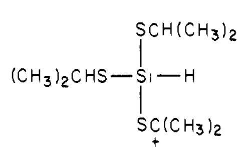
The ionic species does not appear to exhibit appreciable delocalization of positive charge from silicon to sulfur, i.e., the ion is best termed silylenium rather than sulfonium ($RS—^+Si< \leftrightarrow RS^+=Si<$). This conclusion is reached from the resonance position of the methinyl carbon in the isopropyl group, which shifts only from 36.52 to 37.46 ppm on conversion of the silyl hydride to the ionic species. Development of a full positive charge on sulfur is exemplified by the shift of the methinyl resonance from 33.70 to 44.91 ppm on conversion of diisopropyl sulfide to its methylsulfonium salt. If the shift in the silyl ion (0.94 ppm) is multiplied by 3 because the charge is spread over three sulfurs, the value is still only 25% of that for the full sulfonium ion (11.21 ppm). Since the methyl group in the methylsulfonium salt introduces a β effect of unknown size, we also measured the charge on simple protonation of diisopropyl sulfide (CH at δ 33.37 for neat, neutral sulfide, δ 42.43 for protonated sulfide). The 0.94 ppm shift in the silylenium ion, multiplied by 3, is still only 30% of this value.

Finally, tris(2-propylthio)silane could be recovered upon reaction of the ionic solution at −78 °C with diisobutylaluminum hydride. The silane was distilled from the reaction mixture (**Caution**: overheating can cause an explosion) and found to have ^1H NMR and IR spectra identical with those of the starting silane.

The most likely alternative ionic species would involve abstraction of a different hydride (**1**), complexation without abstraction (**2**), or oligomerization (e.g., **3**). The species **1** is eliminated by the ^1H and ^{13}C spectra, which contained only one isopropyl resonance; in addition, **1** retains the SiH, which is clearly lost on formation of the ionic species. The sulfonium ion **2** also has multiple isopropyl groups and would have been formed without loss of the SiH, in contradiction to observation. The dimer **3** has two distinct types of isopropyl groups and deviates significantly from the observed molecular weight. Complexation by the solvent CH_2Cl_2 also is unlikely, because it would add appreciably to the molecular weight.



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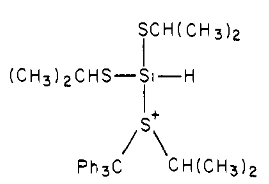

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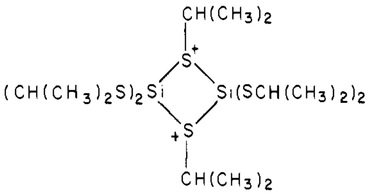

3

In summary, tris(2-propylthio)silane forms a highly conducting solution on reaction with trityl perchlorate. The ^1H spectrum shows complete loss of the SiH resonance, concomitant with gain of the triphenylmethane CH resonance. The ^{13}C spectrum shows resonances of only one isopropyl-containing product with chemical shifts appropriate for silylenium rather than sulfonium character. The molecular weight in sulfolane corresponds to a two-particle monomer. Reaction of the ionic solution with diisobutylaluminum hydride yields only recovered tris(2-propylthio)silane. These observations seem most in accord with a silylenium ion structure. The charge on silicon is sustained by the high polarizability, low electronegativity, and 3p lone-pair donating ability of sulfur.

Acknowledgment. We are grateful to Professors R. L. Burwell, Jr. (Northwestern University), and J. Y. Corey (University of Missouri—St. Louis) for useful suggestions.

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Crystal Structure and Solid-State Reactivity of 4,4'-Methylenebis(phenyl isocyanate) (MDI)

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4,4'-Methylenebis(phenyl isocyanate) ($O=C=N—C_6H_4—CH_2—C_6H_4—N=C=O$, I), a common industrial chemical generally referred to as MDI, has long been known to undergo a reaction in the solid state to give higher molecular weight products formed by intermolecular reaction of the isocyanate groups. The reactivity of MDI has been of particular interest both because it provides a rare example of a reaction that is more rapid in the ordered solid state than in the melt[1] and because little is known about the solid-state chemistry of organic isocyanates. The decreased reactivity of MDI in the melt has been of some industrial importance; Prosser and Seibert have obtained a patent[2] based on the observation that storage of MDI could be improved by keeping it just above its melting point of 42 °C. to minimize the unwanted solid-state reaction. The crystal structure of MDI had not been investigated, and in fact, little is known about the crystal structures of simple isocyanates,[3,4] in part at least because the common members of the family tend to have low melting points and hence do not exist as crystalline solids at room temperature. This communication reports the crystal structure of MDI (I) and examines the relationship of the structure to observed solid-state reactivity.

