

The Crystal and Molecular Structure of 2-*O*-(*p*-Bromobenzenesulphonyl)-1,4:3,6-dianhydro-D-glucitol 5-Nitrate

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Crystals of 2-*O*-(*p*-bromobenzenesulphonyl)-1,4:3,6-dianhydro-D-glucitol 5-nitrate are monoclinic, $a=26.16$, $b=11.11$, $c=5.34$ Å, $\beta=90^\circ 16'$, $Z=4$, space group $P2_1$. The intensities of about 2400 reflexions (1565 observed) were measured with a scintillation counter and Cu $K\alpha$ radiation. The bromine and sulphur positions were determined by Patterson methods, and all the carbon, nitrogen and oxygen atoms were located on successive three-dimensional electron-density distributions. The positional and isotropic thermal parameters of the 46 Br, S, C, N, O atoms in the asymmetric unit were refined by least squares, the final R value being 0.157. The absolute configuration is established since the compound is derived from D-glucose.

The two crystallographically independent molecules have the same conformation; the five-membered rings are non-planar. The bond distances and valency angles are normal; the most significant intramolecular non-bonded contact is 2.9 Å between a nitro group oxygen and the oxygen atom in the other five-membered ring, and this relatively short approach is probably a result of some attractive interaction between the two atoms. The intermolecular separations correspond to van der Waals interactions.

Introduction

Much indirect evidence has been found for intramolecular interaction between contiguous nitroxy groups or between nitroxy groups and neighbouring oxygen atoms (Hayward & Csizmadia, 1963). The only direct structural information is for *cis*-1,2-acenaphthenediol dinitrate (Mak & Trotter, 1964), in which the most significant intramolecular non-bonded distance is 2.91 Å, between an oxygen atom of one nitro group and the neighbouring alkoxy oxygen. This distance of closest approach is slightly greater than the sum of the van der Waals radii of the oxygen atoms (2.8 Å), and indicates the absence of conventional bonding between the *cis* nitroxy groups. However, the molecule could exist in a large number of conformations as a result of rotation about single C–O and O–N bonds, and the adoption of a conformation with a relatively short O...O approach does suggest the possibility of interaction between the relatively positive alkoxy oxygen and the relatively negative oxygen of the nitro group. To substantiate that the close approach is a result of intramolecular rather than intermolecular forces, it was considered necessary to obtain structural information for other molecules of this type. To this end we have determined the structure of 2-*O*-(*p*-bromobenzenesulphonyl)-1,4:3,6-dianhydro-D-glucitol 5-nitrate (I, $R = p$ -bromobenzenesulphonyl).

Experimental

The crystals are colourless needles elongated along c . The unit-cell dimensions and space group were deter-

mined from various rotation, Weissenberg and precession photographs, and on the General Electric Spectrogoniometer.

Crystal data (λ Cu $K\alpha = 1.5418$ Å, λ Mo $K\alpha = 0.7107$ Å)
2-*O*-(*p*-bromobenzenesulphonyl)-1,4:3,6-dianhydro-D-glucitol 5-nitrate, $C_{12}H_{12}O_8NSBr$; mol. wt. 410.2; m.p. 75–76 °C.

Monoclinic, $a = 26.16 \pm 0.04$, $b = 11.11 \pm 0.02$, $c = 5.34 \pm 0.01$ Å,

$\beta = 90^\circ 16' \pm 5'$

$U = 1552$ Å³

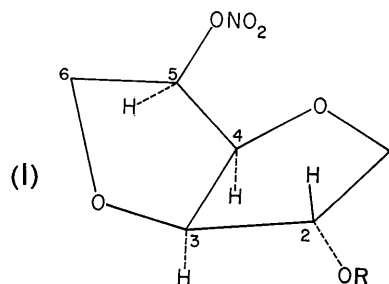
$D_m \sim 1.7$, $Z = 4$, $D_x = 1.755$ g.cm⁻³.

Absorption coefficient for Cu $K\alpha$ radiation, $\mu = 56$ cm⁻¹.

$F(000) = 824$.

Absent spectra: $0k0$ when k is odd. Since the compound is optically active the space group is $P2_1 (C_2^2)$, and there are two molecules in the asymmetric unit.

The intensities of all reflexions with $2\theta(\text{Cu } K\alpha) \leq 119^\circ$ (corresponding to a minimum interplanar spacing $d = 0.9$ Å) were measured on a General Electric XRD 5 Spectrogoniometer, with Single Crystal Orienter, scint-



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Table 1. Measured and calculated structure amplitudes
Unobserved reflexions, for which F_0 is listed as 0, have threshold values in the range 6-10.

