CONFORMATION OF METHYLSULFONYL GROUP: A COMPARISON OF THE DATA FOR 2-CHLOROPHENYL METHYL SULFONE IN SOLUTION AND IN CRYSTAL

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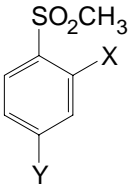*e-mail: [1] vsetecka@prfdec.natur.cuni.cz, [2] cisarova@prfdec.natur.cuni.cz,*
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The conformation of methylsulfonyl group attached to 2-substituted benzene ring was studied in the crystal and in solution. X-Ray crystal structure determination of the title compound demonstrates single conformation with the dihedral angle of 66.9(2)° between the planes defined by the aromatic ring and by the pivot atom of the ring, sulfur and the methyl carbon. In solution, dipole moment measurement leads to the conclusion that the compound also adopts a similar single conformation with slightly different dihedral angle of 53(5)°.
Key words: Methylsulfonyl group, conformation; X-Ray crystal structure.

The determination of molecular conformation represents frequently a complex problem due to many factors involved. For better understanding of the character of these factors it should be wise to determine the conformation of an appropriate model compound in different phases. The present paper deals with the study of conformation of the methylsulfonyl group bonded to a substituted benzene ring – determined independently in the crystal and in solution.

For the determination of the conformation in solution, twelve substituted phenyl methyl sulfones **1–12** were prepared as model compounds and their dipole moments were measured. Substituents X are halogen atoms or a nitrile group (i.e., the groups

	X	Y		X	Y
1	Cl	H	**7**	Br	Br
2	Cl	CH_3	**8**	Br	NO_2
3	Cl	Cl	**9**	CN	H
4	Cl	NO_2	**10**	CN	CH_3
5	Br	H	**11**	CN	Cl
6	Br	CH_3	**12**	CN	NO_2

without their own conformation but of different steric characteristics) and were chosen such as to elucidate their influence on the conformation of the methylsulfonyl group, if any. The choice of substituents Y was such as to provide large changes of the dipole moment and thus enhance the sensitivity of this method with respect to conformational analysis. One of these derivatives, **1**, was subjected to single crystal X-ray structure determination.

RESULTS AND DISCUSSION

Conformation in Solution

Table I summarizes the experimental values of dipole moments. For the determination of conformation, the well-proven graphical method[1] was applied using a comparison of calculated and measured values of dipole moments; the dipole moments expected for the individual conformations were calculated by vector addition of the standard group moments[2]. When the values of μ^2 are plotted on the x-axis for the unsubstituted compound and on the y-axis for its derivative, each presumptive conformation is represented by a point; these points can form either a straight line in the case when the

TABLE I
Experimental dipole moments of substituted phenyl methyl sulfones **1–12**

Compound	α^a	β^a	R_D	$P_{2\infty}$	μ, D/[$(10^{-30}$ C m)]^b
1	12.486	–0.4093	53.47	490.362	4.61/15.37
2	13.916	–0.4713	58.118	578.00	5.03/16.77
3	7.326	–0.5275	58.304	352.251	3.78/12.60
4	5.361	–0.5888	59.794	277.291	3.24/10.80
5	9.973	–0.5312	56.35	484.724	4.57/15.24
6	11.316	–0.3204	60.998	592.231	5.09/16.97
7	5.369	–0.7605	64.064	354.125	3.75/12.50
8	4.815	–0.6032	62.674	288.172	3.30/11.00
9	19.855	–0.156	53.076	731.246	5.75/19.17
10	20.662	–0.6228	57.724	790.096	5.98/19.94
11	12.367	–0.465	57.91	546.375	4.88/16.27
12	7.148	–0.4721	59.4	349.945	3.75/12.50

^{a} Slopes of the plots of ε_{12} and $(d_{12})^{-1}$, respectively, vs weight fraction w_2. ^{b} Correction for atomic polarization was taken as 5% of R_D.

moment of the substituent, the moment of the rest of molecule, and the axis of rotation of the involved group are coplanar, or an ellipse (or even more complex curve) in other cases. The conformation then may be estimated by comparing the calculated point with the experimental value (actually represented by small circle area to take into account the estimated error of measurement).

