyl C and sulphonate O atoms suggests the presence of a C—H...O type hydrogen bond. The crystal structure is stabilized through intermolecular hydrogen bonds formed between the anionic molecules and cationic water species.

Introduction. Intensities of 965 non-zero independent reflections, recorded by usual X-ray diffraction photographic techniques, were estimated visually and corrected for the Lorentz-polarization effects and spot-extension factors. Absorption was neglected (crystal cross-section = 0.2 × 0.3 mm). The coordinates of the heavy atom (S) were determined from a sharpened Patterson map ($E^2 - 1$ map, where E is the normalized structure factor). Starting with the phases of the S atom alone, successive Fourier syntheses revealed all the non-hydrogen atoms. The structure was then refined isotropically to an R value of 0.143 and anisotropically to an R value of 0.113, using a full-matrix least-squares program (Busing, Martin & Levy, 1962). Scale factors and anisotropic temperature factors were refined in alternate cycles (Lingafelter & Donohue, 1966) along with positional parameters. The variations in parameters in the last cycle of anisotropic refinement were less than a tenth of their e.s.d.'s. The final

atomic parameters are given in Table 1.* Bond lengths (with e.s.d.'s) and bond angles are shown in Fig. 1. The average e.s.d. of the bond angles is of the order of 1.5°.

Discussion. As part of our programme to study the effects of substituents on the geometry and biological

* Lists of structure factors, anisotropic thermal parameters and deviations from the least-squares plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33759 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic parameters* ($\times 10^4$) *of non-hydrogen atoms with their e.s.d.'s in parentheses*

	x	y	z
S	1614 (7)	3424 (1)	5395 (7)
O(1)	3799 (16)	5840 (4)	5821 (19)
O(2)	5066 (17)	5241 (5)	8018 (19)
O(3)	1072 (17)	5588 (5)	2661 (18)
O(4)	-287 (16)	3332 (4)	5455 (17)
O(5)	1862 (18)	3058 (5)	4146 (22)
O(6)	3328 (19)	3425 (5)	7219 (21)
O(W1)	-495 (20)	2842 (5)	8269 (30)
O(W2)	2700 (20)	4013 (5)	9970 (19)
O(W3)	4755 (22)	3136 (5)	3009 (29)
O(W4)	6342 (21)	2710 (6)	8366 (29)
C(1)	2588 (23)	4958 (6)	5065 (21)
C(2)	1208 (23)	5087 (6)	3268 (24)
C(3)	-22 (26)	4713 (7)	3074 (27)
C(4)	5 (25)	4189 (6)	2689 (26)
C(5)	1447 (23)	4067 (6)	4547 (26)
C(6)	2667 (24)	4441 (6)	5741 (26)
C(7)	3909 (23)	5400 (6)	6322 (26)
C(8)	-1382 (31)	3773 (8)	1343 (33)