J. Am. Chem. Soc. 1984, 106, 7131-7133

types of molecule not used in determining the parameters, indicates that the parametrization is doing a remarkably good job at coping with the deficiencies of what are admittedly extremely crude approximations to the Schödinger equation. The neglect of overlap in the INDO and NDDO approximations is clearly one of the worst of these deficiencies. The implication is that it is adequately compensated in MINDO/3 and MNDO. Indeed, if the effects of overlap could be allowed for in these treatments without making any other changes, the implication from Houk's work is that they would then *overestimate* the stabilities of symmetrical structures.

If the tendency to make transition states unsymmetrical were universal, or if some predictions of unsymmetrical ones were contrary to the experimental evidence, the situation would of course be different, but this is not the case. Both MINDO/3 and MNDO *do* predict symmetrical transition states in many reactions where unsymmetrical structures would be perfectly feasible, e.g., various ene reactions,[45] and the experimental evidence in other cases is fully consistent with the unsymmetrical structures predicted by MINDO/3 and/or MNDO.[46]

No current theoretical procedure is reliable, and no claims to the contrary could be, or have been, made for MINDO/3 or MNDO. However, attempts to refute conclusions drawn from them, if based on inadequate calculations or specious arguments, are not helpful. What is needed in the present connection is more experimental data and/or a high-level ab initio calculation for the rearrangement of **3**, of the kind reported by Komornicki et al. for the ethylene-fulminic acid cycloaddition.[41]

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract F49620-83-C-0024) and the Robert A. Welch Foundation (Grant F-126). The calculations were carried out on a VAX 11-780 computer provided by grants from the National Science Foundation (Grant CHE82-17948) and The University of Texas at Austin.

Registry No. 3, 3917-15-5; **4**, 2100-17-6; **16**, 92127-02-1; **17**, 92127-03-2; **18**, 92127-04-3; **19**, 60838-52-0; **20**, 92127-05-4; **21**, 60838-49-5; **22**, 79929-67-2; **23**, 79999-08-9.

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(44) Even including positive[27] and negative[45] ions and radicals.[27]

(45) Dewar, M. J. S.; Rzepa, H. S. *J. Am. Chem. Soc.* **1978**, *100*, 784.

(46) See e.g.: Dewar, M. J. S.; Ford, G. P. *J. Am. Chem. Soc.* **1977**, *99*, 8343.

(47) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

A Novel Organic Photochromic

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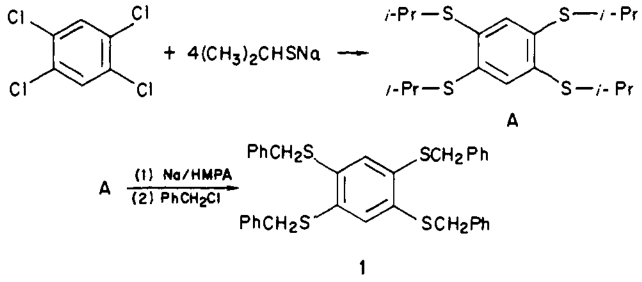
Abstract: Irradiation of 1,2,3,4-tetrakis(benzylthio)benzene with ultraviolet or visible light changes its color from white to dark pink; heating the irradiated sample above ≃80 °C reverts its color to white. It was determined that this phenomenon is due to a solid-state process. Attempts to establish, unambiguously, a mechanism for photochromism were unsuccessful. The X-ray structure determination of the molecular structure of this photochromic material as well as the mode of packing with emphasis on possible intermolecular as well as intramolecular interactions are described.

Photochromic compounds have been studied since the end of the last century in a more or less sporadic manner[1] but have become the subject of very active research in the more recent past because of their potential as photostorage devices.[2]

As part of a different project, was needed to prepare 1,2,4,5-tetrakis(benzylthio)benzene (**1**) as a logical precursor for the preparation of the corresponding benzene-1,2,4,5-tetrathiol[3] via solvated electron reduction.[3] Much to our surprise, a survey of the literature revealed that whereas a number of 1,2,4,5-tetrakis(alkylthio)benzenes had been prepared,[3] compound **1** was unknown. In Scheme I we show how the desired product was obtained.

