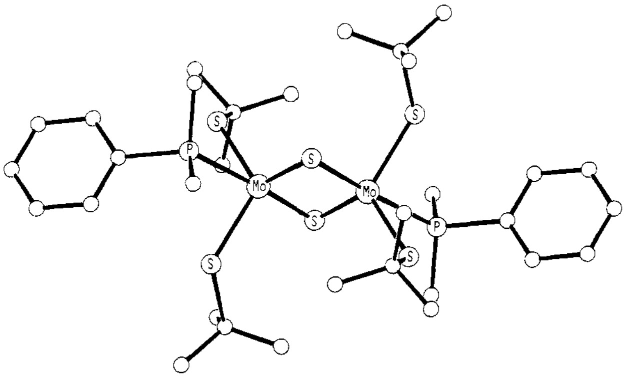
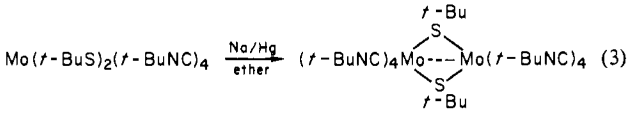


Figure 3. Molecular Structure of $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(PMe_2Ph)_2$ (**5**).

geometry around Mo(I) is distorted octahedral with a large SMoS angle of 106.1 (2)° and a small equatorial CMoC angle of 81.4 (5)°. The average Mo–C(equatorial) distance (2.01 Å) is slightly shorter than the Mo–C(axial) distance (2.05 Å). The Mo–Mo bond [2.984 (2) Å] and Mo–S bond distance (2.48) are comparable to the corresponding parameters [2.923 (1) and 2.40 Å] of a related compound, $Mo_2(\mu\text{-}EtS)_2(\eta\text{-}C_5H_5)_2(NO)_2$.[16]

An alkylisocyanide analogue of **3**, i.e., $Mo_2(\mu\text{-}t\text{-}BuS)_2(t\text{-}BuNC)_8$ (**4**),[5] was obtained from **2**. Thus, a green solution of **2** in ether was stirred with Na/Hg at ambient temperature for 2 h.[4] The solution turned to yellowish brown. After removing precipitated *t*-BuSNa by filtration, the solution was concentrated partially to give an analytically pure, dark brown diamagnetic crystal of **4** (75% yield), mp 165–167° (dec); IR (*n*-hexane) $\nu(N{\equiv}C)$ 2080 (sh), 2000 (vs), 1855 (s) cm^{-1}; ^1H NMR (toluene-d_8) δ 1.30, and 1.56 (*t*-BuNC), 1.82 (*t*-BuS); λ_{max} (toluene) nm (log ϵ) 395 sh (3.59), 480 sh (3.23), 980 sh (2.45). The observation of two singlet ^1H NMR signals for *t*-BuNC ligands and one for *t*-BuS ligands and the IR data are consistent with a *t*-BuS bridged dimeric structure[17] similar to **3**.



$$Mo(t\text{-}BuS)_2(t\text{-}BuNC)_4 \xrightarrow[\text{ether}]{\text{Na/Hg}} (t\text{-}BuNC)_4Mo(\mu\text{-}S\text{-}t\text{-}Bu)_2Mo(t\text{-}BuNC)_4 \quad (3)$$

The observed low $\nu(N{\equiv}C)$ frequencies compared to those found in $Mo_2(\mu\text{-}Cl)_2(t\text{-}BuNC)_8$ (2146, 2123 cm^{-1})[18] again reflect the strong electron-donating property of the thiolate ligand. Further reduction of **4** beyond Mo(I) does not occur by prolonged contact with Na/Hg (24 h). The selective one-electron chemical reduction is amazing.

The reaction of **1** with PMe_2Ph occurs above 50 °C, yielding a Mo(IV) dimeric compound. Thus a toluene solution (20 mL) containing **1** (1.0 mmol) and PMe_2Ph (2.0 mmol) was stirred[4] at 60 °C for 5 h. The initially red solution gradually turned very dark colored and finally dark green. In the vapor and liquid phase of the flask, isobutene and *t*-BuSH were detected, respectively, by GLC. The resulting reaction mixture was evaporated to dryness by vacuum distillation, and the residue was recrystallized to give a myrtle green, diamagnetic crystal of $Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(PMe_2Ph)_2{\cdot}C_6H_5CH_3$ (**5**),[5] mp 180 °C (dec), in 80% yield; λ_{max} (*n*-hexane), nm (log ϵ) 290 (4.49), 329 sh (4.19), 369 (4.01), 425 sh (3.64), 446 (3.11), and 710 (3.65); IR (Nujol) 1153 cm^{-1} $\delta(C(CH_3)_3)$. The ^1H NMR (C_6D_6 at ambient temperature) shows a multiplet centered at δ 2.66 characteristic of an $X_6AA'X'_6$ ($|J_{AA'}| > |J_{AX} - J_{AX'}|$) spin system for the methyl protons of PMe_2Ph, suggesting a strong metal–metal interaction and a singlet at δ 1.16 for the *t*-BuS protons.

