

Packing of the molecules in the crystal is shown in Fig. 2. The molecules are linked into infinite chains by  $N(3) (x, y+1, z+1) - H(N3) (x, y+1, z+1) \cdots O(2) (x, y, z)$  hydrogen bonds [ $N(3) \cdots O(2)$  3.04 (1),  $N(3) - H(N3)$  1.09 (7),  $H(N3) \cdots O(2)$  1.97 (7) Å,  $N(3) - H(N3) \cdots O(2)$  170 (5)°]. The chains are parallel to the [011] direction and the symmetry-equivalent  $[01\bar{1}]$  direction in the layer perpendicular to the *a* axis. On the other hand, in the direction parallel to the *a* axis, packing of molecules is governed only by relatively weak van der Waals contacts. As is expected from these results, the easy cleavage plane is the (100) plane.

It is noticeable that the charge-transfer axis in the pyridine ring [ $N(3) - C(5) - C(1) - N(1)$ ] of each molecule makes a relatively small angle with the twofold screw axis (*b* axis). For this reason, single crystals of this compound may be expected to have very large second-order nonlinear optical susceptibility.

*Acta Cryst.* (1988), **C44**, 104–107

### Structure of a Potential Cross-Linking Reagent: 2,2'-Bis(methoxymethylene)-2,2'-sulfonyldiacetonitrile (MMSBA)

BY UPALI SIRIWARDANE, SHIRLEY S. C. CHU AND NARAYAN S. HOSMANE\*

*Departments of Chemistry and Electrical Engineering, Southern Methodist University, Dallas, Texas 75275, USA*

AND CRAIG M. BERTHA AND RAMACHANDRA S. HOSMANE\*

*Department of Chemistry, University of Maryland, Baltimore County Campus, Catonsville, Maryland 21228, USA*

(Received 14 May 1987; accepted 28 July 1987)

**Abstract.** The title compound (I) was prepared as a potential cross-linking reagent for nucleic acids and/or proteins. The compound is a stable, but reactive, crystalline solid which can be stored indefinitely upon adequate protection. The reagent reacts with amine nucleophiles – primary, secondary as well as heterocyclic – to afford bis-enamines.  $C_8H_8N_2O_4S$ ,  $M_r = 228.23$ , monoclinic,  $C2/c$ ,  $a = 18.031$  (5),  $b = 9.372$  (3),  $c = 13.455$  (6) Å,  $\beta = 108.08$  (5)°,  $V = 2161$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.40$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 2.81$  cm<sup>-1</sup>,  $F(000) = 944$ ,  $T = 295$  K. Final  $R = 0.041$  for 1033 observed reflections. The bond distances in (I) are: S–O, 1.424 (3); S–C, 1.737 (4); C–CN, 1.417 (5); C=C, 1.342 (5); =C(H)–O, 1.295 (4); and  $C \equiv N$ , 1.138 (5) Å. The diagonal distance,  $\alpha - \alpha'$ , between the two *trans* C atoms is 4.976 Å.

**Introduction.** The study of the synthesis, structure and chemistry of novel bifunctional organic reagents is

This work was partially supported by Scientific Research Grant-in-Aid #61460072 from the Ministry of Education, Science and Culture.

#### References

- BETTONI, G., CATSIOTIS, S., PERRONE, R. & TORTORELLA, V. (1977). *Gazz. Chim. Ital.* **107**, 111–116.  
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.  
 MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.  
 SAKURAI, T. & KOBAYASHI, K. (1979). *Rikagaku Kenkyusho Hokoku*, **55**, 69–77.  
 TWIG, R., AZEMA, A., JAIN, K. & CHENG, Y. Y. (1982). *Chem. Phys. Lett.* **92**, 208–211.

important in view of their potential to cross link biomolecules such as nucleic acids and proteins. Cross-linking agents have long been instrumental in investigations relating to structure and function of both nucleic acids and proteins. The recent isolation and structural characterization of a covalent cross-link adduct between the antibiotic mitomycin C and the interstrand guanine residues of DNA have provided direct proof for the long-suspected mode of action of this natural anticancer drug (Tomasz, Lipman, Chowdary, Pawlak, Verdine & Nakanishi, 1987). The above finding has spurred renewed interest in the design and synthesis of synthetic cross-linking reagents. Psoralens, an important class of photochemical cross-linking reagents, have been extensively employed in probing both static and dynamic secondary structural features of DNA/RNA in viral, bacterial and mammalian systems as well as for studying functional properties such as the role of small nuclear RNA's in processing heteronuclear RNA (Cimino, Gamper, Isaacs & Hearst, 1985). Bifunctional reagents such as glutaraldehyde (Hopwood, Allen & McCabe, 1970), diaspirins

\* Authors to whom correspondence should be addressed.