h	k	l	F _{obs}	F _{calc}	7	4	0	7.7	11.4	9	9	0	19.9	17.2	0	1	1	103.8	117.7	20	3	1	16.8	11.6	-7	6	1	45.1	41.2
1	0	0	8.1	6.9	14	4	0	24.6	31.1	15	4	0	51.9	50.5	17	9	0	21.9	19.0	21	3	1	39.4	31.6	-6	6	1	66.1	64.7
2	0	0	3.7	1.3	16	4	0	0	0	10	10	0	21.9	19.0	21	3	1	39.4	31.6	22	3	1	17.4	6.7	-5	6	1	17.7	20.5
3	0	0	30.9	41.4	17	4	0	43.7	45.8	18	4	0	0	0	11	1	1	111.4	128.4	23	3	1	43.0	42.2	-4	6	1	53.4	58.1
4	0	0	21.2	20.8	19	4	0	47.6	48.1	14	9	0	19.0	15.0	4	1	1	94.6	85.4	24	3	1	22.2	8.6	-4	6	1	25.5	23.8
5	0	0	22.2	21.8	20	4	0	21.4	24.8	16	9	0	22.0	13.3	-2	1	1	74.6	66.0	25	3	1	19.6	10.6	-2	6	1	14.0	10.8
6	0	0	36.6	39.3	13	4	0	36.6	39.3	16	9	0	8.6	2.1	6	1	1	55.0	44.2	27	3	1	8.2	7.8	-1	6	1	13.0	7.8
7	0	0	20.8	18.1	17	4	0	20.8	18.1	17	9	0	10.4	5.7	7	1	1	32.4	32.2	-27	4	1	0	3.7	0	6	1	60.3	61.5
8	0	0	51.9	50.5	15	4	0	9.7	7.7	19	9	0	7.7	6.0	8	1	1	86.0	72.3	-36	4	1	0	4.5	2	6	1	6.8	4.3
9	0	0	26.7	27.3	1	10	0	0	0	2	10	0	22.5	24.2	10	1	1	29.5	29.1	-24	4	1	10.7	9.8	3	6	1	35.7	28.2
10	0	0	0	0	7.1	12.5	11	1	42.1	33.4	11	1	0	0	12	1	1	33.5	32.6	-22	4	1	0	8.4	5	6	1	29.2	23.0
11	0	0	16.0	17.6	3	10	0	21.4	25.1	12	1	1	0	0	14	1	1	51.8	34.6	-21	4	1	21.2	13.5	6	6	1	13.1	8.5
12	0	0	20.4	17.0	5	10	0	18.4	16.1	14	1	1	0	0	15	1	1	38.3	31.5	-20	4	1	15.4	8.9	7	6	1	31.2	31.7
13	0	0	16.8	6.7	6	10	0	7.5	5.7	15	1	1	0	0	16	1	1	48.6	32.4	-19	4	1	10.3	13.3	8	6	1	61.6	52.6
14	0	0	6.8	6.1	7	10	0	11.5	5.0	16	1	1	0	0	17	1	1	18.3	15.2	-18	4	1	28.8	28.2	9	6	1	26.7	21.7
15	0	0	36.6	39.3	8	10	0	0	3.0	8	10	0	0	0	9	1	1	25.7	17.0	-17	4	1	0	7.2	10	6	1	11.3	11.5
16	0	0	20.8	18.1	9	10	0	4.5	9.0	10	10	0	9.1	5.1	18	1	1	56.9	40.8	-16	4	1	22.9	24.1	11	6	1	40.2	37.2
17	0	0	51.9	50.5	10	10	0	4.0	4.0	11	10	0	12.4	10.4	20	1	1	31.2	31.4	-15	4	1	0	7.8	12	6	1	17.4	11.6
18	0	0	9.7	7.7	11	10	0	9.7	7.7	11	10	0	19.4	17.2	21	1	1	40.6	30.5	-14	4	1	10.7	6.5	13	6	1	31.7	26.9
19	0	0	26.7	27.3	1	10	0	0	0	12	10	0	23.5	21.3	22	1	1	26.7	21.0	-13	4	1	0	3.4	14	6	1	8.9	6.5
20	0	0	0	0	7.1	12.5	23	1	19.4	15.1	23	1	0	0	23	1	1	19.4	15.1	-12	4	1	37.7	32.5	15	6	1	45.6	39.9
21	0	0	21.2	20.8	22	4	0	16.8	6.7	6	10	0	7.5	5.7	15	1	1	48.6	32.4	-19	4	1	10.3	13.3	9	6	1	26.7	21.7
22	0	0	22.2	21.8	20	4	0	21.4	24.8	16	9	0	11.5	5.0	16	1	1	18.3	15.2	-18	4	1	28.8	28.2	10	6	1	11.3	11.5
23	0	0	36.6	39.3	13	4	0	36.6	39.3	16	9	0	8.6	2.1	6	1	1	55.0	44.2	-27	3	1	8.2	7.8	0	6	1	60.3	61.5
24	0	0	20.8	18.1	17	4	0	20.8	18.1	17	9	0	10.4	5.7	7	1	1	32.4	32.2	-27	4	1	0	3.7	0	6	1	35.7	28.2
25	0	0	51.9	50.5	15	4	0	9.7	7.7	19	9	0	7.7	6.0	8	1	1	86.0	72.3	-36	4	1	0	4.5	2	6	1	6.8	4.3
26	0	0	26.7	27.3	1	10	0	0	0	2	10	0	22.5	24.2	10	1	1	29.5	29.1	-24	4	1	10.7	9.8	3	6	1	35.7	28.2
27	0	0	0	0	7.1	12.5	11	1	42.1	33.4	11	1	0	0	12	1	1	33.5	32.6	-22	4	1	0	8.4	5	6	1	29.2	23.0
28	0	0	16.0	17.6	3	10	0	21.4	25.1	12	1	1	0	0	14	1	1	51.8	34.6	-21	4	1	21.2	13.5	6	6	1	13.1	8.5
29	0	0	20.4	17.0	5	10	0	18.4	16.1	14	1	1	0	0	15	1	1	38.3	31.5	-20	4	1	15.4	8.9	7	6	1	31.2	31.7
30	0	0	16.8	6.7	6	10	0	7.5	5.7	15	1	1	0	0	16	1	1	48.6	32.4	-19	4	1	10.3	13.3	8	6	1	61.6	52.6
31	0	0	6.8	6.1	7	10	0	11.5	5.0	16	1	1	0	0	17	1	1	18.3	15.2	-18	4	1	28.8	28.2	9	6	1	26.7	21.7
32	0	0	36.6	39.3	8	10	0	0	3.0	8	10	0	0	0	9	1	1	25.7	17.0	-17	4	1	0	7.2	10	6	1	11.3	11.5
33	0	0	20.8	18.1	9	10	0	4.5	9.0	10	10	0	9.1	5.1	18	1	1	56.9	40.8	-16	4	1	22.9	24.1	11	6	1	40.2	37.2
34	0	0	51.9	50.5	10	10	0	4.0	4.0	11	10	0	12.4	10.4	20	1	1	31.2	31.4	-15	4	1	0	7.8	12	6	1	17.4	11.6
35	0	0	9.7	7.7	11	10	0	9.7	7.7	11	10	0	19.4	17.2	21	1	1	40.6	30.5	-14	4	1	10.7	6.5	13	6	1	31.7	26.9
36	0	0	26.7	27.3	1	10	0	0	0	12	10	0	23.5	21.3	22	1	1	26.7	21.0	-13	4	1	0	3.4	14	6	1	8.9	6.5
37	0	0	0	0	7.1	12.5	23	1	19.4	15.1	23	1	0	0	23	1	1	19.4	15.1	-12	4	1	37.7	32.5	15	6	1	45.6	39.9
38	0	0	21.2	20.8	22	4	0	16.8	6.7	6	10	0	7.5	5.7	15	1	1	48.6	32.4	-19	4	1	10.3	13.3	9	6	1	26.7	21.7
39	0	0	22.2	21.8	20	4	0	21.4	24.8	16	9	0	11.5	5.0	16	1	1	18.3	15.2	-18	4	1	28.8	28.2	10	6	1	11.3	11.5
40	0	0	36.6	39.3	13	4	0	36.6	39.3	16	9	0	8.6	2.1	6	1	1	55.0	44.2	-27	3	1	8.2	7.8	0	6	1	60.3	61.5
41	0	0	20.8	18.1	17	4	0	20.8	18.1	17	9	0	10.4	5.7	7	1	1	32.4	32.2	-27	4	1	0	3.7	0	6	1	35.7	28.2
42	0	0	51.9	50.5	15	4	0	9.7	7.7	19	9	0	7.7	6.0	8	1	1	86.0	72.3	-36	4	1	0	4.5	2	6	1	6.8	4.3
43	0	0	26.7	27.3	1	10	0	0	0	2	10	0	22.5	24.2	10	1	1	29.5	29.1	-24	4	1	10.7	9.8	3	6	1	35.7	28.2
44	0	0	0	0	7.1	12.5	11	1	42.1	33.4	11	1	0	0	12	1	1	33.5	32.6	-22	4	1	0	8.4	5	6	1	29.2	23.0
45	0	0	16.0	17.6	3	10	0	21.4	25.1	12	1	1	0	0	14	1	1	51.8	34.6	-21	4	1	21.2	13.5	6	6	1	13.1	8.5
46	0	0	20.4	17.0	5	10	0	18.4	16.1	14	1	1	0	0	15	1	1	38.3	31.5	-20	4	1	15.4	8.9	7	6	1	31.2	31.7
47	0	0	16.8	6.7	6	10	0	7.5	5.7	15	1	1	0	0	16	1	1	48.6	32.4	-19	4	1	10.3	13.3	8	6	1	61.6	52.6
48	0	0	6.8	6.1	7	10	0	11.5	5.0	16	1	1																	

