Journal of Chemical Crystallography, Vol. 29, No. 6, 1999

Synthesis and crystal structure of (Z)-1-(phenylsulphenyl)-2-phenylethenyl p-toluenesulfonate

Antonio Luiz Braga,(1)* **Oscar E.D. Rodrigues,**(1) **Daniel J. Emmerich,**(1)
Claudio C. Silveira,(1) **Manfredo Hörner,**(1)* **and Ezequiel M. Vazquez-Lopez**(2)

Received July 3, 1998

The reaction between 1-phenylsulphenyl-2-phenylethyne and *p*-toluenesulfonic acid in methylene chloride gives (Z)-1-(phenylsulphenyl)-2-phenylethenyl p-toluenesulfonate (**1**) in good yields. This reaction is both a regio- and a stereospecific *cis* addition, confirmed by X-ray crystal structure analysis of the title compound. **1** crystallizes in the monoclinic space group $P2_1/n$ with the lattice parameters $a = 10.556(3)$, $b = 9.730(3)$, $c = 19.687(3)$ Å, $\beta = 105.05(2)°$, $V = 1952.7(8)$ Å^3, and $Z = 4$. The results of elemental analysis, IR and NMR spectroscopy are included.

KEY WORDS: Vinilic sulfides; thioacetylenes; tosylates; X-ray structure.

Introduction

Vinilic sulfides are intermediates of great synthetic potential, since they combine the ability of the double bond to form single carbon-carbon bonds with the functional transformation achieved by the well known reactions of organosulfur compounds.[1] (Z)-α-sulfenylvinyl *p*-sulfonates are known,[2] but not yet studied in detail. The crystal structure of this compound was undertaken because a knowledge of its stereochemistry is required to predict successive reaction pathways, and it is not trivial to assign the stereochemistry of trisubstituted olefins by other methods.[3] In this paper we describe the synthesis and the crystal and molecular structure of $Ph(H)C{=}C[OS(O_2)C_6H_4CH_3]SPh$ (**1**), which is a very important precursor for the synthesis of unsaturated and carbonyl compounds.

Experimental

Elemental analysis was performed with a Carlo Erba 1108 analyzer. The IR spectrum was registered using KBr pellets on a Bruker IFS28 spectrometer, and NMR spectra were acquired on a Bruker AC 80 spectrometer. A Büchi apparatus was used for the melting point determination.

All reagents were purchased from Aldrich and used directly from original packages. The starting material, 1-phenysulphenyl-2-phenylethyne, was prepared according to literature.[4]

Preparation of (Z)-1-(phenylsulphenyl)-2-phenylethenyl p-toluenesulfonate

A mixture of the 1-phenysulphenyl-2-phenylethyne (210 mg, 1 mmol) and *p*-toluenesulfonic acid (390 mg, 2.5 mmol) in methylene chloride (5 mL) was stirred at 0°C for 30 min and overnight at room temperature. The reaction mixture was filtered through Al_2O_3 and K_2CO_3 columns and the solvent evaporated. The residue was recrystallized (ethyl ether/

---

(1) Departamento de Química, Universidade Federal de Santa Maria, Caixa Postal 5071, 97.105-900 Santa Maria-RS, Brazil.
(2) Departamento de Química Inorgánica, Universidad de Vigo, E-36200 Vigo, Spain.
* To whom correspondence should be addressed.

1074-1542/99/0600-0677$16.00/0

hexane) to give the product (332 mg, 87%); *mp* = 62.63°C; Anal. Found: C, 65.92; H, 4.75%. $C_{21}H_{18}O_3S_2$ requires: C, 65.95; H, 4.74%. IR (KBr): ν (cm^{-1}): 2975, 1580, 1470, 1370, 1275, 1000. ^1H NMR (80 MHz, $CDCl_3$): 7.64 (d, 2H, J = 8Hz), 7.14-7.28 (m, 12H), 6.95 (1H, s), 2.32 (3H, s). ^{13}C NMR (20 MHz, $CDCl_3$): 145.12, 140.81, 133.36, 132.53, 131.21, 129.89, 129.50, 129.34, 129.20, 128.98, 128.70, 128.49, 128.29, 127.33, 21.63.