The reactions in this approach are based mainly on work described in ref 3. At first sight it would appear that one could have prepared **1** directly from a tetrahalobenzene and benzylmercaptide. Unfortunately, under the conditions required for nucleophilic aromatic substitution (polar aprotic solvent, elevated temperature), debenzylation takes place[4] concomitant with nucleophilic substitution. Previous work showed this to be the case also when methyl mercaptide was used as the nucleophile.[3]

Scheme I



Compound **1** is a white, crystalline solid[5] which quickly turns pink when exposed to light, either fluorescent or solar. It can be shown, as follows, that this change in color is due to a solid-state process: 1. The infrared spectrum of a KBr pellet before and

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(1) Exelby, R.; Grinter, R. *Chem. Rev.* **1965**, *65*, 247. DoMinh, T.; Trozzolo, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 4046.

(2) Brown, G. H., Ed. "Photochromism"; Wiley-Interscience: New York, 1971; Vol. 3.

(3) Preparation of A: Testaferri, L.; Tingoli, M.; Tiecco, M. *J. Org. Chem.* **1980**, *45*, 4376. Reduction of A to a claimed yield of 63% of benzene-1,2,4,5-tetrathiol (in our hands a yield of tetrathiol of, at best, 10%): Maiolo, F.; Testaferri, L.; Tiecco, M.; Tingoli, M. *J. Org. Chem.* **1981**, *46*, 3070. Reduction of tetrakis(alkylthio)benzenes with alkali metals: Odorisio, P. A.; Pastor, S. D.; Spivack, J. D.; Radebaugh, R. K. *Phosphorus Sulfur* **1982**, *13*, 309.

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Table I

compd	photochromicit	color/ avelength,[b] nm	mp, °C	yield,[c] %
o-bis(benzylthio)benzene	no	*d*	73–74	30
m-bis(benzylthio)benzene[a]	no		55–56 (lit. 61–62)	29
p-bis(benzylthio)benzene[a]	no	*d*	123–125.5	50
1,2,4-tris(benzylthio)benzene	no		124.8–126.0	13
hexakis(benzylthio)benzene	no		116–118	44
1	yes	pink/520	147.7–150.0	30

[a] Preliminary results indicate that 1,5-dichloro-2,4-bis(benzylthio)benzene is photochromic. [b] Determined from the UV–vis spectrum of the compounds suspended in KBr pellets. [c] Isolated yields based on polyhalobenzene. [d] Shows no visible color change, but the UV–vis spectrum shows a small absorption at 440 nm upon exposure to UV.

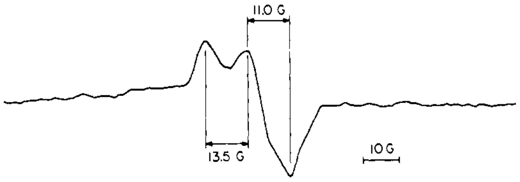

Figure 1. Electron spin resonance of irradiated **1** in the solid state. The signal disappears upon heating to >80 °C.

after coloration is unchanged. 2. Heating of a colored sample pellet returns it to its original (white) color. 3. Dissolution of a colored, powered sample causes immediate bleaching; evaporation of the solvent afforded unchanged **1**. 4. Exposure of solutions of **1** in various solvents to ultraviolet or visible radiation reveals no photochromism. 5. Exposure of a sample to ultraviolet or visible light under strictly anaerobic conditions (degassed sample, argon atmosphere) has no deleterious effect on the photochromism.

The above observations indicate (a) that the photochromism is due to a solid-state transformation and (b) that coloration–decoloration is not the result of a (reversible) surface oxidation reaction. Furthermore, the process must be a relatively low-energy transformation since it requires only temperatures in the range of 80–120 °C to effect bleaching.

