Table III. Irradiation of 36DAF in Methyl Alcohol

	product yields (absolute), %			
[36DAF], M	ketazine 4	diether 6	diazirine 1	ketone 5
5.5×10^{-3}	75	2	20	2
1.2×10^{-3}	40	20	10	10
3.4×10^{-4}	2	30	10	50

isolated by chromatography on silica gel: ^{1}H NMR for **3** δ 1.85 (s, 3 H), δ 2.30 (d, 1 H), δ 2.60 (d, 1 H), δ 5.75 (d, 1 H), δ 7.35 (d, 1 H), δ 8.05 (d, 1 H), δ 8.60 (d, 1 H), δ 9.05 (s, 1 H), δ 9.20 (s, 1 H); MS (EI), *m/e* 284.0; exact MS calcd for $C_{20}H_{16}N_2$ 284.1317, found 284.1307.

Triplet Sensitization of 36DAF with Benzil in Benzene and α-Methylstyrene. A benzene solution of 36DAF (1.03×10^{-3} M) containing 1.0 M AMS and 1.5×10^{-2} M benzil was purged with Ar and irradiated (<380 nm). Analysis of the reaction by ^{1}H NMR spectroscopy showed that the yield of cyclopropane **3** was more than 90%.

Photolysis of 36DAF in Methyl Alcohol. Several samples were prepared, each containing a different concentration of 36DAF (3.4×10^{-4} to 5.5×10^{-3} M). All samples were purged with Ar and then irradiated (Rayonet). The amount of remaining 36DAF and the yields of the products were determined by ^{1}H NMR spectroscopy. The results are summarized in Table III. Ketazine **4** and the dimethoxy ether **6** were isolated from the reaction mixture by chromatography on silica gel. For **6**: ^{1}H NMR δ 2.60 (s, 3 H), δ 6.90 (br, 2 H), δ 8.5 (m, 2 H), δ 8.84 (s, 2 H); MS (EI), *m/e* 394.0; exact MS calcd for $C_{24}H_{18}N_4O_2$ 394.1413, found 394.1421. For **3**: ^{1}H NMR δ 7.85 (d, 2 H), δ 8.00 (d, 2 H), δ 8.70 (d, 2 H), δ 8.85 (d, 2 H), δ 9.15 (s, 4 H); MS (EI), *m/e* 360.0; exact MS calcd for $C_{22}H_{12}N_4$ 360.1115, found 360.1119.

Reaction of 36DAF with Potassium. A 15-mg sample of 36DAF was dissolved in 20 mL of dry, N_2-purged THF. A small piece of potassium (ca. 30 mg) was added to the solution; a blue color developed immediately. A 2.0-mL aliquot of the blue solution was transferred carefully under N_2 to a N_2-purged solution of 36DAF in methyl alcohol (15 mg in 10 mL). After a few minutes, 4.5 mg (determined gravimetrically) of ketazine **4** precipitated from the alcohol solution. This corresponds to a ketazine yield of 300% based upon the maximum quantity of ketazine radical anion that could have been transferred to the methyl alcohol solution of 36DAF.

Acknowledgment. This work was supported by a grant from the National Science Foundation and a fellowship to Y.-Z.L. from the Ministry of Education of the People's Republic of China.

Registry No. 2, 109528-45-2; 3, 109528-46-3; 4, 109528-47-4; 6, 109528-48-5; 7, 109528-44-1; DAF, 832-80-4; 18DAF, 1807-47-2; 36DAF, 109528-41-8; FL, 2762-16-5; 18FL, 103621-90-5; 36FL, 109528-42-9; 2,8-phenanthroline, 230-46-6; 3,6-diaza-9-fluorene, 109528-43-0.