The inspection of Figs 1 and 2 shows that for 2-chlorophenyl methyl sulfone **2** and 2-(methylsulfonyl)benzonitrile **9**, the former case occurs. But there is still one problem to solve: for the straight line relationship, each point can be interpreted either as different mixtures of the two limiting forms or as one non-planar conformation, these two possibilities being undistinguishable. The MM2 molecular mechanics calculation (see below) supports that there is only one prevailing non-planar conformation, most likely as the result of significant steric hindrance.

From Figs 1 and 2, the following can be concluded for the conformation of the methylsulfonyl group in solution: (i) Qualitatively, there is accordance with the results obtained by the single crystal X-ray diffraction. In solution, the dihedral angle between the involved planes in 2-chlorophenyl methyl sulfone (**1**) is 53(5)°, the larger standard deviation being inherent to the dipole moment method. (ii) There is no significant difference between these dihedral angles for 2-chloro- (**1**) and 2-bromophenyl methyl sulfone (**5**). (iii) The somewhat larger dihedral angle in 2-(methylsulfonyl)benzonitrile (**9**) (62(5)°) could be possibly attributed to an attractive interaction between one of the negatively charged oxygen atoms of the sulfonyl group and the positively charged carbon of the nitrile group; this effect was found to operate in related (Z)-3-(methylsulfonyl)propenonitrile[3].
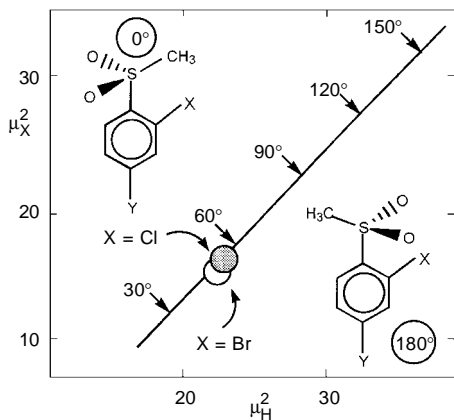

FIG. 1
Plot of squared dipole moments of **1** or **5** (x-axis) and **3** or **7** (y-axis). Small circle areas are experimental points
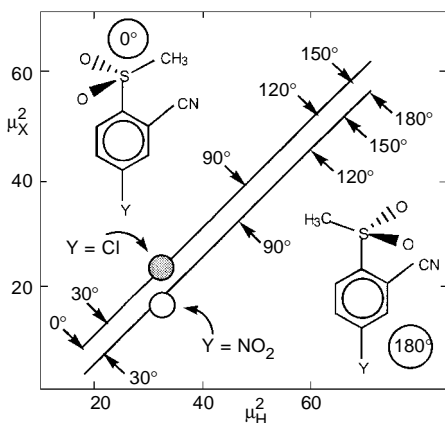
FIG. 2
Plot of squared dipole moments of **9** (x-axis) and **11** or **12** (y-axis). Small circle areas are experimental points

TABLE II
Atomic coordinates (. 10^4) with estimated standard deviations in parentheses. U_{eq} is defined as one third of the trace of the orthogonalized $\boldsymbol{U}_{ij}$ tensor