Table 1 (cont.)

continued:-																													
h	k	l	F	F																									
obs																													
7	9	1	23.1	14.7	-23	1	2	11.2	10.1	4	3	2	24.0	32.2	-4	6	2	0.	13.0	1	10	2	11.6	17.1	-5	2	3	24.0	22.2
8	9	1	14.7	13.7	-22	1	2	17.9	12.3	5	3	2	63.9	65.7	-3	6	2	6.3	9.0	2	10	2	0.	4.2	-4	2	3	28.3	33.1
9	9	1	18.7	14.8	-21	1	2	22.7	20.5	6	3	2	36.5	38.3	-2	6	2	23.7	29.8	3	10	2	0.	4.2	-3	2	3	37.8	36.6
10	9	1	26.0	13.7	-20	1	2	34.1	21.1	7	3	2	29.5	31.3	-1	6	2	19.6	66.0	4	10	2	15.6	16.2	-2	2	3	40.2	55.5
11	9	1	26.4	18.0	-18	1	2	20.4	19.6	8	3	2	22.4	26.0	0	6	2	11.4	9.0	5	10	2	7.8	10.8	-1	2	3	12.7	22.4
12	9	1	11.7		-17	1	2	32.3	27.8	9	3	2	15.4	32.3	1	6	2	55.7	59.3	6	10	2	0.	7.5	0	2	3	26.6	30.1
13	9	1	16.0	4.5	-16	1	2	24.0	19.7	10	3	2	34.6	36.4	2	6	2	9.4	4.4	7	10	2	17.4	17.5	1	2	3	20.5	38.5
14	9	1	14.4	13.9	-15	1	2	45.5	36.6	11	3	2	26.4	20.9	3	6	2	0.	10.1	8	10	2	18.2	13.8	4	2	3	18.1	15.4
15	9	1	9.9	7.7	-14	1	2	39.1	35.1	12	3	2	25.6	22.1	4	6	2	0.	6.2	9	10	2	9.7	10.4	3	2	3	20.2	21.1
16	9	1	9.0	4.2	-13	1	2	23.2	18.4	13	3	2	36.9	32.2	5	6	2	34.8	34.1	10	10	2	0.	4.3	4	2	3	20.5	38.5
17	9	1	14.0	10.1	-12	1	2	45.5	36.6	14	3	2	22.4	21.3	6	6	2	0.	10.1	10	10	2	0.	4.3	5	2	3	18.1	15.4
18	9	1	14.0	10.1	-11	1	2	51.3	50.9	15	3	2	25.6	22.1	7	6	2	0.	6.2	9	10	2	9.7	10.4	3	2	3	20.2	21.1
19	9	1	9.9	7.7	-10	1	2	63.7	54.9	16	3	2	36.9	32.2	8	6	2	27.7	28.0	13	10	2	0.	5.2	7	2	3	14.8	15.5
20	9	1	9.0	4.2	-9	1	2	67.2	64.8	17	3	2	22.4	21.3	9	6	2	16.1	16.1	14	10	2	0.	9.0	8	2	3	29.6	28.4
21	9	1	14.0	10.1	-8	1	2	57.5	49.7	18	3	2	18.6	15.6	10	6	2	20.0	17.5	5	11	2	11.4	11.5	9	2	3	8.2	8.7
22	9	1	14.0	10.1	-7	1	2	80.0	65.8	19	3	2	9.2	9.6	11	6	2	0.	3.1	-25	0	3	9.7	4.0	10	2	3	20.9	22.4
23	9	1	14.0	10.1	-6	1	2	61.6	60.6	20	3	2	12.7	13.6	12	6	2	9.8	19.3	-24	0	3	18.3	13.1	11	2	3	29.7	30.0
24	9	1	14.0	10.1	-5	1	2	95.5	40.2	21	3	2	4.8	13.0	13	6	2	28.6	27.3	-23	0	3	0.	2.1	12	2	3	56.2	61.5
25	9	1	14.0	10.1	-4	1	2	25.2	27.9	22	3	2	5.0	5.0	14	6	2	38.3	35.8	-4	10	2	15.4	15.7	-13	2	3	39.9	40.0
26	9	1	14.0	10.1	-3	1	2	41.2	41.5	-24	4	2	C.	3.3	15	6	2	11.9	10.8	-21	0	3	0.	0.8	14	2	3	15.7	21.4
27	9	1	14.0	10.1	-2	1	2	24.8	22.5	-23	4	2	11.5	5.7	16	6	2	12.8	13.8	-20	0	3	0.	5.4	15	2	3	29.2	27.8
28	9	1	14.0	10.1	-1	1	2	22.5	21.4	-22	4	2	19.3	13.6	17	6	2	0.	8.9	-19	0	3	0.	3.8	16	2	3	0.	7.5
29	9	1	14.0	10.1	0	1	2	62.9	81.9	-21	4	2	18.1	11.3	18	6	2	0.	2.5	-18	0	3	0.	1.3	17	2	3	0.	3.5
30	9	1	14.0	10.1	1	1	2	42.6	51.7	-20	4	2	0.	9.2	19	6	2	9.8	8.9	-17	0	3	0.	12.6	18	2	3	0.	3.5
31	9	1	14.0	10.1	2	1	2	55.9	62.1	-19	4	2	20.4	19.0	20	6	2	0.	8.8	-16	0	3	9.1	3.6	19	2	3	0.	3.9
32	9	1	14.0	10.1	3	1	2	57.7	65.5	-18	4	2	14.1	12.1	21	6	2	17.7	7.7	-15	0	3	10.0	10.1	20	2	3	13.8	61.7
33	9	1	14.0	10.1	4	1	2	25.3	29.7	-17	4	2	16.1	13.6	22	6	2	10.4	9.2	-14	0	3	31.6	37.5	21	2	3	22.7	19.5