A [1,2] and a [1,4] Shift in a Wittig Thioether Rearrangement. Isolation of a [1.1](2,8)Naphthalenophane Tautomer

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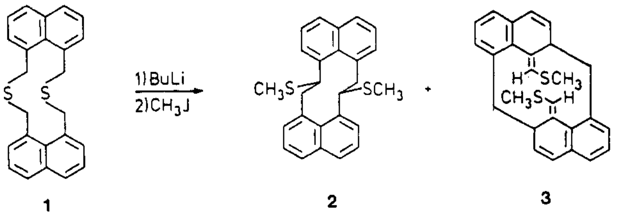
Treatment of 7*H*,9*H*,16*H*,18*H*-dinaphtho[1,8-*cd*:1′,8′-*ij*][1,7]dithiacyclododecin (**1**) with butyllithium and methyl iodide yields as the main product *anti*-7,8,15,16-tetrahydro-7,15-bis(methylthio)cyclodeca[1,2,3-*de*:6,7,8-*d′e′*]-dinaphthalene (**2**) and as a side product 1′,2′,7,8-tetrahydro-1′,8-bis[(methylthio)methylene]-1,2′:7,8′-dimethanodinaphthalene (**3**). The structures of both products have been elucidated by spectroscopic means as well as by X-ray investigations on crystals of **2** and **3**. The origin of **2** and **3** can be rationalized by assuming a [1,2] and a [1,4] shift, respectively, in a Wittig thioether rearrangement. Compound **3** represents the first [1.1](2,8)naphthalenophane tautomer.

The *S* analogue of the Wittig ether rearrangement[1] has been used recently to synthesize cyclophanes.[2,3] Usually [1,2] shifts are observed in this rearrangement;[1–4] in some cases, however, [1,4] shifts also occur.[5] In connection with our efforts to synthesize perpendicular π-systems separated by a four-membered ring,[6] we investigated a Wittig thioether rearrangement and observed a [1,4] shift.

Scheme I



The Wittig thioether rearrangement of 7*H*,9*H*,16*H*,18*H*-dinaphtho[1,8-*cd*:1′,8′-*ij*][1,7]dithiacyclododecin (**1**), prepared according to Kemp et al.[7] has been investigated. The Wittig thioether rearrangement has been carried out according to a procedure described

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[1] Schöllkopf, U. *Angew. Chem.* **1970**, *82*, 795; *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 763.

[2] Mitchell, R. H.; Otsubo, T.; Boekelheide, V. *Tetrahedron Lett.* **1975**, 2193.

[3] Haenel, M. W.; Lintner, B.; Benn, R.; Rufinska, A.; Schroth, G., *Chem. Ber.* **1986**, *118*, 4922.

[4] Biellmann, J. F.; Schmitt, J. L. *Tetrahedron Lett.* **1973**, 4615. Biellmann, J. F., Ducep, J. B.; Schirlin, D. *Tetrahedron* **1980**, *36*, 1249.

[5] Felkin, H.; Tambute, A. *Tetrahedron Lett.* **1969**, 821. Biellmann, J. F.; Ducep, J. B. *Ibid.* **1970**, 2899; **1971**, 33.

[6] Gleiter, R.; Schaaff, H. P.; Götzmann, W.; Rodewald, H.; Jahn, R.; Irngartinger, H. *Helv. Chim. Acta* **1987**, *70*, 480.

[7] Kemp, W.; Storie, I. T.; Tulloch, C. D. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2812.