That all 1-, 2-, 4-, 5-positions on the benzene ring need to be substituted to observe this effect as well as the fact that hexakis(benzylthio) substitution is deleterious can be gathered from examination of Table I.

In order to gain more insight into the mechanism responsible for the observed effect, we performed electron spin resonance (ESR) and electronic spectroscopy experiments together with a single crystal structure determination on samples of solid **1**.

A sample of pristine **1** showed no ESR signal, but pink samples whose color was generated either by exposure to light or X-rays showed a weak, complex signal which increased in intensity and changed shape at 10 K. When a UV-irradiated sample was allowed to remain ("relax") at room temperature for ≃72 h, two closely spaced lines, one at $g = 2.008$ and another at $g = 2.003$ with approximate line widths of 14 and 10 G, respectively were observed at room temperature (cf. Figure 1). These two g values could correspond to unpaired electrons centered on sulfur and carbon, respectively, and the fact that the line width does not change with temperature implies that the electrons are *localized* on these atoms. Alternately, the spectrum could be due to a single species with an anisotropic g tensor. Unfortunately, we could not record the spectrum of a single crystal (the signal was too weak) to test this possibility. Heating this sample above its bleaching temperatures caused the two sharp signals to disappear. In Figure 2, we show UV–vis spectra of pristine, pink, and "cycled" (bleached) **1** in KBr suspension. The first thing to note in this figure is the band at 875 nm in the pristine material. This unusually long-wavelength absorption arises from a solid-state effect because it is absent in solution spectra of **1**. It is also clear from Figure 2 that the absorption responsible for the coloration appears at 520 nm and that "bleaching" results in an increase of overall absorption in the whole region of these spectra.

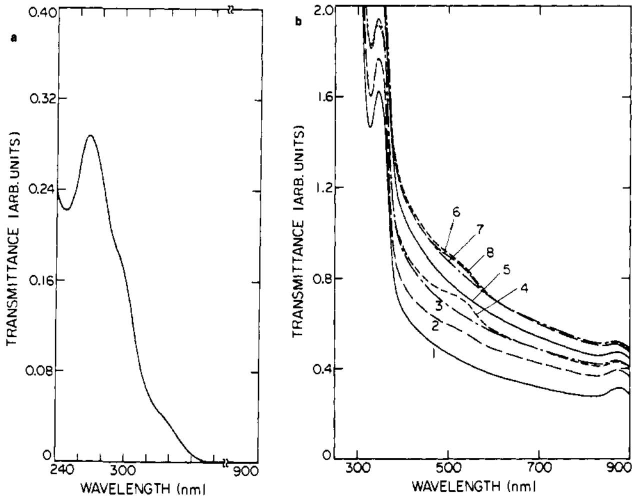

Figure 2. (a) Ultraviolet–visible spectrum of **1** in CH_2Cl_2 solution. There is no absorption in the region 400–900 nm. ϵ (268 nm) = 3 × 10^4. (b) Ultraviolet–visible spectroscopy of **1** in the solid state (KBr pellet): (1) white sample; (2) 5 s of exposure to 2550 Å; (3) heating for 1 min at ≃100 °C; (4) irradiation for 10 s; (5) heating for 1 min; (6) irradiation for 10 s; (7) heating for 1 min; (8) irradiation for 10 s.

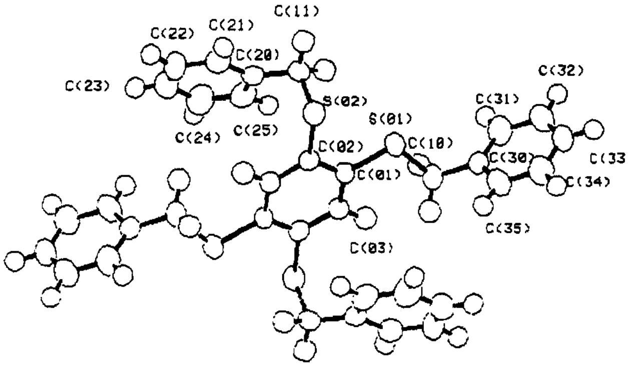

Figure 3. Molecular structure of **1**.