Crystallographic section

Single crystals of **1** were grown from a diethyl ether/n-hexane mixture. A colorless crystal was mounted on a glass fiber and used for intensity data collection. Automatic intensity search and indexing methods indicated a cell belonging to the monoclinic crystal system with a *P* lattice. X-ray intensity data were recorded with a scan speed of 45 sec/reflection. Every 60 min, the intensity and orientation of three standard reflections were confirmed; the observed intensity decay was less than 1.5% over the data collection. From the Bravais lattice and observed reflections conditions, the space group was chosen to be $P2_1/n$. A semi-empirical absorption correction based on *psi*-scans was made on the the intensity data.[5]

The structure was solved using direct methods employing SHELXS-97[7] program and all nonhydrogen atoms were located by subsequent Fourier difference synthesis. For structure refinement the SHELXL-97[8] program was employed and the full-matrix least-squares method minimized on $\Sigma w (F_o^2 - F_c^2)^2$ where w is a weighting scheme indicated

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

Compound	$Ph(H)C{=}C[OS(O_2)C_6H_4CH_3]SPh$
CCDC deposit no.	CCDC-1003/5557
Color/shape	Colorless/prismatic
Formula weight	382.47
Space group	$P2_1/n$
Temperature, °C	20
Cell constants[a]	
a, Å	10.556(3)
b, Å	9.730(3)
c, Å	19.687(3)
β, deg	105.05(2)
Cell volume, $Å^3$	1952.7(8)
Formula units/unit cell	4
D_{calc}, g cm^{-3}	1.301
μ_{calc}, cm^{-1}	2.90
Diffractometer/scan	Enraf-Nonius CAD-4[6]/ω-2θ
Radiation, graphite monochromator	Mo$K\alpha$ (λ = 0.71073 Å)
Max. crystal dimensions, mm	0.35 × 0.30 × 0.15
Scan width	$0.60 + 0.48 \tan \theta$
Standard reflections	208; 43-5; 2-3-2
Decay of standards	±1.5%
Reflections measured	2729
2θ range, deg	$4.70 \leq 2\theta \leq 45.52$
Range, of h, k, l	$-11 \leq h \leq 11, -10 \leq k \leq 0, 0 \leq l \leq 21$
Reflections observed $[I > 2\sigma(I)]$[b]	1037
Computer programs[c]	SHELXL-97[8]
Structure solution	SHELXS-97[7]
No. of parameters varied	239
GOF	1.008
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.0464
R_w	0.0797
Extinction	0.00006(8)
Largest feature final diff. map	0.198 e^- $Å^{-3}$

[a] Least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 25 reflections $\theta > 20$ deg.

[b] Corrections: Lorentz-polarization.

[c] Neutral scattering factors and anomalous dispersion corrections.

below. All nonhydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atom sites were obtained geometrically and their displacement parameters were refined isotropically on a groupwise basis. The hydrogen atom bound to the C(2) atom was found in a difference Fourier map and refined isotropically. The final refinement of the structure includes an isotropic extinction correction and converge to $R = 4.64\%$ and $R_w = 7.97\%$ with the weighting scheme, $w = 1/[s^2(Fo^2) + (0.0608P)^2 + 2.3183P]$, where $P = (F_o^2 + 2F_c^2)/3$. Table 1 summarizes the crystal data and structure refinement parameters for **1.**

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Ph(H)C{=}C[OS(O_2)C_6H_4CH_3]SPh$

	x	*y*	*z*	*U*(eq)[a]
S(1)	5405(2)	1889(2)	1170(1)	72(1)
S(2)	2892(1)	426(2)	1997(1)	71(1)
O(1)	3856(3)	1628(4)	1020(2)	65(1)
O(2)	6011(3)	700(5)	977(2)	91(1)
O(3)	5456(4)	3175(5)	828(2)	87(1)
C(1)	3372(5)	352(8)	1219(3)	60(2)
C(2)	3365(6)	−716(9)	810(4)	66(2)
C(3)	2847(7)	−2104(8)	861(3)	64(2)
C(4)	3467(6)	−3223(9)	656(3)	80(2)
C(5)	3001(8)	−4534(9)	688(4)	101(2)
C(6)	1881(8)	−4770(9)	910(4)	104(3)
C(7)	1240(7)	−3648(10)	1092(4)	92(2)
C(8)	1699(7)	−2342(8)	1074(3)	74(2)
C(11)	5932(5)	2118(7)	2079(3)	57(2)
C(12)	5627(5)	3305(7)	2375(3)	67(2)
C(13)	6097(6)	3522(7)	3086(4)	74(2)
C(14)	6879(7)	2576(9)	3512(4)	73(2)
C(15)	7179(6)	1387(8)	3212(4)	82(2)
C(16)	6725(6)	1147(7)	2493(4)	77(2)
C(17)	7376(6)	2797(7)	4298(3)	116(3)
C(21)	1406(5)	1363(6)	1737(3)	56(2)
C(22)	702(6)	1535(7)	1053(3)	77(2)
C(23)	−475(7)	2259(8)	907(4)	96(3)
C(24)	−956(7)	2745(8)	1429(6)	107(3)
C(25)	−268(8)	2560(8)	2114(5)	108(3)
C(26)	908(6)	1880(7)	2265(3)	77(2)