| Atom	x/a	y/b	z/c	U_{eq} (. 10^3), $\text{Å}^{-2,a}$
S	4655(1)	5000	2827(1)	43.3(2)
Cl	7668(2)	5551(2)	8321(2)	77.0(4)
O1	5042(5)	6473(3)	3072(5)	70.7(8)
O2	3736(3)	4464(4)	421(4)	63.1(7)
C1	6707(4)	4064(3)	4043(5)	38.9(6)
C2	8003(4)	4304(4)	6381(5)	49.8(8)
C3	9601(6)	3544(6)	7127(9)	74(1)
C4	9902(6)	2570(6)	5623(10)	74(1)
C5	8658(5)	2328(5)	3370(9)	66(1)
C6	7043(5)	3059(4)	2573(6)	49.9(7)
C7	3397(6)	4518(5)	4591(8)	58.4(8)
H3	10246(70)	3780(67)	8672(96)	85(16)
H4	10998(69)	2082(81)	6054(101)	103(19)
H5	8915(64)	1685(60)	2318(85)	73(14)
H6	6170(49)	2957(56)	878(75)	63(12)
H7A	3900(47)	4825(48)	6131(70)	48(10)
H7B	2335(57)	4981(58)	3990(72)	58(10)
H7C	3358(73)	3397(62)	4732(91)	81(16)

^{a} U_{iso} for hydrogen atoms.
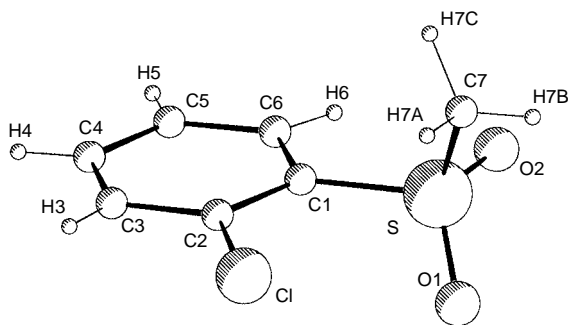
FIG. 3
View of the molecule with atom labelling

Crystal Structure of **1**

The final atom coordinates are summarized in Table II. Bond lengths and bond angles are given in Table III. As the consequence of hindered rotation of the methylsulfonyl group, the molecule exhibits planar chirality. The view of the molecule (the *S*-enantiomer chosen arbitrarily and, hence, the corresponding dihedral angle has opposite sign than that determined in solution) with atom labelling is depicted in Fig. 3. The crowding imposed by the 1,2-substituents has observable effects on the metric parameters of the aromatic ring. The ring remains planar within ±0.008 Å but the endocyclic distances and angles vary within 7 and 5 esd's, respectively, in a manner which relaxes the crowding at least partially. While the chlorine atom is nearly coplanar with the ring (0.016(3) Å), the sulfur atom is slightly displaced from the mean ring plane at 0.065(3) Å. The most interesting feature of the structure is undoubtedly the conformation of the methylsulfonyl group relative to the aromatic ring. The two oxygen atoms (the S–O distances are equal within one esd) are situated on the same side of the ring plane as the

TABLE III
Bond distances (Å) and angles (°) with estimated standard deviations in parentheses. Symmetry code: i, $1 - x$, $-y$, $1 - z$

Atoms	Distances	Atoms	Angles
S–O1	1.434(3)	O1–S–O2	117.6(2)
S–O2	1.429(3)	O1–S–C1	108.6(2)
S–C1	1.772(5)	O1–S–C7	110.3(2)
S–C7	1.751(3)	O2–S–C1	106.5(2)
Cl–C2	1.736(3)	O2–S–C7	107.2(2)
C1–C2	1.405(5)	C1–S–C7	106.1(2)
C1–C6	1.382(7)	S–C1–C2	123.7(3)
C2–C3	1.393(5)	S–C1–C6	117.4(3)
C3–C4	1.364(6)	C2–C1–C6	118.9(4)
C4–C5	1.353(7)	Cl–C2–C1	121.3(3)
C5–C6	1.389(8)	Cl–C2–C3	119.6(2)
C7–H7C	1.07(6)	C1–C2–C3	119.1(3)
O1–H7C[i]	2.34(5)	C2–C3–C4	120.6(3)
		C3–C4–C5	120.7(4)
		C4–C5–C6	120.2(4)
		C1–C6–C5	120.5(4)
		O1–H7C[i]–C7[i]	143(4)

