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)···O(2) (x, y, z) hydrogen bonds [N(3)···O(2) 3·04 (1), N(3)-H(N3) 1·09 (7), H(N3)···O(2) 1·97 (7) Å, N(3)-H(N3)··· O(2) 170 (5)°]. The chains are parallel to the [011] direction and the symmetry-equivalent [011] 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. This work was partially supported by Scientific Research Grant-in-Aid #61460072 from the Ministry of Education, Science and Culture.

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

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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) Å³, Z = 8, $D_x = 1.40$ g cm⁻³, λ (Mo K α) = 0.71069 Å, $\mu = 2.81$ cm⁻¹, 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=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

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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. Psoraleins, 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

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(Walder, Walder & Arnone, 1980) and bisimidates (Mok, Chen & Mazur, 1975) have been used to cross link hemoglobin subunits so as to modify the latter's oxygen-affinity characteristics and retention time. The modified bovine and human hemoglobins were to be adapted as a cell-free oxygen carrier in lieu of blood for emergency transfusions involving rare blood types (Bolin, Beyer & Nemo, 1983). We report herein the structure and properties of a bifunctional organic reagent, 2,2'-bis(methoxymethylene)-2,2'-sulfonyldiacetonitrile (MMSBA) (I). This reagent has potentially useful applications for cross linking proteins and/or nucleic acids.



aminopyridine and 2-aminopyrimidine. The product bis-enamines, obtained in 50-95% yields, were fully characterized by spectroscopy coupled with combustion analyses. We are currently in the process of reacting (I) with nucleic acid bases and amino acids.

The reagent (I) was recrystallized from dry xylene for X-ray analysis. Our main interest was to explore the diagonal distance between the two cross-linking sites α,α' . This distance, among other factors, is crucial in effecting site-directed inter/intrastrand or -subunit crosslink between nucleic acids or proteins as shown below.



Cross Links in Double-Helical DNA: a, interstrand; b, intrastrand

The title reagent (I) was synthesized (Hosmane & Bertha, 1987) by the reaction of 2,2'-sulfonyldiacetonitrile (McCormick & McElhinney, 1972) with excess trimethyl orthoformate, catalyzed by concentrated sulfuric acid. The reagent (I), obtained in 45–50% yield, is a colorless, crystalline solid (m.p. 478–481 K) and can be stored indefinitely in a refrigerator upon adequate protection from moisture. The compound was characterized by IR, 'H NMR and mass spectral data and elemental microanalyses.

The reagent (I) is a bis-enol-ether with each β -C atom flanked by strongly electron-withdrawing nitrile and sulforyl functions, thus causing the α, α' -C atoms to become highly electrophilic. The nucleophilic attack at each α -C atom by amine nucleophiles (e.g. guanine 2-NH₂ in nucleic acids or lysine ε -NH₂ in proteins) will produce an energetically favorable resonancedelocalized zwitterionic species (II). The intermediate (II), upon elimination of a molecule of methanol, would yield the enamine (III). The latter upon reaction with a second molecule of amine would produce the bisenamine (IV). We have thus far studied (Hosmane & Bertha, 1987) the reactivity of (I) with two equivalents each of seven nucleophiles: ammonia, butylamine, dimethylamine, cyclohexylamine, diethylamine, 2-

Experimental. Crystals of the title compound are colorless square plates; a single crystal ($0.42 \times 0.32 \times$ 0.31 mm) was mounted on a goniometer head with an epoxy resin; unit-cell parameters by least-squares fit of 15 reflections in the range $10 < 2\theta < 25^{\circ}$; space group C2/c from systematic absences (0k0, k odd, h0l, l odd, *hkl*, h + k odd); automatic Syntex P2₁ diffractometer, graphite-monochromated Mo K α radiation, $\theta/2\theta$ scan mode; 1627 measured reflections; 1424 independent reflections in the range $3 < 2\theta < 45^{\circ}$; $R_{int} = 0.004$; *hkl* range $h = 18 \rightarrow -19$, $k = 0 \rightarrow 10$, l = 14; 1033 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics; 3 standard reflections remeasured after every 100 reflections did not show any significant change in intensity during data collection; Lorentz-polarization correction, no absorption or extinction corrections; direct methods, MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); refinement by full-matrix least squares using SHELX76 (Sheldrick, 1976), anisotropic, H atoms located in difference Fourier maps, isotropic temperature factors for H; $w = 1/[\sigma^2(F) + 0.003687F^2];$ $\sum w(|F_{o}| - |F_{c}|)^{2}$ minimized; R = 0.041, wR = 0.049; $(\Delta/\sigma)_{max} = 0.15$, $\Delta \rho_{(\text{max,min})} = 0.05, -0.06 \text{ e} \text{ Å}^{-3}$ in final difference Fourier map. Atomic scattering factors for C, H, O, N and S and the effects of the anomalous-dispersion correction for S used were those stored in SHELX76.