A crystal suitable for X-ray diffraction was obtained by slow evaporation of a hexane solution, and the structure, determined from data collected at room temperature, is shown in Figure 1.[5] The molecule lies on a crystallographic 2-fold rotation axis; a most significant feature is that adjacent molecules have isocyanate groups related by an inversion center with intermolecular N--C contacts of only 3.146 (2) Å and with adjacent antiparallel N=C atom pairs forming an approximate square. The phenyl rings attached to the nitrogen atoms of the incipient azetidione ring are nearly in the plane of the four atoms forming that ring.

To investigate the nature of the reaction product from MDI in the solid state, we examined the infrared spectrum of the solid formed after a sample of MDI had stood for 2 years at ambient temperature in the dark.[6,7] In addition to strong absorption at

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(1) Curtin, D. Y.; Paul, I. C.; Duesler, E. N.; Lewis, T. W.; Mann, B. J.; Shiau, W.-I. *Mol. Cryst. Liq. Cryst.* **1979**, *50*, 25.

(2) Prosser, R. M.; Seibert, C. A., Jr. U.S. Patent 2 999 106; *Chem. Abst.* **1962**, *56*, 1606h.

(3) Hargittai, I.; Paul, I. C. "The Chemistry of Cyanates and Their Thio Derivatives"; Patai, S., Ed.; Wiley: Chichester, England, 1977; pp 69–129.

(4) The structure of an azobis(isocyanate) has been reported in a communication: Akers, J.; Dube M. F.; Trefonas, L. M.; Timberlake, J. W.; Majeste, R. *Tetrahedron Lett.* **1978**, 5083.

(5) A colorless monoclinic 12-sided irregular prism approximately 0.52 × 0.40 × 0.28 mm, space group $C2/c$, a = 9.974 (2) Å, b = 8.331 (2) Å, c = 15.199 (3) Å, β = 92.25 (2)°, V = 1262.0 (5) Å^3, Z = 4, mol wt 250.26, ρ(calcd) = 1.318 g cm^{-3}, λ(Mo Kα) 0.710 69 Å, was employed. The space group $C2/c$ was chosen over Cc by a comparison of refinements in the two possibilities. The structure was solved by using 1109 independent reflections (785 observed) [$I > 3\sigma(I)$] measured on a Syntex P2$_1$ automated diffractometer in the range 2θ 2–50°. Data were scaled according to behavior of standard intensities and corrected for Lorentz and polarization effects, but corrections for absorption and/or extinction were not warranted. The structure was solved by direct phasing methods using the MULTAN 80 program (P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.P. Declercq, and M. M. Woolfson) and refined by using SHELX 76 (G. M. Sheldrick). Scattering curves, including anomalous dispersion corrections, were taken from the analytical expressions in "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, AL; Vol IV. Refinement converged at R = 0.036 and R_w = 0.046. The atomic coordinates appear in the supplementary material.

(6) Spectra were measured on Nujol mulls by using a Perkin-Elmer Model 137B Infracord or a Nicolet Model 7000 FT IR instrument.

(7) An estimate of the rate of self-reaction of solid MDI had been made in the patent previously cited.[2] The fraction of reaction calculated from the fraction of toluene-insoluble material was somewhat erratic but was about 1.05%/month at 35 °C and 0.01%/month at 45 °C (mp 42 °C).

