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High Electron-Acceptability of a 2,2-Bis(alkyl- or arylsulfonyl)ethenyl Group

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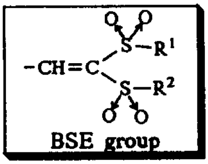
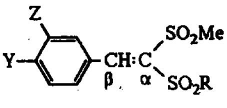
Abstract: A 2,2-bis(alkyl- or arylsulfonyl)ethenyl group (BSE group) exhibits high electron acceptability which can be utilized for an electron-accepting part of second-order nonlinear optical materials.

In this letter, we wish to evaluate an electron-acceptability of 2,2-bis(alkyl- or arylsulfonyl)ethenyl group (BSE group)[1] and its utilization for second-order nonlinear optical materials. The best organic entries in the second-order nonlinear optics are conjugated π-systems in which an electron donating group is separated from an acceptor group.[9] A new type of electron acceptor group opens doors to new nonlinear optics. Our attention was paid to a sulfonyl group which is stable chemically and thermally, easy to deal with, and well crystallizable. Since the sulfonyl group bears two S-O coordinate bonds to strongly stabilize an adjacent anion,[10] the BSE group is anticipated to exhibit unique properties as an electron acceptor.



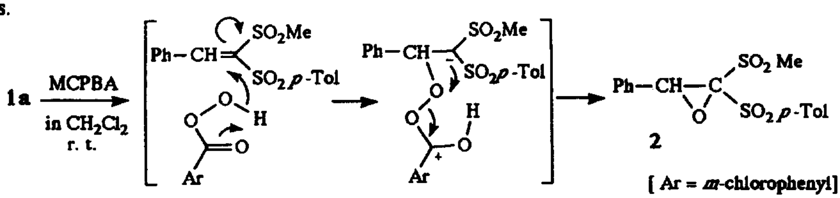
BSE group



1

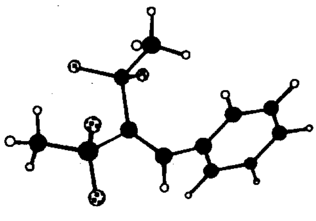
a	Y = Z = H	R = *p*-Tol
b	Y = Z = H	R = Me
c	Y = OMe Z = H	R = *p*-Tol
d	Y = OMe Z = OMe	R = *p*-Tol
e	Y = OMe Z = H	R = Me

To our surprise, high electron acceptability of the BSE group was reflected in a smooth oxidation of 1-(methylsulfonyl)-1-(*p*-tolylsulfonyl)-2-phenylethene (**1a**) with *m*-chloroperbenzoic acid (MCPBA) under neutral conditions.



[Ar = *m*-chlorophenyl]

Treatment of **1a** with MCPBA in CH_2Cl_2 at room temperature for 1 d gave the corresponding epoxide (2) in 87% yield. The present oxidation is rationalized in terms of nucleophilic attack of MCPBA on the C_β carbon followed by elimination of *m*-chlorobenzoic acid. This is in good contrast to the fact that nucleophilic epoxidation of simple α,β–unsaturated sulfones requires an anionic peroxide such as lithium *t*-butyl peroxide.[11,12]



(A)

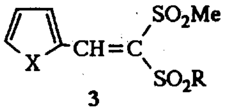
By the MNDO/PM3 method,[13] molecular orbital calculation was performed for 1,1-bis(methylsulfonyl)-2-phenylethene (**1b**). The β-carbon of the most stable conformer (A)[14] is much positive (the charge = +0.2054) and C_β p_z contributes much to the LUMO (the coefficient = 0.6846). In contrast, the β-carbon of 1-(methylsulfonyl)-2-phenylethene is less positive (+0.1000) and the coefficient of the C_β p_z in the LUMO is relatively small (0.4698). These results accord with the nucleophilic oxidation of **1a** with MCPBA.

We measured the molecular polarizability (β value)[15] and second harmonic generation (SHG) efficiency[16] by using Nd:YAG laser (1064 nm) for a variety of **1** and **3** (Table 1). As expected, the methoxyl-substituted ones exhibited large β values. It is noteworthy that the cutoff of uv absorption occurs at a relatively shorter wavelength. The SHG activity of **1e** origins from unsymmetrical array of the molecules in a crystal as shown in Fig. 1.[17] Two molecules of **1e** were arranged in a Λ form through an interaction between the oxygen of the sulfonyl group and the hydrogen of the sulfonyl methyl. We also synthesized two vinylogs (**4** and **5**) of **1**. **4** exhibited a large β value (23.9), but the β value of the branched one (**5**) was small (3.9). Therefore the BSE group appeared to be effective for an acceptor of electrons.

Table 1. Nonlinear Optical Properties of **1** and the Related Compound (**3**)

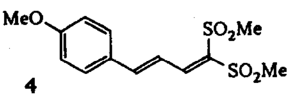
Compound	λ_{max} (nm)^a	λ_{cutoff} (nm)^b	β (10^{-30} esu)^c	SHG Activity^d
1b	282	322	4.7	0
1c	330	---	8.3	0
1d	352	---	10.6	0
1e	325	377	6.4	8.6
3a	329	388	5.2	0
3b	322	380	5.1	0
3c	333	---	4.5	0
3d	327	388	4.0	0

a) In EtOH. b) Evaluated from the wavelength with a transmittance of 95%. c) In dioxane. d) Relative to urea.



