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# STEREOCHEMISTRY OF ERYSULFONE

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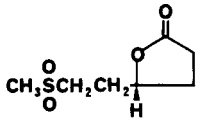
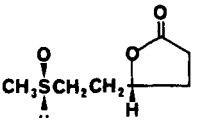
ABSTRACT.—Conformation of the stereochemistry of the chiral center in erysulfone [**1**] has been established by single crystal X-ray characterization and optical rotatory dispersion (ORD) data.

We isolated erysulfone [**1**] and erysulfoxide [**2**] from *Erysimum inconspicuum* but were unable fully to verify the stereochemistry of the chiral centers from the optical rotatory dispersion (ORD) data secured (1,2). Erysulfone [**1**] exhibited a negative plain dispersion curve with $[\Phi]_{589}$ −75.79. Based upon similarities in the signs of the reported rotations (3) of $[\alpha]^{20}D$ −53.2° and −48.8° for (4*S*)-4-methyl-4-hydroxybutanoic acid lactone and (4*S*)-4-butyl-4-hydroxybutanoic acid lactone, respectively, and X-ray structural analysis, a configurational assignment of *R* was made for its C-4 chiral center as depicted in Figure 1.



1



2

Erysulfoxide [**2**], on the other hand, had a positive dispersion curve and $[\Phi]_{589}$ +86.71. If the signs for the rotational value of $[\alpha]^{20}D$ −61.6° (4) for the *R* form of 5-methylsufinylpentylisocyanate and the value of $[\alpha]^{27}D$ +42° for (*S*)-methyl-*n*-butylsulfoxide (5) are compared to the butanoic acid lactones, then the overall positive value for erysulfoxide leads one to conclude an *S* configuration for the sulfoxide moiety.

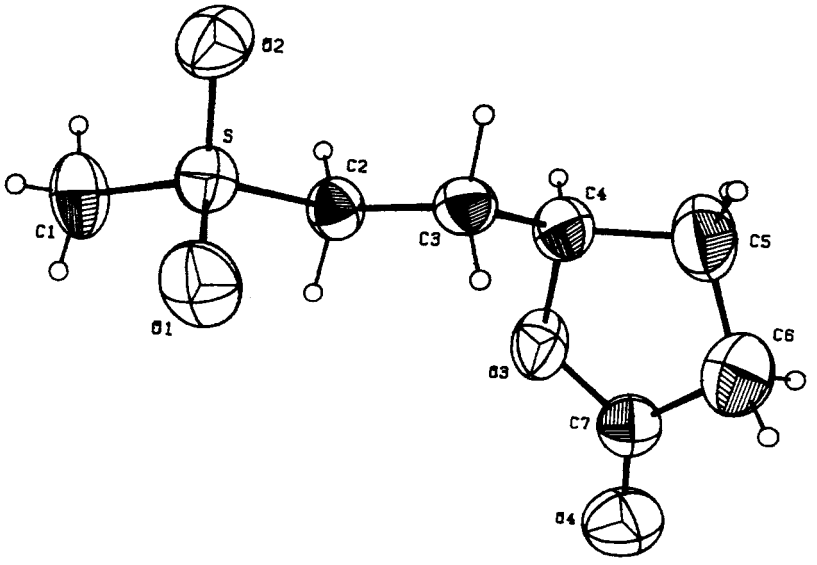



FIGURE 1. ORTEP illustration of erysulfone with 50% probability ellipsoids. The H atom radii have been arbitrarily reduced.

## EXPERIMENTAL

X-RAY DATA COLLECTION, STRUCTURE DETERMINATION, AND REFINEMENT FOR $C_7H_{12}O_4S$.—The isolation and rotations for **1** and **2** have been reported (1,2). A transparent single crystal of **1** was mounted on a pin and transferred to the goniometer. The space group was determined to be either the centric $P2_1/m$ or acentric $P2_1$ from the systematic absences. Statistical tests indicated that the space group was acentric, and the subsequent solution and successful refinement of the structure were carried out in the acentric space group $P2_1$. A summary of data collection parameters is given in Table 1.