[a] *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

*Molecular structure of **1***

Figure 1 shows the ZORTEP[9] plot of the molecular structure and atom numbering of **1.** Atomic positional parameters for non-hydrogen atoms are listed in Table 2 and selected bond distances and bond angles are presented in Table 3. The X-ray structure clearly demonstrates the Z geometry for **1.**

The C(1)—C(2) distance of 1.314(7) Å confirms the expected double-bond character between these atoms. This value is in good agreement with other analogous ethylene compounds, e.g., the observed C—C distance of 1.316 Å in (*E*)-1-chloro-1-(tosyloxy)-3,3-dimethyl-1-butene[10] and 1.34(1) Å in dichloro[(Z)-2-chloro-2-phenylvinyl]-(4-methoxyphenyl) tellurium(IV).[11] A slight deviation from planarity of the trisubstituted ethylene fragment is observed with a C(3)—C(2)—C(1)—S(2) torsion angle of 6.1(10)°. The C=C—SPh and Ph—C=C bond angles opening up to 128.1(6) and 129.0(7)°, and the $C{=}C{-}OS(O_2){-}$tol bond angle decreasing to 117.6(5)°. According to the torsion angles defined by the atoms C(8)—C(3)—C(2)—C(1) [37.0(9)°], C(16)—C(11)—S(1)—O(1) [111.6(4)°], and C(22)—C(21)—S(2)—C(1) [18.0(6)°], the pπ–pπ interaction between the C(2) atom and the C(3)—C(8) phenyl ring and the dπ–pπ interactions between the S(1) atom and the C(11)—C(16) phenyl ring and the S(2) atom and the C(21)—C(26) phenyl ring are weakened. Therefore, the bond lengths C(3)—C(2) = 1.470(8), S(1)—C(11) = 1.746(5), and S(2)—C(21) = 1.770(5) Å, are slightly shorter in comparision with the respective sums of the covalent radii (C···C =

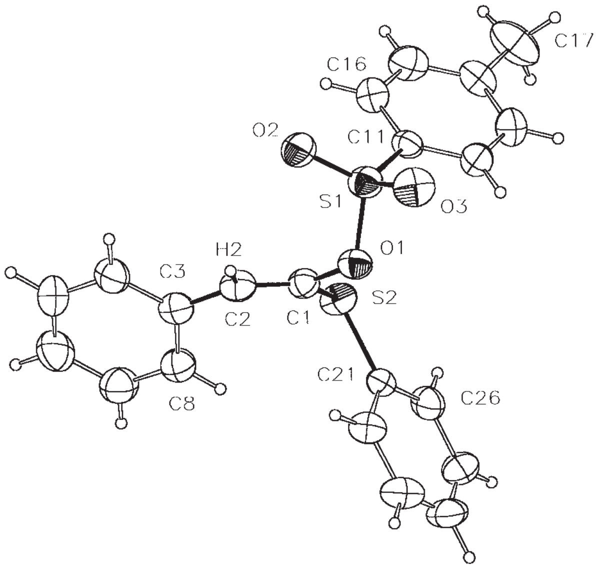

Fig. 1. ZORTEP[9] drawing with atom-labeling scheme of the structure of $Ph(H)C{=}C[OS(O_2)C_6H_4CH_3]SPh$; displacement ellipsoids at the 30% probability level.