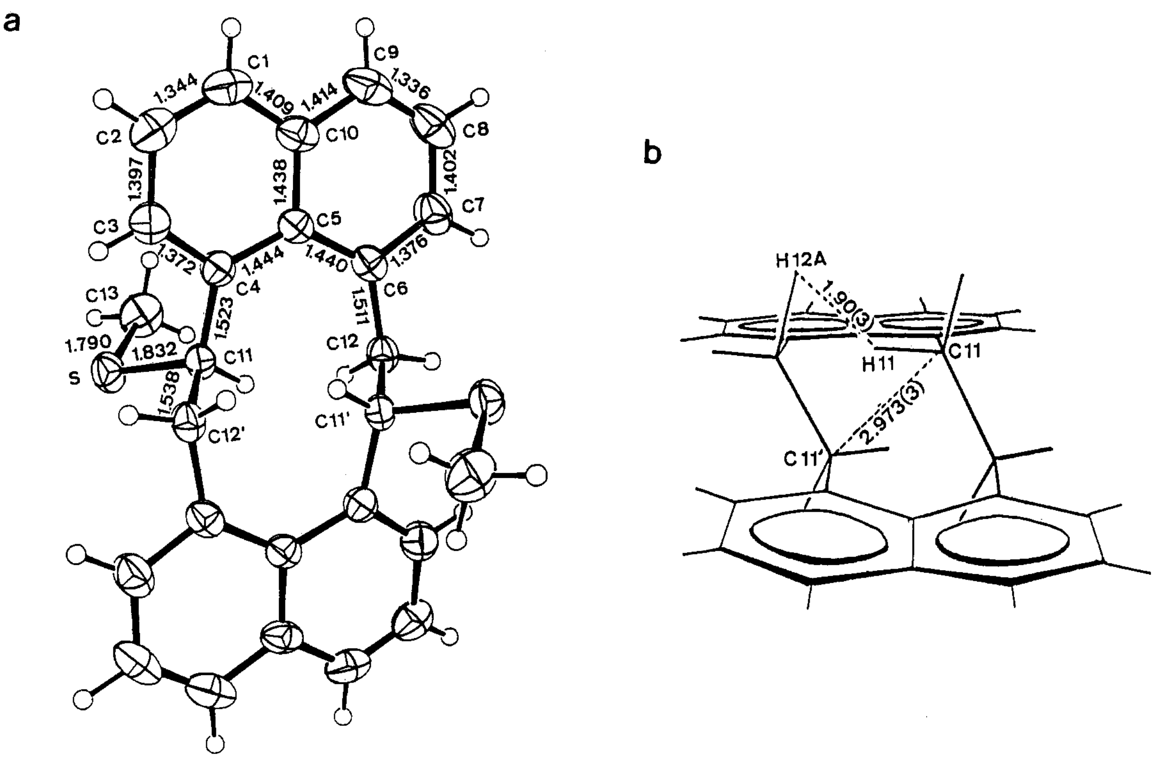
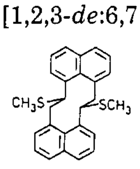
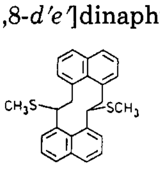


Figure 1. (a) ORTEP drawing of the molecular geometry of **2** with atomic numbering scheme and bond lengths, (b) side view of **2** with transannular contacts in the ten-membered ring.

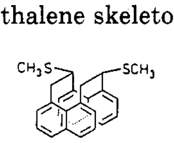
by Mitchell et al.[2] We obtained from **1** after reaction with n-butyllithium and subsequent methylation two isomeric sulfides, **2** and **3**, in the ratio 88:12 (by NMR) as shown in Scheme I. The ^{1}H NMR spectra indicate a considerable difference between both products. The singlet at 1.54 ppm in the spectrum of the main product, **2**, is ascribed to the methylthio protons and the doublet at 5.58 ppm to the proton next to the thiomethyl group (H_c); the doublet and the doublet of doublets (3.49 and 4.44 ppm, respectively) we assign to the remaining benzylic protons (H_a and H_b). The multiplet between 7.4 and 8.3 ppm is typical for a 1,8-disubstituted naphthalene pattern. In line with these arguments are the ^{13}C NMR data indicating three sp^3 and ten sp^2 carbon centers. Our assignment leaves us with the four structural possibilities **2**, **2′**, **2″**, and **2‴** shown below. All have in common the 7,8,15,16-tetrahydrocyclodeca[1,2,3-*de*:6,7,8-*d′e′*]dinaphthalene skeleton.



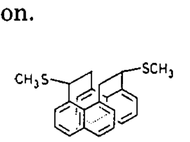
2



2′



2″



2‴

From the observation that one of the coupling constants between the aliphatic protons is large (J_{ac} = 10 Hz) and the other one is small (0 Hz) we rule out the syn isomers **2″** and **2‴**. In these cases we expect[8] for both interactions large coupling constants due to the staggered conformation of the substituents at the C_2 bridge. A discrimination between **2** (C_2) and **2′**(C_s) is not possible with the spectroscopic data available; therefore we undertook a X-ray investigation on **2** (see below).