The investigation of absolute conformation was carried out by the collection of a set of reflections equivalent in $P2_1/m$ (Freidel pair). The

TABLE 1. Crystal Data and Summary of Intensity Data Collection and Structure Refinement.

| | |
|---|---|
| Compound | $C_7H_{12}O_4S$ |
| Mol wt | 192.23 |
| Space group | $P2_1$ (monoclinic) |
| Cell Constants | |
| *a* | 7.193(1) Å |
| *b* | 5.550(1) Å |
| *c* | 11.346(2) Å |
| β | 92.89°(1) |
| Cell vol | 452.4 Å$^3$ |
| Formula units/unit cell | 2 |
| D | 1.41 g·cm$^{-3}$ |
| Radiation, graphite monochromator | MoKα (λ = 0.71073) |
| Reflections observed [$F_o \geq 5\sigma(F_o)$] | 641 |
| $R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$ | 0.039 |
| $R_w$ | 0.054 |

TABLE 2. Final Fractional Coordinates for $C_7H_{12}O_4S$.

| Atom | *x/a* | *y/b* | *z/c* | B (eqv)[a] |
|---|---|---|---|---|
| S | 0.7676(2) | 0.2500 | 0.1094(1) | 2.39 |
| O-1 | 0.6343(6) | 0.372(1) | 0.1759(5) | 3.88 |
| O-2 | 0.8080(7) | 0.355(1) | −0.0019(4) | 3.42 |
| O-3 | 1.2057(7) | 0.3097(7) | 0.4083(4) | 3.25 |
| O-4 | 1.2034(7) | 0.359(1) | 0.6007(4) | 4.18 |
| C-1 | 0.700(1) | −0.051(1) | 0.0868(8) | 3.46 |
| C-2 | 0.9784(8) | 0.223(1) | 0.1959(5) | 2.42 |
| C-3 | 1.0547(9) | 0.469(1) | 0.2297(5) | 2.55 |
| C-4 | 1.2352(9) | 0.447(1) | 0.3023(5) | 2.75 |
| C-5 | 1.315(2) | 0.687(2) | 0.3465(8) | 4.14 |
| C-6 | 1.282(2) | 0.690(2) | 0.4736(9) | 4.56 |
| C-7 | 1.2275(9) | 0.440(1) | 0.5056(6) | 2.77 |
| H-1 (C-1) | 0.79(1) | −0.14(2) | 0.032(9) | 8(2)[b] |
| H-2 (C-1) | 0.60(1) | −0.04(2) | 0.048(8) | 8(3)[b] |
| H-3 (C-1) | 0.65(2) | −0.11(3) | 0.14(1) | 10(4)[b] |
| H-1 (C-2) | 1.04(1) | 0.13(2) | 0.150(8) | 7(2)[b] |
| H-2 (C-2) | 0.940(9) | 0.13(1) | 0.266(6) | 3(1)[b] |
| H-1 (C-3) | 0.975(8) | 0.56(1) | 0.281(6) | 3(1)[b] |
| H-2 (C-3) | 1.07(1) | 0.58(1) | 0.155(7) | 5(2)[b] |
| H-1 (C-4) | 1.33(1) | 0.36(2) | 0.270(7) | 6(2)[b] |
| H-1 (C-5) | 1.28(1) | 0.84(2) | 0.301(7) | 6(2)[b] |
| H-2 (C-5) | 1.41(2) | 0.66(3) | 0.328(9) | 10(4)[b] |
| H-1 (C-6) | 1.38(1) | 0.69(2) | 0.51(1) | 9(3)[b] |
| H-2 (C-6) | 1.21(2) | 0.78(5) | 0.52(1) | 16(4)[b] |

[a] $B(eqv) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.
[b] Isotropic refinement.

structure was then solved and analyzed by refinement in $P2_1$ first as solved and then by inversion of all coordinates through 0,0,0. The differences between the refinements were small; however, slightly lower R values and estimated standard deviations were noted for the conformation chosen. This conformation is supported by the observed ORD spectra.

Least-squares refinement with isotropic thermal parameters led to R = 0.088. The geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and then fully refined. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C-H = 0.95 Å, B = 5.5 Å$^2$) for three least-squares cycles and then fully refined. Refinement of nonhydrogen atoms with anisotropic temperature factors and hydrogen atoms with isotropic thermal parameters led to the final values of R = 0.039 and $R_w$ = 0.054. The final values of the positional parameters are given in Table 2.[1]

## ACKNOWLEDGMENTS

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[1]Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.