$$2Mo(t\text{-}BuS)_4 + 2PMe_2Ph \rightarrow Mo_2(\mu\text{-}S)_2(t\text{-}BuS)_4(PMe_2Ph)_2 + 2(CH_3)_2C{=}CH_2 + 2t\text{-}BuSH \quad (4)$$

The molecular structure of **5** was determined by X-ray studies[19] and is centrosymmetric (Figure 3). The geometry around Mo(IV) ion is best described as a distorted trigonal bipyramid with the axial phosphine and sulfide ligands. The average Mo–S(*t*-Bu) distance of 2.31 Å is longer than that of **1**.[3] The Mo–Mo distance of 2.741 (1) Å is consistent with metal–metal bonding.

The formation of this sulfide-bridged dimer indicates facile dealkylation of the $t\text{-}BuS^-$ ligand. Apparently the strong electron-donating property of PMe_2Ph is responsible for the preferential formation of Mo(IV) rather than the lower valent ions. PPh_3 reacts with **1** (60 °C, 5 h), resulting in a mixture of products we have not identified yet.

Preparative appliations of **1** are of course not limited to the four reactions so far described in this paper. For example, it may be useful as a molybdenum component to synthesize Mo–Fe–S mixed clusters.[20] Thus **1** is a versatile starting material offering a rich thiolatomolybdenum chemistry.

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(16) Clark, G. R.; Hall, D.; Marsden, K. *J. Organometall. Chem.*, **1979**, *177*, 411–434.

(17) An X-ray crystallographic analysis of **4** has been undertaken.

(18) King, R. B.; Saran, M. S. *Inorg. Chem.* **1974**, *13*, 2453–2457.

(19) Single crystals of **5** were grown from toluene. They belong to $P\bar{1}$ with $a = 13.331$ (8), $b = 10.343$ (5), $c = 9.553$ (5) Å; $\alpha = 97.58$ (4), $\beta = 108.62$ (4), $\gamma = 98.57$ (4)°; V (for $Z = 2$) = 1211 (1) Å^3. $R = 4.1\%$ for 2681 reflections with $I > 3\sigma(I)$.

(20) Otsuka, S.; Kamata, M., ref 2, pp 229–238.

Photochemistry of Stilbene-Capped Cyclodextrins. Exclusive Ring Closure of Cis Cap and Direct Evidence for Trans A,D Structure

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Since the first member of rigidly capped cyclodextrin family appeared,[1] these compounds have been gradually recognized as important key intermediates for di- (poly-) functional catalysts of various enzyme activities.[2] Problems of less regioselective capping by the original diphenylmethane cap elegantly displayed by Breslow[2b] have been solved by the recent discovery of regioselective A,C- and A,D-capping reagents, benzophenone-3,3′-disulfonyl chloride and stilbene-4,4′-disulfonyl chloride,[3] respectively (see Figure 1). Now we wish to report the unique photochemistry of *trans*- and *cis*-stilbene-4,4′-disulfonyl-capped β-cyclodextrins.

This photochemistry originates in our finding very efficient energy transfer between benzophenone-capped β-cyclodextrin and an appropriate naphthalene derivative;[4] further investigations of modified cyclodextrins have been extensively pursued, such as the

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(1) (a) Tabushi, I.; Shimokawa, K.; Shimizu, N.; Shirakata, H.; Fujita, K. *J. Am. Chem. Soc.* **1976**, *98*, 7855. (b) Tabushi, I.; Shimokawa, K.; Fujita, K. *Tetrahedron Lett.* **1977**, 1527–1530.

(2) (a) Tabushi, I.; Kuroda, Y.; Mochizuki, A. *J. Am. Chem. Soc.* **1980**, *102*, 1152–1153. (b) Breslow, R.; Doherty, J. B.; Guillot, G.; Hersh, C. L. *Ibid.* **1978**, *100*, 3227–3229. (c) Breslow, R.; Bovy, P.; Hersh, C. L. *Ibid.* **1980**, *102*, 2115–2117.