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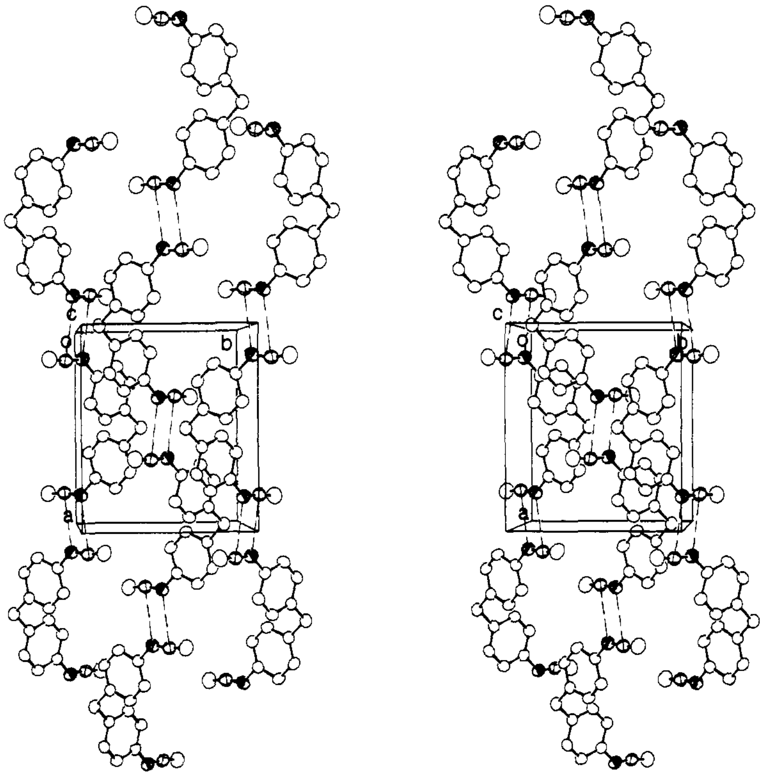
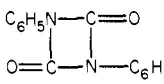


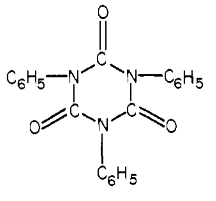
Figure 1. Stereoscopic view of the crystal structure of MDI viewed along the *c* axis. Dashed lines are drawn between the potentially reacting C–N groups.

2300 cm^{-1} attributed to unreacted isocyanate groups of the MDI, there was a new absorption at 1770 cm^{-1} (Nujol) characteristic of the azetidione functional group.[8]

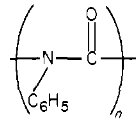
Isocyanates have been shown to undergo at least three kinds of self-addition reaction in solution, illustrated here with the reaction products from phenylisocyanate. Reaction catalyzed by pyridine or phosphines leads to the dimeric azetidione (II) and a trimer (III). The third type of product, whose formation is catalyzed by sodium in dimethylformamide, is the vinyl polymer (IV) with a 1-nylon structure. The infrared spectrum of the solid-state reaction product of MDI showed no absorption maximum in the region 1700–1710 cm^{-1} as might have been expected if trimerization to give a product analogous to III had occurred.



II: IR 1770 ($CHCl_3$),[9] 1773, 1756 (Nujol),[10] 1775, 1750 (KBr)[12] cm^{-1}



III: IR 1685 ($CHCl_3$),[9] 1711 (Nujol),[10] 1705 (KBr)[12] cm^{-1}



IV: IR 1709 (KBr)[11] cm^{-1}

The uncatalyzed dimerization of other isocyanates appears not to have been reported, although the reverse reaction, the dissociation of the azetidione to the isocyanate, is well-known and occurs when the dimer is heated.[13]

A rationale for the formation of azetidione rings in the solid-state reaction of MDI but not in solution or in the melt solution is provided by the crystal structure. In Figure 1 it can be seen that there is alignment of adjacent isocyanate groups in the correct orientation for four-membered ring formation with distances between the carbon and nitrogen atoms that are to become bonded of only 3.146 Å. In addition the geometry of the incipient four-membered azetidione ring and its two attached phenyl groups is remarkably similar to the molecular structure that has been found in the crystalline dimer of phenylisocyanate.[14] The conversion of isocyanates to azetidiones is a 2 + 2 cycloaddition and a thermal concerted $[_{\pi}2_s + {}_{\pi}2_s]$ addition is forbidden by the conservation of orbital symmetry.[15] There is no evidence that this solid-state reaction is concerted, however, and furthermore it was proposed by Woodward and Hoffman that the formally analogous addition of ketenes to olefins is a $[_{\pi}2_s + {}_{\pi}2_a]$ process and therefore thermally allowed.[15b]

Irradiation of MDI crystals with a UV light or sunlight had no noticeable effect on the rate of development of the azetidione absorption, showing that the solid-state reaction was not due to a photochemical reaction. It was also noted that X-rays had no effect on the MDI crystals during the collection of data for the X-ray structure determination.