Table 3. Selected Bond Lengths (Å), Angles (°) and Torsional Angles (°) for $Ph(H)C{=}C[OS(O_2)C_6H_4CH_3]SPh$

S(1)−O(1)	1.604(3)
S(1)−O(2)	1.421(4)
S(1)−O(3)	1.428(4)
S(1)−C(11)	1.746(5)
S(2)−C(1)	1.736(6)
S(2)−C(21)	1.770(5)
O(1)−C(1)	1.435(6)
C(1)−C(2)	1.314(7)
C(2)−C(3)	1.470(8)
C(2)−H(2)	0.88(4)
O(2)−S(1)−O(3)	120.9(3)
O(2)−S(1)−O(1)	109.3(2)
O(3)−S(1)−O(1)	102.3(2)
O(2)−S(1)−C(11)	109.4(3)
O(3)−S(1)−C(11)	109.3(3)
O(1)−S(1)−C(11)	104.3(2)
C(1)−S(2)−C(21)	101.9(3)
C(1)−O(1)−S(1)	120.4(3)
C(2)−C(1)−O(1)	117.6(5)
C(2)−C(1)−S(2)	128.1(6)
O(1)−C(1)−S(2)	114.3(5)
C(1)−C(2)−C(3)	129.0(7)
C(1)−C(2)−H(2)	114(3)
C(3)−C(2)−C(1)−S(2)	6.1(10)
C(8)−C(3)−C(2)−C(1)	37.0(9)
C(16)−C(11)−(1)−O(1)	111.6(4)
C(22)−C(21)−S(2)−C(1)	18.0(6)
O(2)−O(3)−O(1)−C(11)	70.0(2)

1.54 and S···C = 1.80 Å). The S(1) atom shows a distorted tetrahedral configuration, with a O(2)−O(3)−O(1)−C(11) torsion angle of 70.0(2)°. The S(1)−O(1) distance [1.604(3) Å] and the O(1)−C(1) distance [1.435(6) Å] are in good agreement with the values found for analogous bonds in (*E*)-1-Chloro-1-(tosyloxy)-3,3-dimethyl-1-butene.[10] Two lone pairs together with the C(1) and the C(21) atoms impose a typical tetrahedral configuration to the S(2) atom. As expected by the valence-shell electron-pair-repulsion model (VSEPR)[12] the C(1)−S(2)−C(21) angle of 101.3(9)° becomes appreciably deviated from the ideal internal angle of a tetrahedron as result of the repulsion between both of the lone pairs of electrons and from those on the S−C bonds. The three phenyl rings are essentially planar with an average RMS deviation of 0.0068 Å and their interplanar angles are 84.8(2)° between the C(3)−C(8) and C(11)−C(16) phenyl rings and 33.6(2)° between the C(11)−C(16) and C(21)−C(26) phenyl rings.

Acknowledgments

The authors thank the CNP_q for financial support, and Prof. Dr. Alfonso Castiñeiras Campos, University of Santiago de Compostela, Spain for the diffractometer facilities.

References

1. Kuwajima, I.; Tanino, K. *J. Synth. Org. Chem. Jpn.* **1996,** *54,* 929.
2. Braga, A.L.; Rodrigues, O.E.D.; Avila, E.; Silveira, C.C. *Tetrahedron Lett.* **1998,** *39,* 3395.
3. Braga, A.L.; Andrade, L.H.; Zeni, G.Z.; Silveira, C.C.; Stefani, H. A. *Synthesis* **1998,** 39.
4. Braga, A.L.; Silveira, C.C.; Reckziegel, A.; Menezes, P.H. *Tetrahedron Lett.* **1993,** *34,* 8041.
5. North, A.C.T.; Phillips, D.C.; Scott Mathews, F. *Acta Crystallogr.* **1968,** *A24,* 351.
6. Enraf-Nonius, *CAD-4-Express Software;* Enraf-Nonius Inc.: Delft, The Netherlands, 1992.
7. Sheldrick, G.M. *SHELXS-97, Program for Crystal Structure Solution;* University of Göttingen: Germany, 1990.
8. Sheldrick, G.M. *SHELXL-97, Program for Crystal Structure Refinement;* University of Göttingen: Germany, 1997.
9. Zsolnai, L.; Pritzkow, H. *ZORTEP, Program for Personal Computer;* University of Heidelberg: Germany, 1996.
10. Stang, J.P.; Roberts, K.A. *J. Org. Chem.* **1997,** *52,* 5213.
11. Zuckerman-Schpector, J.; Comasseto, J.V.; Stefani, H.A. *Acta Crystallogr.* **1995,** *C51,* 861.
12. Gillespie, R.J. *Molecular Geometry;* van Nostrand-Reinhold, 1972.