sulfur atom (O1 at 1.156(4) Å, O2 at 0.081(4) Å) and the dihedral angle of the ring and SO$_2$ planes is 50.6(7)°. The methyl carbon C7 is then, of course, located on the opposite side of the ring plane at 1.458(4) Å and tilted towards O2 (the corresponding torsional angles C2–C1–S1–O2 and C2–C1–S1–C7 are 179.2(4) and –66.9(2)°, respectively). Obviously, this arrangement results from rotation of the methylsulfonyl group around
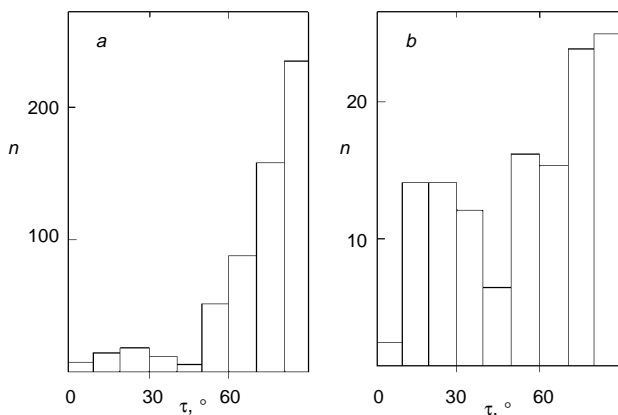

Fig. 4

Histogram of dihedral angles defined in text: *a* sulfones void of *ortho* substituents; *b* sulfones bearing at least one *ortho* substituent
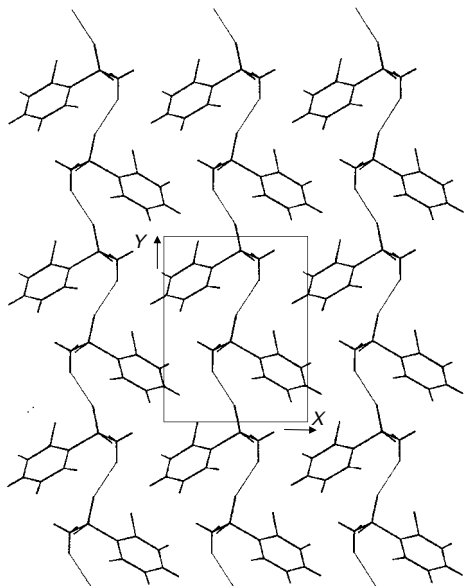

Fig. 5

Projection of structure onto *ab* plane with intermolecular contacts shown as thin lines

the S1–C1 bond such as to put the involved atoms into van der Waals contacts: e.g., the nonbonding distance O1–C1 becomes 3.153(3) Å compared to the van der Waals sum of 3.2 Å etc. Nearly the same geometry (within ±1° in torsional angles) results from MM2 molecular mechanics calculations[4,5] providing one flat minimum of energy. The search of Cambridge Structural Database[6] revealed that this effect is common among *ortho* substituted phenyl alkyl sulfones. Figure 4 depicts the distribution of the dihedral angle (defined in the 0–90° quadrant) between the ring plane and the plane defined by the pivot carbon of the phenyl ring C1, sulfur and the aliphatic carbon C7. The distribution strongly prefers an almost perpendicular arrangement of the planes for unhindered sulfones bearing no *ortho* substituens (histogram *a*, 580 fragments) but is considerably more spread with a pronounced tendency to the conformation in which the terminal carbon atom is tilted towards the *ortho* substituent (histogram *b*, 199 fragments).

In the crystal, the molecules are arranged into zig-zag chains running along the crystallographic *b*-direction (Fig. 5). There is one remarkable intermolecular contact within this chain which is shorter by 0.26 Å than the sum of the van der Waals radii of involved atoms, namely that between O1 and H7C (at $1 - x$, $-y$, $1 - z$). In accord with the generally accepted criteria[7], this interaction is to be regarded as hydrogen bonding.