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(8) Spectra of several analogues of II all had absorption in the 1770-cm^{-1} region; in some cases there was one peak, in other examples there was a second peak. It has been pointed out (see: Bellamy, L. J. "Advances in Infrared Group Frequencies"; Methuen and Co.: 1968, pp 127 ff; "The Infrared Spectra of Complex Molecules", 3rd ed.; Chapman and Hall: London, 1975; p 248) that azetediones can be expected to show two carbonyl bands. The band associated with the symmetric stretching vibration should, however, be absent when the carbonyl groups are precisely aligned in opposite directions as is the case here.

(9) Richter, R.; Ulrich, H. *Synthesis* **1975**, 463.

(10) Jones, J. I.; Savill, N. G. *J. Chem. Soc.* **1957**, 4392.

(11) Shashoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960**, *82*, 866; **1959**, *81*, 3156.

(12) Boutevin, B.; Hugon, J. P. *Tetrahedron Lett.* **1978**, 129.

(13) (a) Richter, R.; Ulrich, H. "The Chemistry of Cyanates and Thier Thio Derivatives", Patai, S. Ed.; Wiley: New York, 1977; Capter 17. (b) Smith, P. A. S. "Open Chain Nitrogen Compounds"; W. A. Benjamin: New York, 1965; Vol. 1, pp 234 ff. (c) Ozaki, S. G.; *Rev.* **1972**, *72*, 457. (d) Arnold, R. G.; Nelson, J. A.; Verbang, J. J. *Ibid.* **1957**, *57*, 47. (e) Saunders, J. H.; Slocombe, R. J. *Ibid.* **1948**, *43*, 203.

(14) (a) Brown, C. J. *J. Chem. Soc.* **1955**, 2931. (b) Baudour, J.-L.; Delugeard, Y.; Sanquer, M. *Acta Crystallogr. Sect. B.* **1974**, *B30*, 691.

(15) (a) Woodward, R. B.; Hoffman, R. "The Conservation of Orbital Symmetry"; Academic Press: New York 1971; pp 64 ff. (b) pp 163 ff.

The spontaneous formation of azetidione groups in crystalline MDI thus appears to provide what is at present a rare example of a *thermal* reaction that proceeds in the solid because of the proper alignment of the reacting functional groups by the solid matrix.[16]

Acknowledgment. We are indebted to the National Science Foundation (CHE-79-05-04871 and CHE 82-09-393) for support of this work. We would like to thank Dr. David Chadwick for calling this problem to our attention and to Dr. Chadwick and Dr. Ronald Taylor of the Mobay Chemical Corp. for samples of MDI.

Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, and observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(16) Preliminary examination of the reaction of single crystals of MDI with the nucleophilic reagents methanol, ammonia, and pyridine has shown evidence of gas–solid reactions whose anisotropic behavior can be correlated with the internal structure of the crystal.

Isolation and Characterization of Two New Bacteriochlorophylls *d* Bearing Neopentyl Substituents

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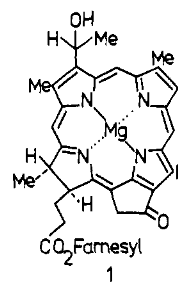
Received December 6, 1982

The bacteriochlorophylls *c* and *d* are found in a variety of photosynthetic green sulfur bacteria. They differ structurally from the plant chlorophylls in several ways, a remarkable feature of which is the presence of ethyl, *n*-propyl, or isobutyl substituents at position 4 (where chlorophyll *a* bears ethyl), and either methyl or ethyl at position 5 (in place of methyl); the source of the additional methyl groups has been shown to be methionine.[2] Intriguingly, the bacteriochlorophylls *c* exhibit[3] a further variance in the chirality of the 2-(1-hydroxyethyl) substituent, which changes from *R* to *S* as the size of the 4-substituent increases upon successive additions of methyl groups to a presently undefined precursor related to chlorophyll a. The chirality of the 2-substituents of the bacteriochlorophylls *d* (Table I, **1**) extracted from *Chlorobium vibrioforme* forma *thiosulfatophilum* (NCIB No. 8327) varies similarly:[4] it is *R* for the 4-Et,5-Me, 4-Et,5-Et, 4-*n*-Pr,5-Me, and 4-*n*-Pr,5-Et pigments (**1a–d**), but *S* for the 4-*i*-Bu,5-Me and 4-*i*-Bu,5-Et compounds (**1e** and **1f**, respectively). We describe here the isolation and characterization of two additional pigments from the same organism. The new bacteriochlorophylls possess a neopentyl substituent at position 4, and the *S* stereochemistry at the 2-(1-hydroxyethyl) group.