34	9	1	14.0	10.1	5	1	2	20.9	27.9	-16	4	2	18.8	18.7	23	6	2	0.	4.3	-13	0	3	18.0	16.9	22	2	3	12.5	8.3
35	9	1	14.0	10.1	6	1	2	39.3	40.1	-15	4	2	27.4	26.9	-22	7	2	11.0	12.0	-12	0	3	24.1	22.3	23	2	3	9.9	14.5
36	9	1	14.0	10.1	7	1	2	16.9	16.2	-14	4	2	17.2	16.7	-18	7	2	17.7	15.7	-11	0	3	21.2	21.1	24	2	3	19.1	17.8
37	9	1	14.0	10.1	8	1	2	46.6	42.3	-13	4	2	37.8	36.8	-27	7	2	22.3	15.3	-10	0	3	23.3	17.1	-24	3	3	11.3	11.0
38	9	1	14.0	10.1	9	1	2	34.7	33.4	-12	4	2	21.6	22.7	-14	7	2	20.0	20.8	-9	0	3	23.4	26.4	-23	3	3	10.6	7.2
39	9	1	14.0	10.1	10	1	2	41.8	32.2	-11	4	2	21.4	22.6	-13	7	2	24.5	25.8	-8	0	3	55.7	5.1	-21	3	3	20.2	13.6
40	9	1	14.0	10.1	11	1	2	33.0	28.2	-10	4	2	33.2	32.2	-12	7	2	17.7	17.7	-7	0	3	47.7	44.8	-20	3	3	12.6	6.0
41	9	1	14.0	10.1	12	1	2	47.8	39.9	-9	4	2	0.	3.2	-11	7	2	20.1	18.1	-6	0	3	71.3	70.6	-18	3	3	16.3	9.6
42	9	1	14.0	10.1	13	1	2	8.4	11.7	-8	4	2	20.1	19.2	-8	7	2	28.1	27.0	-5	0	3	41.5	39.7	-17	3	3	12.8	13.7
43	9	1	14.0	10.1	14	1	2	18.9	17.4	-7	4	2	17.8	19.3	-9	7	2	38.3	35.8	-6	0	3	21.2	21.1	-16	8	3	19.1	17.8
44	9	1	14.0	10.1	15	1	2	18.1	18.8	-6	4	2	25.5	28.6	-5	7	2	20.5	22.8	-3	0	3	26.0	26.5	-15	3	3	25.5	23.7
45	9	1	14.0	10.1	16	1	2	23.3	19.2	-5	4	2	25.8	27.6	-4	7	2	27.8	29.4	-2	0	3	0.	7.5	-14	3	3	25.2	18.1
46	9	1	14.0	10.1	17	1	2	31.3	29.4	-4	4	2	80.0	82.7	-3	7	2	28.4	32.0	-1	0	3	0.	6.0	-13	3	3	39.0	34.8
47	9	1	14.0	10.1	18	1	2	20.1	13.3	-3	4	2	46.6	52.5	-2	7	2	62.6	62.5	0	0	3	0.	2.9	-12	3	3	19.1	17.8
48	9	1	14.0	10.1	19	1	2	12.0	11.9	-2	4	2	47.1	54.0	-1	7	2	11.4	9.9	1	0	3	37.5	38.3	-11	3	3	16.1	13.8
49	9	1	14.0	10.1	20	1	2	16.2	11.6	-1	4	2	10.9	9.5	1	7	2	12.7	14.4	2	0	3	39.8	40.4	-10	3	3	26.9	24.8
50	9	1	14.0	10.1	21	1	2	14.6	9.7	0	4	2	49.8	92.1	2	7	2	20.5	18.3	3	0	3	59.8	58.1	-9	3	3	32.8	34.8
51	9	1	14.0	10.1	22	1	2	14.8	9.4	1	4	2	40.3	3.3	3	7	2	17.7	17.7	4	0	3	31.7	31.7	-8	3	3	19.1	13.0
52	9	1	14.0	10.1	23	1	2	10.5	6.0	2	4	2	26.2	38.3	5	7	2	17.2	23.9	5	0	3	53.0	52.6	-7	3	3	13.0	21.7
53	9	1	14.0	10.1	24	1	2	0.	5.4	3	4	2	15.6	12.1	8	7	2	15.6	11.3	6	0	3	0.	4.4	-6	3	3	23.4	21.8
54	9	1	14.0	10.1	25	1	2	0.	10.7	4	4	2	55.3	66.0	10	7	2	17.9	18.7	7	0	3	56.4	49.8	-5	3	3	18.6	17.2
55	9	1	14.0	10.1	26	1	2	0.	5.9	5	4	2	35.9	35.9	11	7	2	17.5	12.8	8	0	3	12.8	8.8	-4	3	3	14.9	14.9
56	9	1	14.0	10.1	27	1	2	17.7	14.4	6	4	2	20.3	28.8	12	7	2	21.3	22.6	9	0	3	30.2	30.5	-3	3	3	35.2	40.3
57	9	1	14.0	10.1	28	1	2	0.	3.2	7	4	2	8.3	10.6	14	7	2	22.4	18.1	10	0	3	14.1	9.3	-2	3	3	19.1	23.3
58	9	1	14.0	10.1	29	1	2	0.	6.2	8	4	2	7.5	7.6	15	7	2	22.4	13.0	11	0	3	29.6	27.3	-2	3	3	13.0	13.0
59	9	1	14.0	10.1	30	1	2	25.3	20.2	-2	4	2	19.3	15.5	16	7	2	20.8	17.0	12	0	3	20.0	17.0	0	3	3	36.0	44.9
60	9	1	14.0	10.1	31	1	2	12.1	14.3	10	4	2	40.7	47.0	17	7	2	11.7	13.1	13	0	3	0.	5.5	2	3	3	24.9	30.7
61	9																												