Table 1. Fractional atomic coordinates with equivalent isotropic thermal parameters for the non-H atoms and isotropic thermal parameters for H atoms with *e.s.d.*'s in parentheses

	x	y	z	$U_{eq}/U(\text{\AA}^2)$
S	0.29586 (5)	0.8163 (1)	0.2250 (1)	0.0541 (2)
O(1)	0.2305 (1)	0.8110 (3)	0.1327 (2)	0.0724 (7)
O(2)	0.2843 (2)	0.8256 (3)	0.3247 (2)	0.0821 (7)
O(3)	0.4233 (1)	1.1601 (3)	0.2859 (2)	0.0592 (6)
O(4)	0.3698 (1)	0.4642 (2)	0.1345 (2)	0.0578 (6)
N(1)	0.3823 (3)	0.9837 (4)	0.0419 (2)	0.1057 (14)
N(2)	0.4763 (2)	0.6386 (4)	0.3796 (2)	0.0822 (10)
C(1)	0.3536 (2)	0.9602 (4)	0.2149 (2)	0.0434 (7)
C(2)	0.3821 (2)	1.0514 (4)	0.2947 (2)	0.0473 (7)
C(3)	0.3527 (2)	0.6672 (4)	0.2225 (2)	0.0496 (8)
C(4)	0.3308 (2)	0.5794 (4)	0.1399 (2)	0.0490 (7)
C(5)	0.3701 (2)	0.9741 (4)	0.1192 (2)	0.0624 (10)
C(6)	0.4530 (2)	1.2503 (5)	0.3776 (3)	0.0727 (10)
C(7)	0.4210 (2)	0.6483 (4)	0.3090 (3)	0.0573 (8)
C(8)	0.3406 (2)	0.3811 (5)	0.0403 (3)	0.0733 (10)
H(1)	0.372 (2)	1.041 (3)	0.353 (2)	0.041 (7)
H(2)	0.286 (1)	0.598 (3)	0.092 (2)	0.039 (7)
H(3)	0.4863 (2)	1.337 (1)	0.3599 (3)	0.177 (24)
H(4)	0.4900 (2)	1.188 (1)	0.4413 (3)	0.126 (17)
H(5)	0.4048 (2)	1.293 (1)	0.3998 (3)	0.091 (13)
H(6)	0.3774 (2)	0.289 (1)	0.0448 (3)	0.193 (24)
H(7)	0.3408 (2)	0.446 (1)	-0.0262 (3)	0.213 (32)
H(8)	0.2818 (2)	0.347 (1)	0.0318 (3)	0.181 (24)

\* The standard deviations of  $U_{eq}$  were calculated according to Schomaker & Marsh (1983).

Table 2. Bond lengths ( $\text{\AA}$ ), bond angles ( $^\circ$ ) and selected torsion angles ( $^\circ$ )

S—O(1)	1.424 (3)	O(4)—C(8)	1.441 (5)
S—O(2)	1.423 (3)	N(1)—C(5)	1.131 (5)
S—C(1)	1.734 (4)	N(2)—C(7)	1.148 (5)
S—C(3)	1.739 (4)	C(1)—C(2)	1.344 (5)
O(3)—C(2)	1.288 (4)	C(1)—C(5)	1.415 (5)
O(3)—C(6)	1.454 (5)	C(3)—C(4)	1.340 (5)
O(4)—C(4)	1.303 (4)	C(3)—C(7)	1.419 (5)
O(1)—S—O(2)	120.0 (2)	S—C(1)—C(5)	116.3 (3)
O(1)—S—C(1)	108.3 (2)	C(2)—C(1)—C(5)	122.2 (3)
O(1)—S—C(3)	106.8 (2)	O(3)—C(2)—C(1)	121.2 (3)
O(2)—S—C(1)	107.1 (2)	S—C(3)—C(4)	119.1 (3)
O(2)—S—C(3)	109.1 (2)	S—C(3)—C(7)	116.8 (3)
C(1)—S—C(3)	104.6 (2)	C(4)—C(3)—C(7)	124.1 (3)
C(2)—O(3)—C(6)	116.9 (3)	O(4)—C(4)—C(3)	122.0 (3)
C(4)—O(4)—C(8)	116.2 (3)	N(1)—C(5)—C(1)	178.9 (4)
S—C(1)—C(2)	121.5 (3)	N(2)—C(7)—C(3)	177.4 (4)
S—C(1)—C(2)—O(3)	-178 (3)	O(1)—S—C(3)—C(7)	-178 (3)
S—C(3)—C(4)—O(4)	-178 (3)	O(2)—S—C(1)—C(2)	3 (4)
O(1)—S—C(1)—C(2)	134 (3)	O(2)—S—C(1)—C(5)	-177 (3)
O(1)—S—C(1)—C(5)	-47 (3)	O(2)—S—C(3)—C(4)	133 (3)
O(1)—S—C(3)—C(4)	2 (3)	O(2)—S—C(3)—C(7)	-47 (3)

