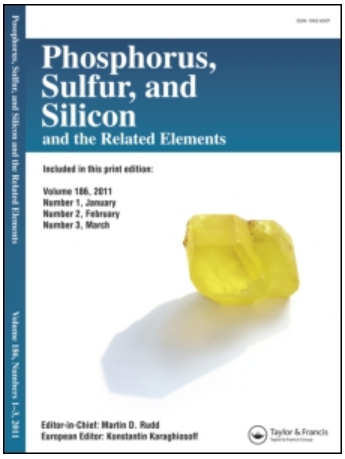

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ABSOLUTE CONFIGURATION OF (+)2-(3'- NITROBENZYLSULFINYL)-BENZOIC ACID

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ABSOLUTE CONFIGURATION OF (+)2-(3′-NITROBENZYLSULFINYL)-BENZOIC ACID

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Using single crystal X-ray diffraction technique the R configuration has been assigned to a (+)2-(3′-nitrobenzylsulfinyl)-benzoic acid. In the molecule an extended chain C8—S—C1—C2 is observed. Both phenyl rings lie on almost one plane. O1 and O5 atoms are involved in attractive interactions.

Key words: 2-(3′-Nitrobenzylsulfinyl)-benzoic acid; X-ray structure analysis; absolute configuration

INTRODUCTION

The problem of the influence of position isomerism of certain substituents and functional groups in aromatic rings on the optical properties of aromatic-aliphatic systems containing heteroatomic chirality centers separated from aromatic fragments of the molecules by methylene groups has been studied by us on the examples of benzylsulfinylacetic and orthobenzylsulfinylbenzoic acids and their derivatives. The observed optical order in the group of isomeric bromobenzylsulfinylacetic acids[1–4] as well as in the group of isomeric bromobenzylsulfinylbenzoic acids[5–8] suggested that a single methylene group did not isolate completely the chiral sulfoxide system from the effects caused by substituents in the aromatic ring. The observed optical and stereochemical relationships encouraged us to further study the group of compounds with nitro groups as substituens in the arene nuclei.

Our investigations started with a comparative study of principal chiroptical properties of 2-(benzylsulfinyl)-benzoic acids and their nitro derivatives with nitrogroup in the benzene ring of benzyl moiety i.e., isomeric 2-(nitrobenzylsulfinyl)-benzoic acids. Until now we have synthesized the enantiomeric 2-(3′-nitrobenzylsulfinyl)-benzoic acids and we have determined their spatial configurations[9] as R(+) and S(−) on the basis of the Freudenberg optical shifts rule taking R(+) 2-(3′- and 4′- bromobenzylsulfinyl)-benzoic acids[6,7] as configuration standards. This configuration correlation was confirmed by present X-ray analysis of (+) 2-(3′-nitrobenzylsulfinyl)-benzoic acid.

RESULTS AND DISCUSSION

The molecular structure of (+)-2-(3′-nitrobenzylsulfinyl)-benzoic acid is displayed in Figure 1 which shows also its absolute configuration.

According to Cahn-Ingold-Prelog rules[10] the configuration at sulphur atom is R. In the molecule under investigation, an extended chain C8—S—C1—C2 is observed [C8—S—C1—C2 = 178.4(2)°]. This conformation is entirely different from (−)-methyl 2-(4-bromobenzylsulfinyl) benzoate, where the conformation around the S—C_{sp^3} bond is sc—sc.[11]

The situation of phenyl ring **I** relative to the extended chain C8—S—C1—C2 is the same as that of the bromophenyl ring in (−)-m-bromobenzylsulfinylacetic acid.[12] The torsion angle S—C1—C2—C3 in both compounds is 88.6(3) and 88.6(11)°, respectively, and in the molecule of (−)-methyl 2-(4-bromobenzylsulfinyl) benzoate it equals 73.6(6)°. The situation of benzoate ring in this molecule and ring **II** in the molecule under study is also similar. Torsion angles C1—S—C8—C9 and C1—S—C8—C13 are 81.7(5), 99.3(5)° and 95.3(2), 91.7(2)°, respectively. Phenyl ring **I** is ideally flat. The maximum deflection from the plane is observed for atom C4 (0.004(4)Å), while atoms of ring **II** deviate significantly from planarity. Atoms C13, C12 and C10 are most out of plane (−0.016(3), 0.015(3) and −0.011(3)Å, respectively). Three hydrogen atoms of this ring are involved in attractive interactions of C—H . . . O type; two are intramolecular C13—H131 . . . O1 and C10—H101 . . . O5 and one is intermolecular C11—H111 . . . O1. Atom O5 occurs also as a donor in a strong, almost linear intermolecular hydrogen bond O5—H5 . . . O1 (Figure 2). The details of this bonding are listed in Table I.