Table 2. Final fractional positional parameters and standard deviations (each $\times 10^4$), and thermal parameters and standard deviations(\AA^2)

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	$\sigma(B)$
Br(1)	1991	2609	11127	2	7	10	5.95	0.11
Br(2)	3240	9980	3876	2	7	10	6.17	0.11
S(3)	3442	5152	3096	4	13	22	3.95	0.25
S(4)	1345	7673	9639	4	15	24	5.75	0.29
O(5)	3534	4396	1111	10	28	57	5.38	0.74
O(6)	3243	6308	2717	10	28	53	4.32	0.67
O(7)	3956	5267	4588	9	25	46	3.57	0.61
O(8)	4889	5936	6903	10	26	49	3.73	0.63
O(9)	4160	8146	7688	10	27	52	4.43	0.68
O(10)	5249	7838	9323	10	29	51	5.04	0.69
O(11)	5879	7020	7296	10	27	55	5.03	0.73
O(12)	5795	6890	11461	11	31	61	6.45	0.84
O(13)	0902	8317	8955	11	31	59	6.13	0.79
O(14)	1442	7566	11857	12	42	61	8.43	0.89
O(15)	1321	6341	8490	11	30	57	5.58	0.76
O(16)	1187	4006	6251	10	29	54	4.76	0.69
O(17)	0130	5440	5626	10	29	54	5.41	0.79
O(18)	0409	2910	4043	10	27	51	4.79	0.70
O(19)	0826	1505	6270	12	34	62	6.70	0.83
O(20)	0846	1584	2159	11	33	60	6.19	0.82
N(21)	5721	7074	9378	13	36	71	5.46	0.91
N(22)	0778	1812	4289	13	37	74	5.87	0.97
C(23)	2396	3331	8665	15	42	81	4.39	1.06
C(24)	2780	2695	7543	15	49	76	4.68	0.99
C(25)	3111	3143	5608	15	42	82	4.64	1.07
C(26)	3027	4348	5221	15	41	80	4.46	1.04
C(27)	2636	5176	6270	14	41	73	3.82	0.91
C(28)	2336	4537	8227	16	41	81	4.47	1.07
C(29)	3997	6048	6805	15	40	76	3.66	0.98
C(30)	4430	5632	8314	16	43	81	4.29	1.06
C(31)	4798	6945	5582	15	40	81	4.37	1.03
C(32)	4223	7216	5396	13	34	70	2.55	0.86
C(33)	4573	9069	7553	17	48	93	6.32	1.22
C(34)	5022	8143	6960	14	39	74	3.57	0.93
C(35)	2705	9305	6016	14	37	74	3.33	0.91
C(36)	2808	8492	7519	17	46	90	5.67	1.24
C(37)	2400	8074	8986	17	47	90	6.24	1.25
C(38)	1868	8345	8145	14	39	76	3.68	0.95
C(39)	1773	9196	6402	19	50	99	7.23	1.39
C(40)	2179	9707	5130	15	42	81	4.60	1.06
C(41)	0941	6123	6527	16	42	80	4.44	1.09
C(42)	1225	5117	4876	15	46	77	4.53	0.97
C(43)	0748	4047	8077	16	45	85	5.20	1.11
C(44)	0530	5377	7650	13	33	68	2.37	0.81
C(45)	-0151	4250	6278	16	42	81	4.58	1.08
C(46)	0280	3268	6441	15	40	75	3.98	0.99

Table 3. Bond distances (\AA) and valency angles ($^\circ$)

Standard deviations are 0.03–0.06 \AA and 2° – 4° . The short intramolecular non-bonded distances are also given.