Table 1. Fractional atomic coordinates with equivalentisotropic thermal parameters for the non-H atoms andisotropic thermal parameters for H atoms with e.s.d.'sin parentheses

	x	У	Ζ	$U_{\rm eq}^{*}/U({\rm \AA}^2)$
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 (Å), bond angles (°) and selected
torsion angles (°)

S-O(1) S-O(2) S-C(1) S-C(3) O(3)-C(2) O(3)-C(6)	1 · 424 (3) 1 · 423 (3) 1 · 734 (4) 1 · 739 (4) 1 · 288 (4) 1 · 454 (5)	O(4)-C(8) N(1)-C(5) N(2)-C(7) C(1)-C(2) C(1)-C(5) C(3)-C(4)	1.441 (5) 1.131 (5) 1.148 (5) 1.344 (5) 1.415 (5) 1.340 (5)
O(4)–C(4)	1.303 (4)	C(3)–C(7)	1.419 (5)
$\begin{array}{c} O(1) - S - O(2) \\ O(1) - S - C(1) \\ O(1) - S - C(3) \\ O(2) - S - C(3) \\ O(2) - S - C(3) \\ C(1) - S - C(3) \\ C(2) - O(3) - C(6) \\ C(4) - O(4) - C(8) \\ S - C(1) - C(2) \end{array}$	120.0 (2) 108.3 (2) 106.8 (2) 107.1 (2) 109.1 (2) 104.6 (2) 116.9 (3) 116.2 (3) 121.5 (3)	$\begin{array}{l} S-C(1)-C(5)\\ C(2)-C(1)-C(5)\\ O(3)-C(2)-C(1)\\ S-C(3)-C(4)\\ S-C(3)-C(7)\\ C(4)-C(3)-C(7)\\ O(4)-C(4)-C(3)\\ N(1)-C(5)-C(1)\\ N(2)-C(7)-C(3) \end{array}$	116.3 (3) 122.2 (3) 119.1 (3) 116.8 (3) 124.1 (3) 122.0 (3) 178.9 (4) 177.4 (4)
$\begin{array}{l} S-C(1)-C(2)-O(3)\\ S-C(3)-C(4)-O(4)\\ O(1)-S-C(1)-C(2)\\ O(1)-S-C(1)-C(5)\\ O(1)-S-C(3)-C(4)\\ O(1)-S-C(4)\\ O(1)-S-C(4$	$\begin{array}{c} -178 (3) \\ -178 (3) \\ 134 (3) \\ -47 (3) \\ 2 (3) \end{array}$	O(1)-S-C(3)-C(7 O(2)-S-C(1)-C(2 O(2)-S-C(1)-C(5 O(2)-S-C(3)-C(4 O(2)-S-C(3)-C(7	$\begin{array}{c} -178 (3) \\ 3 (4) \\ -177 (3) \\ 133 (3) \\ -47 (3) \end{array}$

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.



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 α, α' C atoms is trans as predicted.

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^{*} 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.

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

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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) Å³, Z = 4, $D_x =$ 1.245 g cm⁻³, λ (Mo K α) = 0.7107 Å, μ (Mo K α) = 0.73 cm⁻¹, F(000) = 664, T = 140 K, R = 0.047 for 2241 reflections with $I \ge 3\sigma(I)$. 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 $C=CH_2$ and $C-CH_3$, 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-(α,α -dimethylbenzyl)phenyl methacrylate at room tem-

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perature (Viersen, Tan, van Bolhuis & Zwiers, 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=CH₂ and C-CH₃ bonds. In order to establish the true reason, measurements were made at 140 K.



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 N₂ 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

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^{*} IUPAC name: m-terphenyl-2'-yl methacrylate.