**Discussion.** The final atomic parameters are given in Table 1.\* The identification of the atoms and the configuration of the molecule are shown in the *ORTEP* (Johnson, 1965) drawing of Fig. 1.

\* Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44291 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

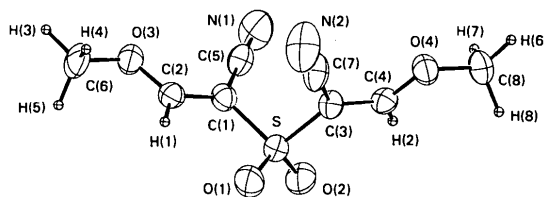


Fig. 1. *ORTEP* drawing of the molecule. Thermal ellipsoids scaled to enclose 30% probability. H atoms are represented as spheres of arbitrary radii.

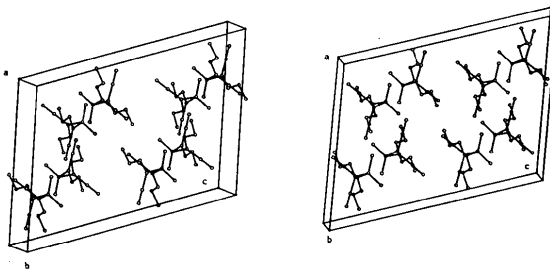


Fig. 2. Stereoscopic drawing of the molecular packing in the unit cell. Atoms are represented as circles of arbitrary radii.

The bond lengths, bond angles and selected torsion angles with their standard deviations are given in Table 2. The packing of eight molecules in the unit cell is shown in Fig. 2. There are no other intermolecular contacts less than van der Waals distances. The geometry of the title compound is in good agreement with the data we have recently obtained for 2,2'-bis(dimethylaminomethylene)-2,2'-sulfonyldiacetonitrile (Siriwardane, Chu, Hosmane, Bertha & Hosmane, 1987), where the bond distances are: S—O, 1.433 (3); S—C, 1.744 (4); C—CN, 1.415 (6), C=C, 1.377 (6); C≡N, 1.139 (6) Å; and the angle O—S—O is 118.9 (2)°. In the title compound, the corresponding values are 1.424 (3), 1.737 (4), 1.417 (5), 1.342 (5), 1.138 (5) Å and 120.0 (2)°. The diagonal distance  $\alpha$ - $\alpha'$ , computed from the observed sets of fractional coordinates and unit-cell measurements, is 4.976 Å. The conformational relationship between  $\alpha$ ,  $\alpha'$  C atoms is *trans* as predicted.

This work was supported by grants from the National Science Foundation (No. CHE-84-18874) (NSH), the National Institutes of Health (Nos. CA36154 and HL 33629) (RSH), American Heart Association—Maryland Affiliate (RSH), and the Robert A. Welch Foundation (Nos. N-1016 and N-495) (NSH and SSCC).

#### References

- BOLIN, R. B., BEYER, R. P. & NEMO, G. J. (1983). Editors. *Advances in Blood Substitutes Research*. New York: Alan R. Liss Inc.
- CIMINO, G. D., GAMPER, H. B., ISAACS, S. T. & HEARST, J. E. (1985). *Annu. Rev. Biochem.* **54**, 1151–1193.