Br–C	1.87, 1.96, mean 1.92
S–C	1.81, 1.75, mean 1.78
S–O	1.57, 1.60, mean 1.59
S=O	1.38, 1.40, 1.41, 1.22
C–O	mean 1.35 [1.40, omitting O(14)] 1.35–1.61 (12 bonds)
C _{ar} –C _{ar}	1.24–1.52 (12 bonds)
C _{sp³} –C _{sp³}	mean 1.41 1.46–1.73 (10 bonds)
O–N	mean 1.58
N=O	1.50, 1.56, mean 1.53 1.19, 1.15, 1.12, 1.18 mean 1.16
O–S–C	104; 104; mean 104
O=S–C	107, 109; 108, 109; mean 108

Table 3 (cont.)

O=S–O	107, 108; 107, 110; mean 108
O=S=O	121; 118; mean 120
\angle at O (in ring)	109, 109, 111, 97, mean 107
\angle at O (not in ring)	121, 119, 117, 108, mean 116
\angle at C _{ar}	110–131 (20 angles), mean 119
\angle at C _{sp³}	96–116 (28 angles), mean 101
O–N=O	107, 105, 113, 101, mean 107
O=N=O	147, 146, mean 147
O(11)···O(8)	2.86
O(19)···O(16)	2.94
O(12)···O(8)	3.55
O(20)···O(16)	3.58
O(10)···O(8)	2.65
O(18)···O(16)	2.65
N(21)···O(8)	2.84
N(22)···O(16)	2.86

Various mean planes were computed. Each aromatic ring, with the attached bromine and sulphur atoms, is approximately planar. The nitrate groups are also

planar within experimental error (deviations from best planes are O(10), 0.01 Å; O(11), 0.02 Å; O(12), 0.02 Å; N(21), -0.03 Å; and O(18), -0.01 Å; O(19), -0.02 Å; O(20), -0.02 Å; N(22), 0.04 Å). All the five-membered rings are significantly non-planar. Each ring may be described in terms of planes through four atoms – the two atoms which are common to two five-membered rings, and the two atoms bonded to these; the fifth atoms are displaced from these planes by about $\frac{1}{2}$ Å. However, some of the four-atom planes are not very satisfactory, and other descriptions taking planes through various sets of four or of three atoms could be given.

All the intermolecular distances less than 4.0 Å were calculated. There are a large number of short contacts, nearly all involving oxygen atoms, and those distances less than 3.4 Å are listed in Table 4. The shortest Br...C and C...C separations are 3.65 Å and 3.47 Å respectively. The packing of the molecules in the unit cell is illustrated in Fig. 2.

Finally it may be noted that, since the compound is derived from *D*-glucose, the absolute configuration is established; the parameters of Table 2 referred to a right-handed set of axes give the true absolute configuration. Figs. 1 and 3, and (I), also depict the correct absolute configuration.

Discussion

The two molecules in the asymmetric unit are of course crystallographically independent. Projections of the two molecules in similar orientations were constructed, and are shown in a composite diagram in Fig. 3. It is clear that the nitrate group conformation is exactly the same in both molecules, and that the conform-

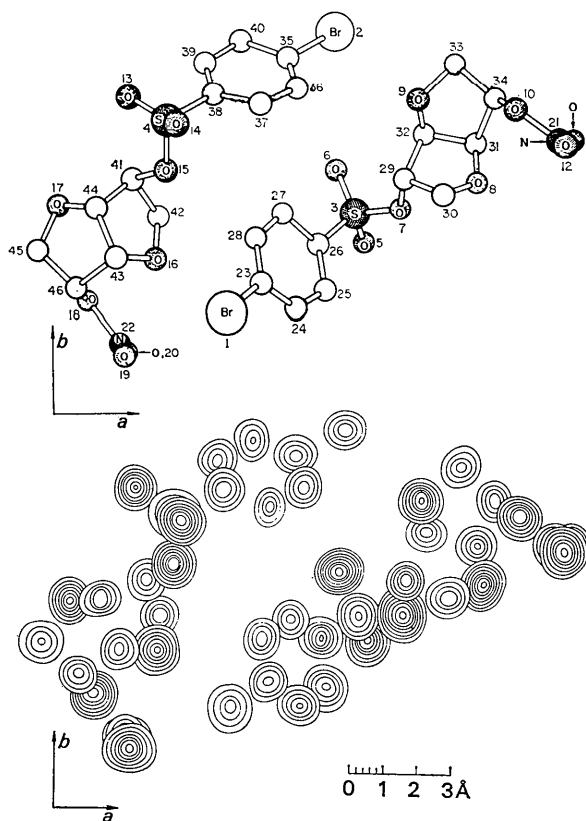


Fig. 1. Superimposed sections of the third three-dimensional electron-density distribution, taken through the atomic centres parallel to (001). Contours are at intervals of 2, 3, 4... $e.\text{Å}^{-3}$ for C, N, O; 2, 5, 10, 15... $e.\text{Å}^{-3}$ for S and 10, 20, 30... $e.\text{Å}^{-3}$ for Br. A perspective drawing of the two molecules in the asymmetric unit is also shown; the atom numbering is for convenience in the crystallographic analysis, and has no chemical significance.