Figure 1A shows the reverse-phase HPLC[4] trace of an intact mixture of methyl bacteriopheophorbides *d* (**2**) from *C. vibrioforme*; these were obtained from the corresponding bacteriochlorophylls (**1**) by treatment with sulfuric acid in methanol.[2] The traces in Figure 1, B and C, show the 5-methyl (**2a,c,e**) and 5-ethyl (**2b,d,f**) series, respectively, after a preliminary separation using a silica gel column.[4,5] Two additional pigments, not previously reported, are apparent in the chromatograms (arrows in Figure 1, B and C). After isolation by preparative HPLC,[6] the new pigments (one from the 5-methyl and one from the 5-ethyl series) were subjected to spectroscopic analysis.

Table I



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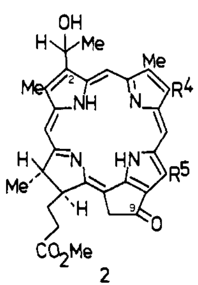

2

	R^4	R^5	confign at position 2
a	Et	Me	*R*
b	Et	Et	*R*
c	*n*-Pr	Me	*R*
d	*n*-Pr	Et	*R*
e	*i*-Bu	Me	*S*
f	*i*-Bu	Et	*S*
g	neoPn	Me	*S*
h	neoPn	Et	*S*

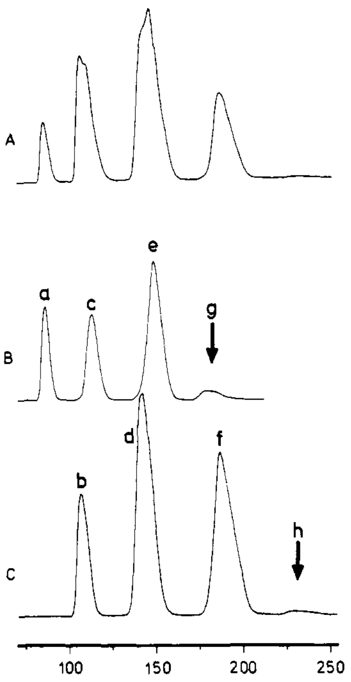

Figure 1. HPLC traces[4] of the methyl bacteriopheophorbides *d*: (A) complete mixture from *C. vibrioforme*; (B) the 5-methyl series, after preliminary separation by chromatography on silica; (C) the 5-ethyl series, after preliminary separation by chromatography on silica. The neopentyl derivatives are indicated by the arrows in B and C.

The methyl series bacteriopheophorbide (mp 181 °C) showed a molecular ion at *m/e* 608 (100%) in its mass spectrum, together with a large ion (*m/e* 551, 65%) indicating cleavage of a fragment of mass 57 Daltons. Assuming normal benzylic cleavage,[7] this suggested the presence of a neopentyl substituent in the molecule. Likewise, the ethyl series bacteriopheophorbide (mp 218°C)

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[1] Address correspondence concerning the X-ray structure to this author.

[2] Kenner, G. W.; Rimmer, J.; Smith, K. M.; Unsworth, J. F. *J. Chem. Soc., Perkin Trans. 1* **1978**, 845–852.

[3] Smith, K. M.; Kehres, L. A.; Tabba, H. D. *J. Am. Chem. Soc.* **1980**, *102*, 7149–7151.

[4] Smith, K. M.; Goff, D. A.; Fajer, J.; Barkigia, K. M. *J. Am. Chem. Soc.* **1982**, *104*, 3747–3749.

[5] Kemmer, T.; Brockmann, H., Jr.; Risch, H. *Z. Naturforsch., B* **1979**, *34B*, 633–637.

[6] A Waters Associates Prep 500A chromatograph equipped with an ISCO 1840 variable-wavelength detector set at 650 nm was used. Reverse-phase cartridges were used, and the solvent was 15% water in methanol (flow rate 150 mL/min, with recycling).

[7] Jackson, A. H.; Kenner, G. W.; Smith, K. M.; Aplin, R. T.; Budzikiewicz, H.; Djerassi, C. *Tetrahedron* **1965**, *21*, 2913–2924.

0002-7863/83/1505-1674$01.50/0