- HOPWOOD, D., ALLEN, C. R. & MCCABE, M. (1970). *Histochem. J.* **2**, 137–150.
- HOSMANE, R. S. & BERTHA, C. M. (1987). In preparation.
- JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- MCCORMICK, J. E. & MCELHINNEY, R. S. (1972). *J. Chem. Soc. Perkin Trans. 1*, pp. 1335–1342.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- MOK, W., CHEN, D.-E. & MAZUR, A. (1975). *Fed. Proc. Fed. Am. Soc. Exp. Biol.* **34**, 1458–1460.
- SCHOMAKER, V. & MARSH, R. E. (1983). *Acta Cryst. A* **39**, 819–820.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SIRIWARDANE, U., CHU, S. S. C., HOSMANE, N. S., BERTHA, C. M. & HOSMANE, R. S. (1987). *Acta Cryst. C* **43**, 1823–1826.
- TOMASZ, M., LIPMAN, R., CHOWDARY, D., PAWLAK, J., VERDINE, G. L. & NAKANISHI, K. (1987). *Science*, **235**, 1204–1208.
- WALDER, J. A., WALDER, R. Y. & ARNONE, A. (1980). *J. Mol. Biol.* **141**, 195–216.

*Acta Cryst.* (1988). **C44**, 107–109

## (2,6-Diphenyl)phenyl Methacrylate.\* 1. Synthesis and Crystal Structure

BY FRITS JAN VIersen, WIRO M. P. B. MENGE AND YOE-YONG TAN†

Laboratory of Polymer Chemistry, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

AND FRÉ VAN BOLHUIS

Chemical Laboratory, State University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

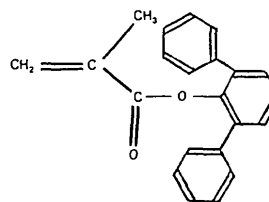
(Received 13 October 1986; accepted 15 September 1987)

**Abstract.**  $C_{22}H_{18}O_2$ ,  $M_r = 314.4$ , monoclinic,  $P2_1/c$ ,  $a = 14.214$  (2),  $b = 7.259$  (3),  $c = 16.369$  (2) Å,  $\beta = 96.80$  (1)°,  $V = 1677.1$  (1.1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.245$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu(\text{Mo } K\alpha) = 0.73$  cm<sup>-1</sup>,  $F(000) = 664$ ,  $T = 140$  K,  $R = 0.047$  for 2241 reflections with  $I \geq 3\sigma(I)$ . Prepared by reaction of *m*-terphenyl-2'-ol or its K salt with methacryloyl chloride in ether or in tetrahydrofuran. The monomer (m.p. 374.6–375.6 K) was not polymerizable owing to steric hindrance of the bulky ester group.

**Introduction.** In the search for methacrylate monomers that on polymerization produce as little shrinkage as possible, the title compound (1) seems a most attractive candidate. This monomer has not been described before. It can be readily synthesized by reacting methacryloyl chloride with the appropriate phenol, either as such or as its K salt.

Besides characterization by IR and NMR, its crystal structure has been determined. When this was done at room temperature it was difficult to assign unambiguously the two adjacent bonds C=CH<sub>2</sub> and C-CH<sub>3</sub>, since they gave approximately identical bond-distance values, *viz.* 1.433 and 1.442 Å. The same problem was encountered in determining the structure of 4-( $\alpha,\alpha$ -dimethylbenzyl)phenyl methacrylate at room tem-

perature (Viersen, Tan, van Bolhuis & Zwieters, 1985). Two explanations were forwarded: one was rapid rotation around the C-C ester bond, the other was a 50–50 disorder placement of C=CH<sub>2</sub> and C-CH<sub>3</sub> bonds. In order to establish the true reason, measurements were made at 140 K.



(1)

**Experimental. Synthesis.** To a 200 ml ether solution of 12.8 g (0.052 mol) of *m*-terphenyl-2'-ol and 51.3 g (0.052 mol) of triethylamine under a N<sub>2</sub> blanket, 6.3 g (0.061 mol) of methacryloyl chloride was added dropwise. After 24 h the reaction mixture was filtered, washed with water, *etc.* On cooling the concentrated ether solution to 253 K pure crystals of (1) were obtained. Yield: 4.0 g (22%). Alternatively (1) could be synthesized in a much better yield as follows. To a solution of 24.6 g (0.1 mol) of *m*-terphenyl-2'-ol in 100 ml absolute ethanol 5.8 g (0.1 mol) of powdered KOH was added. After 15 min stirring the yellowish

\* IUPAC name: *m*-terphenyl-2'-yl methacrylate.

† To whom correspondence should be addressed.