Both phenyl rings are almost coplanar, the dihedral angle between them is 1.7(2)°.

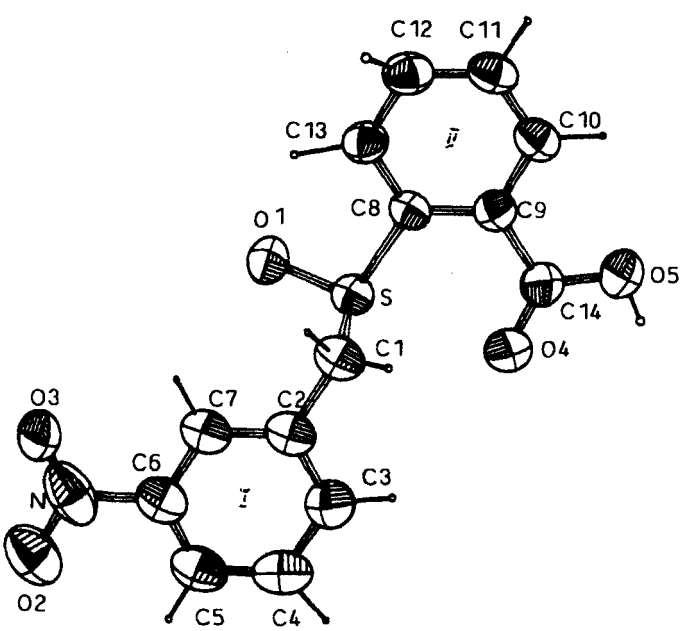

FIGURE 1 Projection of the molecule.

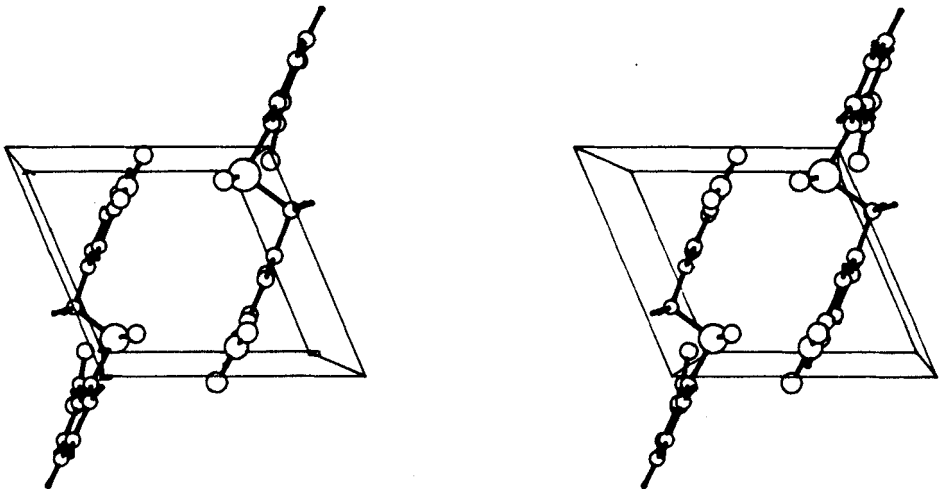

FIGURE 2 The packing in the unit cell along the b axis.

TABLE I
Details of hydrogen bonding

	Distance (Å)			Angle (°)	
D-H...A	D-H	D...A	H...A	D-H...A	
C13-H131...O1	0.97(4)	2.844(3)	2.33(4)	112(3)	
	1.08		2.29	109	(*)
C10-H101...O5	1.01(4)	2.764(4)	2.38(4)	101(3)	
	1.01		2.37	99	(*)
O5-H5...O1[a]	1.02(7)	2.560(4)	1.55(7)	177(7)	
	0.94		1.62	177	(*)
C11-H111...O1[b]	1.03(4)	3.295(3)	2.33(4)	155(4)	
	1.08		2.29	154	(*)

Symmetry code: none x, y, z

[a] -x,y-1/2,-z

[b] x-1,y,z-1

(*) Values normalized following Jeffrey and Lewis, Carbohydr.Res (1978) 60, 179; R.Taylor, O.Kennard, Acta Cryst.(1983) B 39, 133.

The NO_2 group is inclined by 6.7(2)° to phenyl ring **I** while the carboxyl group forms with phenyl ring **II** an angle of 12.8(1)°.

S=O1 bond is of a length typical for sulfoxide groups[13-15] and its inclination to phenyl ring **I** equals 17.3(1)°.

EXPERIMENTAL SECTION

Crystal data: $C_{14}H_{11}NO_5S$, M = 305.3. Monoclinic. a = 7.310(1), b = 13.557(1), c = 7.686(1)Å, β = 113.16(1)°. Space group $P2_1$, V = 700.3(2)Å^3, d_x = 1.448 Mgm^{-3}, d_m = 1.45 Mgm^{-3}, Z = 2, μ = 22.11 cm^{-1}, F(000) = 316.