EXPERIMENTAL

2-Chloro- and 2-bromophenyl methyl sulfones and their substituted derivatives were prepared from 2-chloro- and 2-bromoanilines or their substituted derivatives via the corresponding sulfinic acid[8]; sodium salts of these acids were converted to the substituted phenyl methyl sulfones by the reaction with iodomethane. 2-(Methylsulfonyl)benzonitrile and its substituted derivatives were prepared from 2-bromo- or 2-iodophenyl methyl sulfone and its derivatives by the reaction with copper(I) cyanide in HMPA or DMF. Elemental analyses for the new compounds are given below.

2-Chlorophenyl methyl sulfone (**1**), m.p. 90 °C, (ref.[9] gives 93.5–94.2 °C). ^{1}H NMR spectrum: 3.28 s, 3 H; 7.57 m , 3 H; 8.21 m, 1 H. Mass spectrum, *m/z* (%): 192 (22), 190 (M[+]), 177 (14), 175 (35), 130 (17), 128 (52), 126 (41), 113 (31), 111 (100), 99 (20), 85 (7), 75 (50), 74 (14), 63 (8), 50 (22).

2-Chloro-4-methylphenyl methyl sulfone (**2**), m.p. 55–56 °C. ^{1}H NMR spectrum: 2.32 s, 3 H; 3.26 s, 3 H; 7.46 dd, 1 H, $J = 8.38$ and 2.55; 7.58 d, 1 H, $J = 1.77$; 8.21 d, 1 H. Mass spectrum, *m/z* (%): 206 (16), 204 (M[+]), 191 (15), 189 (41), 143 (32), 141 (100), 127 (29), 125 (94), 113 (10), 99 (20), 91 (14), 89 (66), 77 (46), 73 (12), 63 (53), 51 (19), 39 (31). For $C_8H_9ClO_2S$ (204.7) calculated: 46.95% C, 4.43% H; found: 46.81% C, 4.52% H.

2,4-Dichlorophenyl methyl sulfone (**3**), m.p. 72 °C (ref.[10] gives 74–75 °C). ^{1}H NMR spectrum: 3.26 s, 3 H; 7.46 dd, 1 H, $J = 8.38$ and 2.55; 7.58 d, 1 H, $J = 1.77$; 8.21 d, 1 H. Mass spectrum, *m/z* (%): 226 (27), 224 (M[+]), 211 (22), 209 (30), 163 (62), 161 (100), 147 (49), 145 (68), 135 (15), 133 (22), 111 (15), 109 (41), 79 (84), 76 (31), 74 (38), 63 (13), 50 (13), 45 (5).

2-Chloro-4-nitrophenyl methyl sulfone (**4**), m.p. 147–149 °C. ^{1}H NMR spectrum: 3.32 s, 3 H; 8.35 m, 3 H. Mass spectrum, *m/z* (%): 237 (18), 235 (M[+]), 222 (9), 220 (21), 175 (32), 173 (100), 158 (13), 156 (36), 143 (22), 126 (16), 110 (27), 109 (18), 95 (8), 84 (9), 79 (27), 73 (39), 63 (69), 50 (9). For $C_7H_6ClNO_4S$ (235.7) calculated: 35.68% C, 2.57% H, 5.95% N; found: 35.55% C, 2.68% H, 5.80% N.

2-Bromophenyl methyl sulfone (**5**), m.p. 101 °C (ref.[11] gives 108.5 °C). ^{1}H NMR spectrum: 3.29 s, 3 H; 7.50 m, 2 H; 7.78 m, 1 H; 8.15 m, 1 H. Mass spectrum, *m/z* (%): 236 (70), 234 (M[+]), 221 (30), 174 (45), 173 (46), 172 (46), 171 (47), 157 (99), 155 (100), 145 (20).