The solid-state structure of **1** was determined by a single crystal X-ray diffraction analysis.[6,7] A drawing of the structure depicting

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(4) Under conditions described in ref 3, reaction of 2 or 4 equivs of sodium benzyl mercaptide with either tetrafluoro- or tetrachlorobenzene afforded only dichloro- (or difluoro-) dibenzylmercaptobenzenes as the major product together with minor amounts of monosubstitution and trisubstitution products as well as substantial amounts of variously substituted (but uncharacterized) phenyl mercaptides.

(5) Compound **1**: mp 147–150 °C; soluble $CHCl_3$, EtOAc, acetone, slightly soluble Et_2O, insoluble hexane, MeOH. Elemental analysis calcd for $C_{34}H_{30}S_4$: C, 72.04; H, 5.33; S, 22.63. Found: C, 71.94; H, 5.35; S, 22.55. NMR ($CDCl_3$, ppm relative to Me_4Si) 3.84 (s, 4 H), 6.87 (s, 1 H), 7.23 (s, 10 H). IR (KBr) 3070 w, 3035 w, 1495 m, 1455 m, 1425 m, 690 s.

(6) Crystal data for **1**: $S_4C_{34}H_{30}$, M_r 566.85, triclinic, $P1$, $a = 5.358$ (6) Å, $b = 10.80$ (1) Å, $c = 14.77$ (1) Å, $\alpha = 106.02$ (2)°, $\beta = 89.84$ (2)°, $\gamma = 117.22$ (2)°, $V = 722.76$ Å^3, $Z = 1$, $D_x = 1.30$ gcm^{-3}. Diffraction intensities were measured with a modified Picker diffractometer (graphite monochromatized Mo Kα radiation). Intensities of 2705 reflections with 2 less than 50° were collected; 1400 were considered observed [I greater than $3\sigma(I)$] and used in the refinement. The structure was solved by direct methods (MULTAN78) and refined by full matrix least squares to final values of the residuals $R = 0.047$ and $R_w = 0.053$.

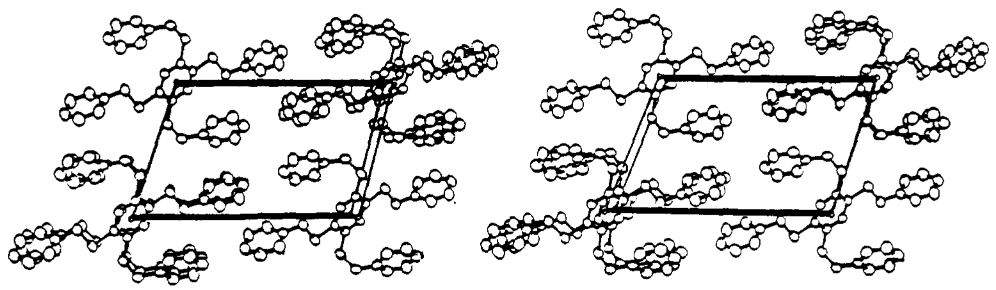

Figure 4. Stereoview of a unit cell depicting molecular packing.

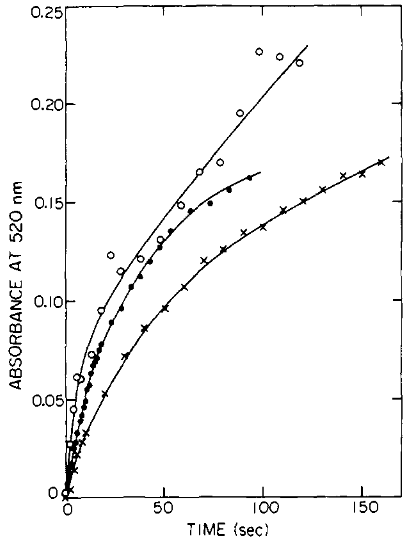

Figure 5. Rate of color development as determined by the rate of appearance of a 520-nm band as a function of time: (•) first coloring cycle of sample A; (×) second coloring cycle of sample A, after bleaching by heating; (○) second coloring cycle of sample B. The figure clearly indicates sample dependence as rate of heating is probably due to inhomogeneity of particle size and dispersion in KBr.