Accurate cell dimensions were obtained by a least-squares fit to the θ value of 25 reflections measured on an Enraf Nonius CAD 4 diffractometer. The intensity data were collected using CuKα radiation

TABLE II

Positional parameters ($\times 10^4$) for the nonhydrogen atoms

	x	y	z
S	973(1)	2555(0)	921(1)
O(1)	1314(3)	3503(2)	2010(2)
O(2)	10405(4)	3981(3)	5689(4)
O(3)	8102(5)	4900(3)	3783(7)
O(4)	124(3)	788(2)	-777(4)
O(5)	-2918(4)	214(3)	-2476(5)
N	8808(4)	4098(3)	4351(4)
C(1)	2634(3)	2622(3)	-349(3)
C(2)	4741(3)	2521(3)	1084(3)
C(3)	5593(4)	1589(3)	1567(5)
C(4)	7519(5)	1488(3)	2964(5)
C(5)	8572(5)	2309(3)	3875(4)
C(6)	7712(4)	3221(3)	3380(4)
C(7)	5814(4)	3339(2)	1994(4)
C(8)	-1385(3)	2727(2)	-1049(3)
C(9)	-2498(4)	1927(2)	-2053(3)
C(10)	-4426(4)	2098(2)	-3428(4)
C(11)	-5170(4)	3048(3)	-3797(4)
C(12)	-4035(4)	3831(2)	-2809(4)
C(13)	-2148(4)	3675(2)	-1391(4)
C(14)	-1646(4)	928(2)	-1703(4)

TABLE III
Bond lengths (Å) and angles (°)

O(1)	---S	1.500(3)		C(1)	---S	1.835(3)	
C(8)	---S	1.807(2)		N	---O(2)	1.225(3)	
N	---O(3)	1.209(6)		C(14)	---O(4)	1.222(3)	
C(14)	---O(5)	1.312(4)		C(6)	---N	1.464(5)	
C(2)	---C(1)	1.501(3)		C(3)	---C(2)	1.393(5)	
C(7)	---C(2)	1.379(4)		C(4)	---C(3)	1.402(4)	
C(5)	---C(4)	1.378(5)		C(6)	---C(5)	1.371(6)	
C(7)	---C(6)	1.387(3)		C(9)	---C(8)	1.393(3)	
C(13)	---C(8)	1.384(4)		C(10)	---C(9)	1.409(3)	
C(14)	---C(9)	1.471(4)		C(11)	---C(10)	1.383(5)	
C(12)	---C(11)	1.377(4)		C(13)	---C(12)	1.397(3)	

C(1)	-S	-O(1)	104.4(2)	C(8)	-S	-O(1)	104.6(1)
C(8)	-S	-C(1)	99.2(1)	O(3)	-N	-O(2)	123.4(4)
C(6)	-N	-O(2)	118.2(3)	C(6)	-N	-O(3)	118.4(3)
C(2)	-C(1)	-S	107.9(2)	C(3)	-C(2)	-C(1)	119.9(3)
C(7)	-C(2)	-C(1)	120.8(3)	C(7)	-C(2)	-C(3)	119.3(3)
C(4)	-C(3)	-C(2)	120.1(3)	C(5)	-C(4)	-C(3)	120.2(4)
C(6)	-C(5)	-C(4)	118.9(3)	C(5)	-C(6)	-N	119.5(3)
C(7)	-C(6)	-N	118.7(3)	C(7)	-C(6)	-C(5)	121.9(3)
C(6)	-C(7)	-C(2)	119.6(3)	C(9)	-C(8)	-S	121.4(2)
C(13)	-C(8)	-S	117.3(2)	C(13)	-C(8)	-C(9)	120.9(2)
C(10)	-C(9)	-C(8)	118.8(2)	C(14)	-C(9)	-C(8)	120.2(2)
C(14)	-C(9)	-C(10)	121.0(3)	C(11)	-C(10)	-C(9)	120.2(3)
C(12)	-C(11)	-C(10)	120.1(3)	C(13)	-C(12)	-C(11)	120.6(3)
C(12)	-C(13)	-C(8)	119.3(2)	O(5)	-C(14)	-O(4)	123.3(3)
C(9)	-C(14)	-O(4)	121.7(3)	C(9)	-C(14)	-O(5)	115.0(3)

and a graphite monochromator in an $\omega - 2\theta$ scan mode. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The 1503 reflections with $I > 2\sigma(I)$ were used in the subsequent analysis. The structure was solved by direct methods, using the SHELXS-86 program [16] and refined by the full-matrix least-squares method.