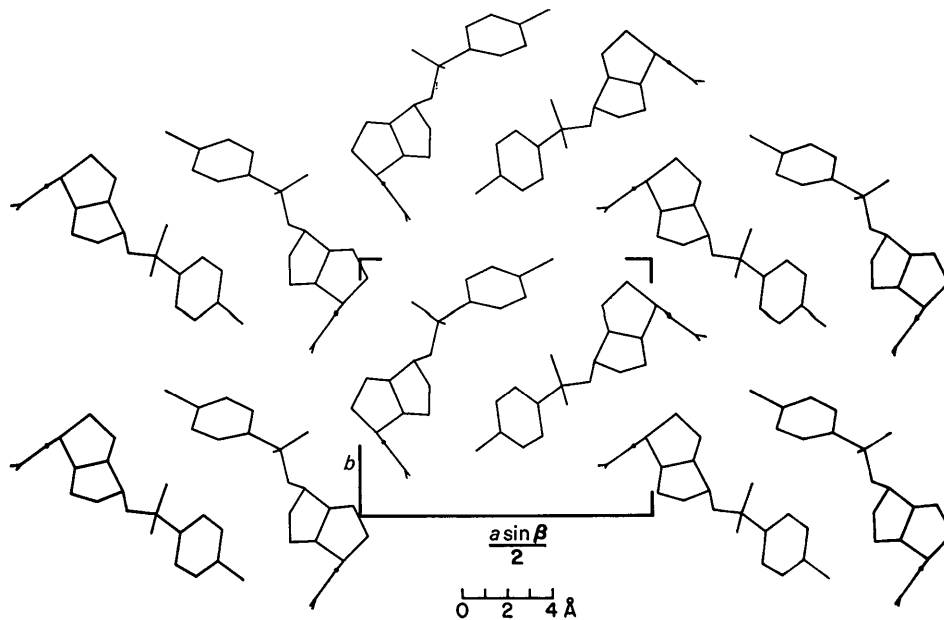


Fig. 2. Projection of the structure along [001], showing the molecular packing.

ations of the *p*-bromobenzenesulphonyl groups differ slightly. The aromatic ring of each derivative group is planar together with its attached bromine and sulphur atoms. The five-membered rings are non-planar; the rings may be described in terms of various planes through sets of four or of three atoms, or in terms of various dihedral angles, so that it is not useful to give any of these in detail. Any information required can be derived readily from Table 2. The dihedral angle

between the five-membered rings cannot be given precisely because of the impossibility of defining the rings by any unique planes, but the value is about 110° . The ONO_2 groups are planar. These and various other features of the molecule can be seen from Figs. 1 and 3.

The bond distances and valency angles in the molecule do not differ significantly from normal values. The mean distances are $C_{\text{ar}}-C_{\text{ar}}=1.41 \text{ \AA}$, $C_{sp^3}-C_{sp^3}=1.58 \text{ \AA}$, $C-O=1.47 \text{ \AA}$, $S-C=1.78 \text{ \AA}$, $S-O=1.59 \text{ \AA}$, $S=O=1.35 \text{ \AA}$, $\text{Br}-C_{\text{ar}}=1.92 \text{ \AA}$, and in the nitrate group, $O-N=1.53 \text{ \AA}$, $N=O=1.16 \text{ \AA}$. The mean angle at C_{sp^2} is 119° , at C_{sp^3} 101° , at ring oxygen atoms 107° , and at side-chain oxygen atoms 116° . At the sulphur atom the $O=S=O$ angle (120°) is very significantly larger than the other angles, as is usual in this type of derivative (compare, for example, Camerman & Trotter, 1965; Macdonald & Trotter, 1965). In the nitrate group the $O=N \rightarrow O$ angle (147°) is very significantly larger than the value of about 130° in nitric acid (Millen & Morton, 1960), in pentaerythritol tetranitrate (Trotter, 1963), and in *cis*-acenaphthenediol dinitrate (Mak & Trotter, 1964).

The most significant non-bonded intramolecular distances involve the nitrate group and the oxygen atom in the other five-membered ring, and these approaches are the same in both molecules. The shortest contact (2.65 \AA) involves the ring oxygen and the first side chain oxygen, but these atoms are constrained to be relatively close together as a result of the rigid molecular framework. The next shortest distances are $O \cdots N$ (2.85 \AA) and $O \cdots O$ (2.90 \AA), as given in Table 3, and illustrated in Fig. 3. The other nitrate oxygen atom is 3.57 \AA from the oxygen of the other five-membered ring (Table 3). As with *cis*-acenaphthenediol dinitrate (Mak & Trotter, 1964), the molecule can adopt a large number of conformations as a result of rotations about C-O and O-N bonds, and the adoption of the same conformation in two crystallographically independent molecules is virtually conclusive evidence that intramolecular forces are involved. Again the $O \cdots O$ contact (2.90 \AA) is only a little greater than the van der Waals distance, and is almost certainly a result of attractive forces between the relatively negative nitro oxygen and the relatively positive ring oxygen.

There are a large number of relatively short intermolecular contacts (Table 4), but on the basis of the van der Waals radii (Br, 1.95 \AA ; S, 1.85 \AA , C, 1.7 \AA ; N, 1.5 \AA ; O, 1.4 \AA , Pauling, 1960), these approaches all correspond to normal van der Waals interactions, and require no special comment.

The authors are indebted to Dr L. D. Hayward and Mr D. J. Livingstone for the crystal sample and for much helpful discussion, to the staff of the U.B.C. Computing Centre for assistance with the computations on the IBM 7040 computer, and to the National Research Council of Canada for financial support and for the award of research studentships (to A. C. and N. C.).