2-Bromo-4-methylphenyl methyl sulfone (**6**), m.p. 93 °C. ^{1}H NMR spectrum: 2.35 s, 3 H; 3.22 s, 3 H; 7.30 m, 1 H; 7.60 m, 1 H; 8.15 d, 1 H, $J = 8.05$. Mass spectrum, *m/z* (%): 250 (M[+]), 248 (82), 235 (45), 233 (44), 187 (95), 185 (100), 171 (79), 169 (76), 90 (73), 88 (69), 78 (39), 76 (23), 63 (48), 62 (16), 51 (14), 39 (26). For $C_8H_9BrO_2S$ (249.1) calculated: 38.57% C, 3.64% H; found: 38.68% C, 3.69% H.

2,4-Dibromophenyl methyl sulfone (**7**), m.p. 122 °C. ^{1}H NMR spectrum: 3.27 s, 3 H; 7.66 dd, 1 H, $J = 8.33$ and 1.71; 7.95 d, 1 H, $J = 1.71$; 8.05 d, 1 H, $J = 8.33$. Mass spectrum, *m/z* (%): 316 (25), 314 (M[+]), 312 (23), 301 (13), 299 (23), 297 (11), 253 (50), 251 (100), 249 (54), 237 (31), 235 (60), 233 (30), 223 (19), 156 (20), 154 (21), 75 (72), 73 (62), 63 (22), 50 (11), 45 (6). For $C_7H_6Br_2O_2S$ (314.0) calculated: 26.78% C, 1.93% H; found: 26.85% C, 2.00% H.

2-Bromo-4-nitrophenyl methyl sulfone (**8**), m.p. 155–157 °C. ^{1}H NMR spectrum: 3.33 s, 3 H; 7.25 s, 1 H; 8.39 s, 1 H; 8.62 s, 1 H. Mass spectrum, *m/z* (%): 281 (M[+]), 279 (31), 266 (12), 219 (64), 217 (61), 202 (25), 200 (25), 189 (14), 187 (14), 172 (10), 170 (11), 156 (16), 154 (17), 107 (7), 95 (12), 79 (37), 75 (100), 73 (71), 63 (90), 50 (10), 39 (8). For $C_7H_6BrNO_4S$ (218.1) calculated: 38.55% C, 2.77% H, 6.42% N; found: 38.44% C, 2.86% H, 6.39% N.

2-(Methylsulfonyl)benzonitrile (**9**), m.p. 100–101 °C (ref.[12] gives 103–104 °C). IR spectrum: 2 233 w (CN). ^{1}H NMR spectrum: 3.29 s, 3 H; 7.83 m, 3 H; 8.19 m, 1 H. Mass spectrum, *m/z* (%): 181 (M[+]), 166 (16), 119 (100), 102 (81), 76 (18), 75 (26), 63 (17), 51 (16).

2-(Methylsulfonyl)-5-methylbenzonitrile (**10**), m.p. 106–108 °C. IR spectrum: 2 235 w (CN). ^{1}H NMR spectrum: 2.50 s, 3 H; 3.248 s, 3 H; 7.59 m, 1 H; 7.70 m, 1 H; 8.05 m, 1 H. Mass spectrum, *m/z* (%): 195 (M[+]), 180 (24), 133 (100), 132 (39), 116 (75), 88 (45), 77 (15), 63 (27), 39 (18). For $C_9H_9NO_2S$ (195.2) calculated: 55.37% C, 4.65% H, 7.17% N; found: 55.19% C, 4.86% H, 7.22% N.

2-(Methylsulfonyl)-5-chlorobenzonitrile (**11**), m.p. 110–112 °C. IR spectrum: 2 235 vw (CN). ^{1}H NMR spectrum: 3.271 s, 3 H; 7.76 dd, 1 H, $J = 8.7$ and 2.2; 7.87 d, 1 H, $J = 2.2$; 8.14 d, 1 H, $J = 8.79$. Mass spectrum, *m/z* (%): 217 (8), 215 (M[+]), 200 (16), 155 (37), 153 (100), 151 (29), 138 (16), 136 (49), 124 (13), 100 (39), 75 (22), 63 (28), 50 (21). For $C_8H_6ClNO_2S$ (215.7) calculated: 44.56% C, 2.80% H, 6.50% N; found: 44.43% C, 2.87% H, 6.40% N.