3

a X = O R = *p*-Tol
b X = O R = Me
c X = S R = *p*-Tol
d X = S R = Me



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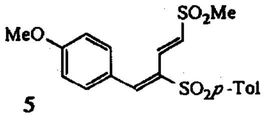

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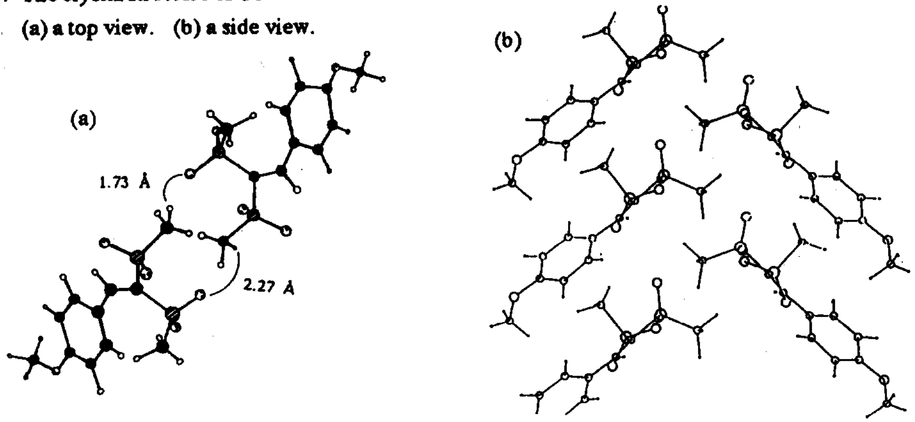
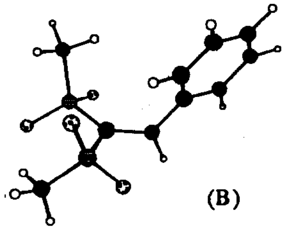
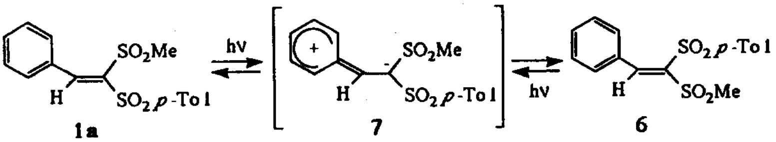
Fig. 1. The crystal structure of **1e**
(a) a top view. (b) a side view.



The MNDO/PM3 calculation[13] also showed that, in the lowest excited singlet state of **1b**, the C_α-C_β bond twists by about 90° [see a formula (B)] and the β-carbon is less positive (+0.0948) by donation of the π-electrons into the C_α-C_β double bond. The UV spectrum of **1a** in THF showed a benzenoid band with a *large* absorption coefficient (ε 20000) at 289 nm which was somewhat shifted to 291 nm (ε 4000) in ethanol. Irradiation (>290 nm)[19] at this absorption caused isomerization around the C_α-C_β double bond to afford quantitatively a 44 : 56 mixture of the (*E*) and (*Z*)-isomers at a photostationary state.[20]



(B)



In a methoxyl(s)-substituted derivative (**1c** or **1d**), electron donation from the methoxyl group into the C_α-C_β double bond was observed in its uv and ^{1}H NMR spectra. The uv absorptions of **1c** and **1d** appeared at longer wavelengths (327 and 351 nm, respectively, in THF). The chemical shift of the proton on the C_β carbon was at a higher field (in $CDCl_3$: δ 8.55 for **1c** and δ 8.54 for **1d**) than that of **1a** (δ 8.70), implying the increase of the electron density around the C_β proton. These observations are in good coincidence with the fact that MCPBA could not oxidize **1c** to afford the corresponding epoxide.

In conclusion, high electron acceptability of 2,2-bis(alkyl- or arylsulfonyl)ethenyl (BSE) groups was ascertained from its chemical and physical properties. Now we are investigating further development of new nonlinear optical materials utilizing the BSE group as an electron acceptor.

REFERENCES AND NOTES

1. The BSE group was easily prepared by peracid oxidation of the corresponding 2,2-bis(alkyl- or arylthio)-ethenyl group,[2] its monosulfinyl derivative,[3] or its monosulfonyl derivative.[4] A Knoevenagel-type con-

densation of benzaldehyde with bis(alkylsulfonyl)methane in the presence of piperidine was also reported.[5] This method is ambiguous since it is accompanied by the rearrangement of the sulfonyl group.[6]

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14. The dihedral angle of C_α-C_β-C(phenyl)-C(phenyl) is 66.4°. The most stable conformer of **1e** was calculated to be similar to its X-ray structure (Fig. 1), whose skeleton resembles A, except for somewhat different dihedral angle (41.8°) of C_α-C_β-C(phenyl)-C(phenyl) (Cf. that of the X-ray structure = 22.9°).
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17. Crystal data are as follows: $C_{12}H_{14}O_5S_2$, F.W.=234.21, orthorhombic, space group $Pna2_1$, a=14.3796 (30) Å. b=15.3706 (42) Å, c=5.8784 (32) Å; α=90.0 (0)°, β=90.0(0)°, γ=90.0 (0)°; V=1299.25 Å^3; D_x=1.484 g cm^{-3}; Z=4. A computer program UNICS III[18] MULTAN Set No. 1896/2048 run on a HITACHI M680 at Tokyo University was employed for the analysis. The intensity data were collected in the region $3° < 2\theta < 120°$. For a structure analysis, 1112 independent reflections with $I_o > 3\sigma(I_o)$ were used. The final refined R value was 0.040.
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19. With a high pressure Hg lamp through a Pyrex glass. This isomerization was also induced by sunlight.
20. In DMSO, this isomerization occurred in the dark. Since other solvents such as chloroform and acetone were ineffective, the isomerization may be induced by the addition-elimination of the oxygen of DMSO at the C_β position of **1a**.

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