(3) Tabushi, I.; Kuroda, Y.; Yokota, K.; Yuan, L. C. *J. Am. Chem. Soc.* **1981**, *103*, 711–712.

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cis–trans isomerization[5] or dye-sensitized photooxygenation.[6] Later Ueno reported an azobenzene cap[7] but without any investigation on AC/AD regioselectivity.

Treatment of 3.04 g of β-cyclodextrin with 1.11 g of purified *trans*-stilbene-4,4′-disulfonyl chloride in 150 mL of dry pyridine gave the trans cap (**1**) in 20% yield. This trans cap was irradiated with a high-pressure mercury lamp by use of a Toshiba UV-D33S filter glass, a K_2CrO_4 and potassium biphthalate salt solution, and a $NiSO_4$ aqueous solution to give the corresponding cis cap (**2**) in practically quantitative yield. Interestingly, the trans isomer was completely converted to the cis, and no photostationary state was observed, in a marked and interesting contrast to the photoisomerization of sodium *trans*-stilbene-4,4′-disulfonate (like other simple stilbene derivatives) which leads to a stationary state (trans/cis = 53/47).

$$\mathbf{1} \rightarrow \mathbf{2}/\mathbf{1} \sim \infty \text{ (no photostationary state)}$$

$$\textit{trans}\text{-}NaO_3S\text{-}p\text{-}C_6H_4CH{=}CHC_6H_4\text{-}p\text{-}SO_3Na \rightarrow \text{cis/trans} \sim 47/53$$

This unique photochemistry of the stilbene cap was concluded to be due to the extremely low quantum yield of the trans cap formation from the cis cap. The latter, instead, was found to give a ring closure product (**4**) in a moderate quantum yield, most probably via **3** (Scheme I). Continued irradiation of the cis cap (or trans cap also) finally gave **4** as a sole detectable product.[8] This type of photo ring closure is known[9] but only as a side reaction, except in a micelle where it is the major pathway.[10]

The unique behavior of the stilbene cap seems to be due to the unique nature of its singlet excited state,[11] since the quantum yield of trans–cis isomerization of **1** by direct irradiation at 3126–3132 Å ($\phi = 0.40$) was much higher than that of a model compound (**5**) ($\phi = 0.10$), while benzophenone-sensitized isomerization at 3650–3663 Å gave very similar quantum yields, 0.45 and 0.49 for **1** and **5**, respectively.

$$\underset{\mathbf{5}}{\textit{trans}\text{-}HOCH_2CH_2OSO_2\text{-}p\text{-}C_6H_4CH{=}CHC_6H_4\text{-}p\text{-}SO_2OCH_2CH_2OH} \xrightleftharpoons{\text{direct or } Ph_2CO \text{ sensitized}} \underset{\mathbf{6}}{\text{cis isomer}}$$

Treatment of 0.4 g of β-cyclodextrin with 0.14 g of *cis*-stilbene-4,4′-disulfonyl chloride in 30 mL of dry pyridine gave the corresponding cis cap (in 20% combined yield after isolation)[12] which, interestingly, consisted of two well-resolved peaks, P_1 and P_2, in HPLC. The second peak P_2 was identical with the cis cap obtained from photoisomerization of **1** in every respect. These two cis caps P_1 and P_2 were converted exclusively to the corresponding phenanthrene derivatives but at remarkably different rates (P_2 was ca. 10 times faster), and the resultant phenanthrene caps showed much better separation than the cis caps, allowing precise determination of P_1/P_2 ratio which was found to be 1.38. The phenanthrene caps were identical with those independently prepared from phenanthrene-3,6-disulfonyl chloride (P_1'/P_2' = 8.1); IR 1346 and 1175 cm^{-1} with cyclodextrin absorptions, ^{1}H NMR (Me$_2$SO-d_6) δ 8.0–8.5 and 9.0–9.3 (8 H), 4.90 (7 H), centered at 3.5 (others). Since A,B structure should be excluded from candidates for P_1 or P_2 on the basis of ^{13}C NMR spectra,[13] P_1 or P_2 should be A,C and A,D, respectively, or vice versa. The fact that ready formation of a double cap was observed for the mixture ($P_1 + P_2$) but not for pure P_2 (eq 1 and 2) strongly demonstrates that P_2 is A,D and P_1 is A,C,[14] which is in accord with the reasonable expectation from CPK model where the cis disulfonyl chloride (7.8–10.7 Å) is much shorter in looper's walk than the trans (ca. 13.5 Å).