Table 4. Shortest intermolecular distances (\AA)

All distances $\leq 4.0 \text{ \AA}$ were calculated; only the crystallographically independent contacts $< 3.4 \text{ \AA}$ are listed

Atom (Molecule 1) to	Atom in Molecule	<i>d</i>
C(28)	O(15)	1 3.33 \AA
C(28)	O(16)	1 3.24
Br(1)	O(20)	2 3.25
Br(2)	O(11)	6 3.30
O(11)	O(5)	6 3.17
O(11)	C(25)	6 3.32
O(12)	O(11)	2 3.12
O(14)	C(39)	2 3.15
O(14)	C(41)	2 3.25
O(14)	C(42)	2 3.22
O(17)	O(18)	4 3.09
O(17)	O(19)	4 2.94
O(17)	O(20)	4 3.09
O(17)	N(22)	4 2.82
O(19)	O(20)	2 3.15
N(21)	O(5)	6 3.25
C(24)	O(5)	2 3.33
C(29)	O(5)	2 3.19
C(30)	O(5)	2 3.11
C(33)	O(12)	7 3.32
C(45)	O(19)	4 3.35
C(45)	O(20)	4 3.28
C(45)	N(22)	4 3.30

Molecule	1	<i>x</i>	<i>y</i>	<i>z</i>
2	<i>x</i>	<i>y</i>	$1+z$	
3	$-x$	$\frac{1}{2}+y$	$-z$	
4	$-x$	$\frac{1}{2}+y$	$1-z$	
5	$1-x$	$\frac{1}{2}+y$	$-z$	
6	$1-x$	$\frac{1}{2}+y$	$1-z$	
7	$1-x$	$\frac{1}{2}+y$	$2-z$	

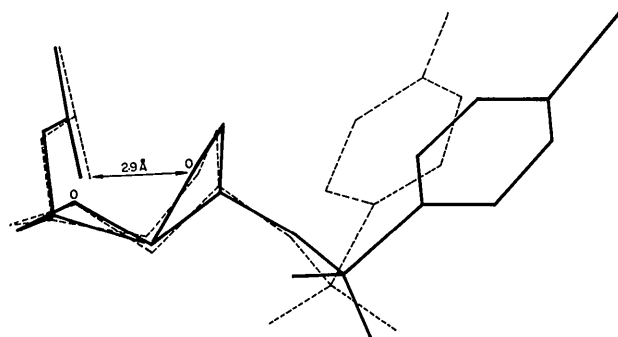


Fig. 3. Composite projection of the two independent molecules in the asymmetric unit, showing the similar conformation of the nitrate groups, and the short intramolecular non-bonded contact.

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The Crystal and Molecular Structure of *anti*-7-Norbornenyl *p*-Bromobenzoate

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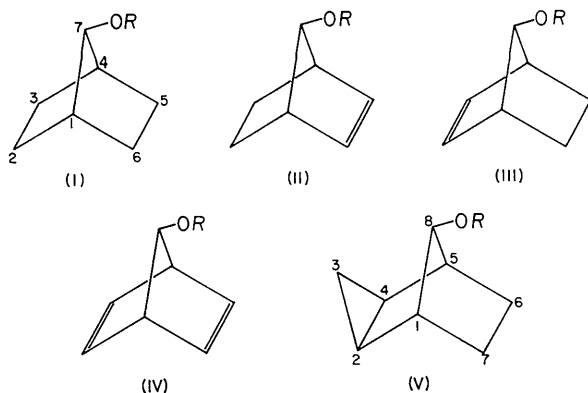
(Received 15 December 1964)

The crystal structure of *anti*-7-norbornenyl *p*-bromobenzoate, $C_{14}H_{13}O_2Br$, has been determined to provide further quantitative molecular data to assist in the interpretation of rates of solvolysis of norbornane derivatives. The crystals are monoclinic, $a=8.81$, $b=10.17$, $c=14.10$ Å, $\beta=99^\circ 51'$, $Z=4$, space group $P2_1/a$. The intensities of 2506 reflexions were measured with a scintillation counter using Cu $K\alpha$ radiation; 2059 reflexions had an intensity greater than background. The structure was determined by heavy-atom Patterson and Fourier methods, and the positional and anisotropic thermal parameters were refined by differential syntheses and least squares. The final R was 0.18.

The bond distances in the molecule are all normal, but the valency angles in the norbornene nucleus are all less than the tetrahedral value. The angles at the double bond are 107° ; the bridgehead angle is 96° , not significantly different from the corresponding angle in the *anti*-8-tricyclo-octane nucleus. All the intermolecular distances correspond to van der Waals interactions.

Introduction

The rates of solvolysis of the compounds (I), (II), (III), (IV) ($R=p$ -bromobenzenesulphonyl) are in the ratio 1: 10^4 : 10^{11} : 10^{14} . It has been postulated as one possible reason for this remarkable variation in solvolytic reactivity that, since the transition state involves sp^2 hybridization at atom 7, an increase in this bridgehead angle would facilitate formation of the transition state and hence increase the solvolysis rate. No real quantitative assessment of this factor is possible owing to a lack of molecular structure data, and the angle has generally been estimated from models, or derived from empirical relations involving infrared stretching frequencies (see *e.g.* Schleyer & Nicholas, 1961).



Recently we have determined the structure of *anti*-8-tricyclo[3,2,1,0^{2,4}]-octyl *p*-bromobenzenesulphonate (V, $R=p$ -bromobenzenesulphonyl), and found that the bridgehead angle, C(1)–C(8)–C(5), is 97° (Macdonald & Trotter, 1965); this compound has a solvolysis rate comparable to that of (I), so that an angle of about 97° would appear to be characteristic of a lack of solvolytic reactivity. We have now investigated the structure of *anti*-7-norbornenyl *p*-bromobenzoate (III, $R=p$ -bromobenzoyl); if the variation of bridgehead angle controls the solvolysis rate, then the angle should be considerably greater than 97° . We find that the angle is 96° .

Experimental

Crystals of *anti*-7-norbornenyl *p*-bromobenzoate are colourless plates elongated along a with (001) developed. The density was measured by flotation in aqueous potassium iodide, and the unit-cell dimensions and space group were determined from various rotation and Weissenberg photographs, and on the General Electric Spectrogoniometer.

Crystal data (λ , Cu $K\alpha=1.5418$ Å).

anti-7-Norbornenyl *p*-bromobenzoate, $C_{14}H_{13}O_2Br$;
 M.W. 293.2; m.p. 70–73 °C.

Monoclinic, $a=8.81 \pm 0.02$, $b=10.17 \pm 0.02$, $c=14.10 \pm 0.03$ Å, $\beta=99^\circ 51' \pm 5'$.
 $U=1245$ Å³.