All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were located from a difference Fourier map and their positional and individual isotropic thermal parameters were refined. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, and in the final cycles of calculation a weighting scheme based on counting statistics was used with $w = [\sigma^2(F_o) + 0.0068(F_o)^2]^{-1}$. An empirical isotropic extinction correction was introduced, and the parameter x was refined to the value 0.037(5). The final difference Fourier synthesis showed only peaks with an electron density ≤ 0.15 eÅ^{-3}. Most of the computations were performed with SHELX-76 crystal structure determination program[17] on an AMSTRAD-1512 microcomputer. Convergence was obtained at R = 0.036, R_w = 0.038.

Absolute Configuration

The R (at sulphur atom) configuration was confirmed with the Hamilton R-test.[18] The final R(R_w) factor is 0.036 (0.038) for a refinement of the structure with an R (at sulphur atom) configuration and

TABLE IV

Anisotropic thermal parameters ($\times 10^4$) for the nonhydrogen atoms

	U 11	U 22	U 33	U 23	U 13	U 12
S	295(3)	622(3)	435(3)	86(2)	85(2)	17(2)
O(1)	447(9)	693(9)	523(8)	-3(7)	92(7)	-18(7)
O(2)	473(12)	156(27)	692(12)	-110(16)	65(9)	-111(16)
O(3)	705(18)	1018(20)	1392(30)	-88(20)	150(18)	-160(17)
O(4)	412(10)	690(11)	1042(16)	-48(11)	48(10)	78(9)
O(5)	483(12)	657(11)	1207(19)	-94(12)	98(12)	-48(9)
N	446(13)	1105(22)	683(14)	-66(15)	209(11)	-116(13)
C(1)	333(10)	941(16)	483(11)	112(12)	135(8)	14(13)
C(2)	332(10)	836(14)	524(10)	120(12)	175(8)	22(12)
C(3)	465(14)	774(15)	699(15)	87(13)	219(11)	21(13)
C(4)	510(16)	932(22)	765(18)	239(16)	261(14)	191(15)
C(5)	350(12)	1101(25)	616(13)	217(15)	164(11)	82(14)
C(6)	336(11)	962(18)	543(13)	73(12)	173(10)	-34(11)
C(7)	329(11)	814(16)	533(13)	130(10)	140(9)	23(10)
C(8)	288(9)	662(15)	438(9)	42(8)	97(7)	1(9)
C(9)	328(11)	658(12)	481(10)	2(8)	124(9)	-5(9)
C(10)	316(12)	842(16)	496(11)	-4(11)	82(10)	-10(11)
C(11)	368(11)	934(17)	473(11)	67(12)	69(9)	129(12)
C(12)	436(13)	773(15)	553(13)	102(11)	100(11)	151(12)
C(13)	435(12)	643(13)	547(13)	57(10)	120(10)	41(10)
C(14)	390(12)	645(13)	672(13)	-15(11)	147(10)	-24(10)

TABLE V

Positional parameters ($\times 10^3$) and U_{iso} ($\times 10^3$) for hydrogen atoms

	x	y	z	U
H(5)	-224(10)	-46(5)	-228(10)	103(13)
H(11)	240(6)	326(3)	-87(5)	56(8)
H(12)	228(8)	219(4)	-141(7)	96(13)
H(31)	498(7)	98(4)	100(6)	76(12)
H(41)	788(10)	82(5)	297(8)	107(13)
H(51)	984(6)	219(3)	490(5)	54(8)
H(71)	517(6)	399(3)	167(5)	60(8)
H(101)	-519(6)	149(3)	-409(6)	67(10)
H(111)	-655(7)	314(4)	-489(7)	94(13)
H(121)	-469(7)	448(4)	-312(7)	84(11)
H(131)	-134(6)	418(3)	-54(6)	65(9)

R^- (R_w^-) is 0.040 (0.042) for the opposite configuration. The resulting R^- and R_w^- values showed that the model with inverse configuration had to be rejected with very high probability. The R_{ratio} ($R_{w\ ratio}$) is 1.111 (1.105) for N = 1269 independent parameters. According to the Pearson and Hartley tables of R_{ratio} values[19] as the function of the significance level α, and number of independent parameters, the significance level $\alpha < 10^{-6}$.

Tables II, IV and V give the final atomic positional and thermal parameters and Table III the bond lengths and angles. The molecular structure is displayed in Figure 1, which shows also its absolute configuration. Figure 1 presents the numbering of atoms and rings used in the discussion. Figure 2 shows a view of the molecular packing in the unit cell along the b axis.

Tables listing anisotropic thermal parameters and hydrogen atoms parameters have been deposited with the Cambridge Crystallographic Data Centre.

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