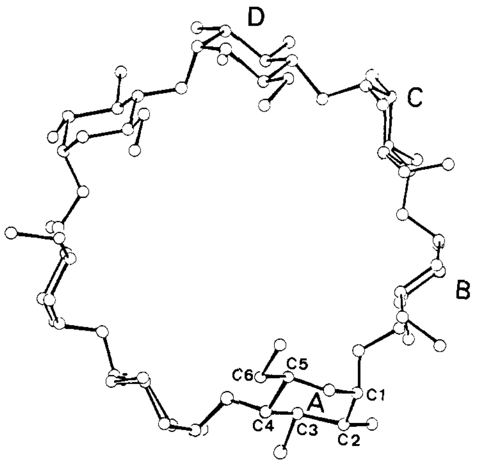
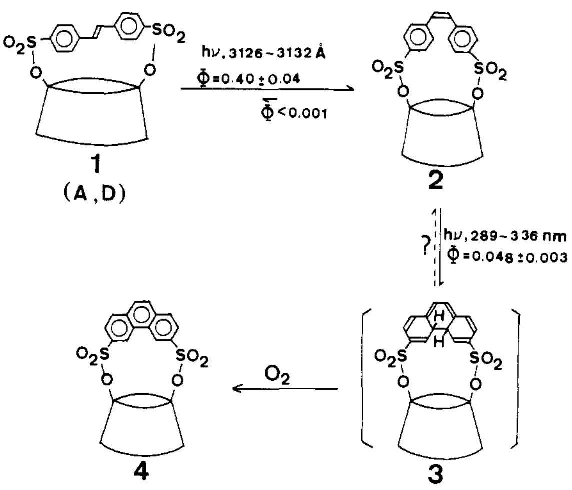


Figure 1. β-Cyclodextrin. The ABCDEFG nomenclature was originally presented by Breslow. See ref 2b,c.

Scheme I



$$cis\text{-stilbene-4,4'-disulfonyl chloride} + \beta\text{-CD} \rightarrow P_1 + P_2$$

$$trans\text{-stilbene-4,4'-disulfonyl chloride} + \beta\text{-CD} \rightarrow P_2$$

$$P_1 + \text{capping reagent} \rightarrow \text{double cap}$$

$$P_2 + \text{capping reagent} \not\rightarrow \text{double cap}$$

Thus, a firm evidence for the A,D structure of *trans*-stilbene-4,4′-disulfonyl cap was not obtained, strongly supporting our previous conclusion that stilbene-4,4′-disulfonyl chloride was the regiospecific A,D transannular capping reagent.[3]

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(5) Tabushi, I.; Fujita, K.; Yuan, L. C. 36th Annual Meeting of the Chemical Society of Japan, Osaka, Apr 1977, Abstr. II, p 791.

(6) Tabushi, I.; Yamamura, K.; Yuan, L. C. Symposium on Photochemistry, Japan, Kyoto, Nov 1978, Abstr., p 16.

(7) (a) Ueno, A.; Yoshimura, H.; Saka, R.; Osa, T. *J. Am. Chem. Soc.* **1979**, *101*, 2779–2780. (b) Ueno, A.; Saka, R.; Osa, T. *Chem. Lett.* **1979**, 841–844. (c) *Ibid.* **1979**, 1007–1010. (d) *Ibid.* **1979**, 29–32.

(8) Ueno[7] did not detect any ring closure product.

(9) (a) Smakula, A. *Z. Phys. Chem.* **1934**, *B25*, 90–98. (b) Buckles, R. E. *J. Am. Chem. Soc.* **1955**, *77*, 1040–1041. (c) Mallory, F. B.; Wood, C. S.; Gordon, J. T. **1964**, *86*, 3094–3102.

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(12) If the solvent and/or cyclodextrin used for the cap preparation is not dry enough or if workup was not quick enough, some half-ester (monosulfonate ester monosulfonic acid) was formed as a byproduct. Also a considerable amount of polymeric material was formed.

(13) (a) Boger, J.; Brenner, P. G.; Knowles, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 7630–7631. (b) Boger, J.; Knowles, J. R. *Ibid.* **1979**, 7631–7633.

(14) Careful consideration of all the possibilities leads to the presence conclusion, P_1 = A,C and P_2 = A,D.