2-(Methylsulfonyl)-5-nitrobenzonitrile (**12**), m.p. 160–162 °C. IR spectrum: 2 235 vw (CN). ^{1}H NMR spectrum: 3.35 s, 3 H; 8.42 dd, 1 H, $J = 8.7$ and 1; 8.63 dd, 1 H, $J = 8.7$ and 3; 8.7+ dd, 1 H, $J = 3$ and 1. Mass spectrum, *m/z* (%): 226 (M[+]), 164 (20), 147 (12), 100 (12), 79 (20), 75 (17), 63 (100), 50 (16). For $C_8H_6N_2O_4S$ (226.2) calculated: 53.10% C, 2.67% H, 12.39% N; found: 53.29% C, 2.76% H, 12.48% N.

Melting points were determined on a Boetius block and are uncorrected. ^{1}H NMR spectra (δ, ppm; *J*, Hz) were measured in CDCl₃ solutions on a Bruker FX-80 instrument with TMS as internal standard and IR spectra (ṽ, cm⁻¹) on a Perkin–Elmer 684 instrument in CHCl₃ solutions. Mass spectra were measured using a GC/MS spectrometer; GC: Varian 3400, capillary column 30 m × 0.32 mm, DB 5. MS: Finnigan MAT (70 eV). Dipole moments were determined at 25 °C in benzene solutions (usually five concentrations in the range of weight fraction 0.0005–0.006) using the method of Halverstadt and Kumler[13]. Relative permittivities (ε_{12}) were measured on an instrument with direct frequency reading[14], densities (d_{12}) were determined in an Ostwald–Sprengel pycnometer. Molar refractions (R_D) were calculated from the published increments[15]; the correction of 5% of R_D was applied for the atomic polarization.

Single-crystal X-ray diffraction – crystal and measurement data: $C_7H_7ClO_2S$ 190.6, monoclinic, space group $P2_1$ (No. 4), $a = 7.9970(5)$, $b = 9.5396(6)$, $c = 5.8844(4)$ Å, $\beta = 111.520(5)°$, $V = 417.61(5)$ Å³, $Z = 2$, $D_c = 1.516$ g cm⁻³, $F(000) = 196$. A prismatic crystal of the dimensions

$0.32 \times 0.18 \times 0.14$ mm grown from aqueous methanol was measured at room temperature on a CAD4 diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). Absorption was neglected ($\mu = 0.65$ mm^{-1}). The lattice parameters were determined from 24 reflections in the 17.2–19.7° θ-range. The intensities of reflections were measured between $h \langle 0,10 \rangle$, $k \langle 0,13 \rangle$, $l \langle -7,8 \rangle$, $(\sin \theta/\lambda)_{max} = 0.68$ Å^{-1}. Three standard reflections monitored during the measurement every 1 h showed an intensity decrease up to 9% because of crystal decomposition; the intensities were corrected appropriately. From 1 497 measured reflections, 1 097 were unique ($R_{int} = 0.03$) and 937 were regarded as "observed" according to the $I \geq 2\sigma(I)$ criterion. The structure was solved by direct methods (SHELXS86, ref.[16]) and refined by SHELXL93 (ref.[17]) using a full-matrix least squares procedure based on F^2. The refinement was anisotropic for non-H and isotropic for H-atoms (127 parameters) and the function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2(F_c^2) + (0.0543P)^2 + 0.0035P]$, $P = (F_o^2 + 2F_c^2)/3$. The refinement converged to $R = 0.032$, $R_w = 0.086$, $S = 1.066$ with $(\Delta/\sigma)_{max} = \pm 0.001$ for non-H atoms. The final difference electron density map was featureless with extreme values of 0.22; –0.20 e Å^{-3}. The tables of observed and calculated structure factors and of anisotropic displacement parameters as well as the standard CIF files produced by SHELXL93 can be obtained from the authors upon request.

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