the numbering system used is shown in Figure 3, and a stereoview depicting the mode of packing is shown in Figure 4. Average S–C(sp^2) and S–C(sp^3) distances observed in the structure are 1.771 (4) and 1.830 (5) Å, respectively. The C–C distances in the benzene ring do not differ significantly from the mean of 1.391 Å. The inversion-related C(1) substituents adopt an extended configuration with a C(1)–S(1)–C(10) angle of 103.1 (2)°, while the C(2) substituents fold back to position the phenyl groups above and below the benzene ring. The C(2)–S(2)–C(11) bond angle is 98.6 (2)°. The only significant intermolecular interaction is that between extended phenyl groups on the molecules related by the translation a + c. The interplanar spacing between these two parallel groups is 3.54 Å, but the overlap involves only the meta and para carbon atoms.

Taken together, the above results point to three hypotheses to explain the photochromic behavior of **1**: (a) intermolecular charge transfer between tetrathiobenzenes, (b) intramolecular charge transfer involving the tetrathiobenzene and phenyl rings above and below it, and (c) homolytic cleavage of benzyl–sulfur bonds to produce relatively stable thiyl radicals (but rather unstable benzyl radicals).

While an ongoing detailed exploration (see below) is necessary to distinguish between conjectures a, b, and c, above, on the basis of ease of reversibility, one could have considered mechanism c the least likely. However, HPLC of a cycled sample showed detectable amounts of three new components.[8]

A qualitative study of the rate of coloration (growth rate of the 520-nm band) of **1** as a KBr suspension is shown in Figure 5. As can be seen, the initial rate is quite fast, but ≃50% "coloration" occurs after ca. 40 s for all runs. "Saturation" seems to be sample dependent but appears to occur at >180 s.

As far as technological potential is concerned, solid suspensions of **1** in poly(vinyl chloride) form tough, free-standing photochromic films which are somewhat more sluggish in their coloration–decoloration cycles than the pristine material. Suspensions of **1** in KBr can be cycled at least 16 times without visible fatigue.[9]

In conclusion, we have discovered a new photochromic organic solid which appears to be unique. The species responsible for the photochromism exhibit an absorption at 520 nm and ESR signals compatible with two radicals: one with an unpaired electron localized on sulfur and another with an electron localized on carbon. While the solid-state structure implies the possibility of a charge-transfer state, the nature of the colored state is unknown at this time.[10]

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Registry No. 1, 91900-07-1.

Supplementary Material Available: X-ray structural data for **1**—atomic coordinates and thermal parameters, bond distances and angles, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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(7) All calculations were performed with a DEC VAX 11/780 computer operated by the UCLA Department of Chemistry and Biochemistry. The UCLA Crystallographic Computing Package includes local versions of CARESS, PROFILE, MULTAN, ORFLS, ORTEP, ORFFE, ORTEP, and ABSN.

(8) Mass spectral analysis of these fractions was hampered by extraneous materials such as dialkyl phthalates, etc., resulting from concentration of these highly dilute HPLC fractions. Only one peak gave an identifiable mass spectrum corresponding to tris(benzylthio)benzene. The other peaks were definitely not due to dibenzyl sulfide or dibenzyl disulfide.

(9) Upon cycling manually, the base line of the UV–vis spectra rose from 0.4 to 1.0 A at 600 nm in the course of 16 color-bleach cycles. The increase in "background" absorption was observed to be most pronounced in the first 2–3 cycles. However, the color of the bleached sample remained white.

(10) Preliminary results indicate a profound effect on the absorption wavelength of the photochromicity upon incorporation of substituents in the para position of the benzyl groups of **1**.