A comparison of the ^{1}H NMR spectrum of **2** with that of **3** shows large differences in the downfield region, indicating that both π-systems are rather different. This comparison points to a deep skeletal rearrangement during the generation of **3**. The singlet at 1.95 ppm we ascribe to the methylthio group. The three signals at 2.76, 3.25, and 3.60 ppm indicate three aliphatic protons, while the three features between 5.5 and 6.5 ppm (H_d–H_f) are indicative of three olefinic protons. This leaves us with three signals around 7 ppm (H_g–H_i), which can be assigned to three aromatic protons in vicinal positions.

Double resonance experiments on proton H_c reveal a coupling between H_a and H_b on one side and with H_e on the other. NOE experiments indicate a close proximity between the protons at 1.95 ppm and H_d. These data are compatible with 1′,2′,7,8-tetrahydro-1′,8-bis[(methylthio)methylene]-1,2′:7,8′-dimethanodinaphthalene (**3**) in so far as this structure provides two aliphatic (H_a, H_b) and one allylic proton (H_c), one vinylic proton with no neighbors (H_d), two olefinic protons (H_e, H_f), one of which is adjacent to the allylic proton (H_c), and three vicinal aromatic protons (H_g–H_i). In line with these arguments are the ^{13}C NMR data listed in the Experimental Section. Due to the low solubility of **3** in the usual solvents and the low yield of pure product we refrained from further NMR experiments to prove the structure of **3** but carried out a X-ray analysis.

X-ray Investigations on 2 and 3. In order to assure the conformation of the ten-membered ring and the configuration of the methylthio groups in **2** as well as to determine the structure of **3** we have carried out X-ray investigations on crystals of both compounds.

Our investigations of **2** reveal that the molecule is situated on a crystallographic center of symmetry which implies a trans orientation of the methylthio groups at the atoms C(11) and C(11′) of the ten-membered ring (see Figure 1). In Figure 1a the bond lengths obtained are shown as well as the conformation of the ring system.

Because of transannular nonbonding H···H contacts, the ten-membered ring is twisted out of a conformation with mirror symmetry (mirror plane perpendicular to the ring)

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[8] Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11; *J. Am. Chem. Soc.* **1963**, *85*, 2870. Conroy, H. *Adv. Org. Chem.* **1960**, *2*, 310. Bothner-By, A. A. *Adv. Magn. Reson.* **1965**, *1*, 195.

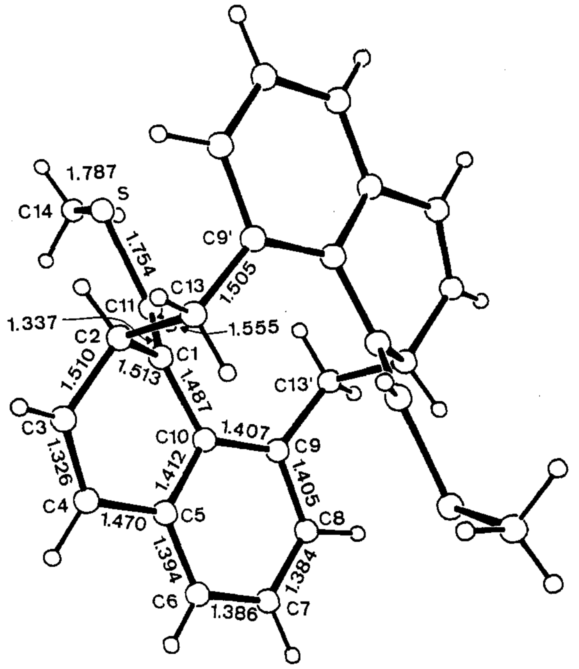


Figure 2. Drawing of the molecular geometry of 3 with atomic numbering scheme and bond lengths.

to allow gearing of the opposite CH_2 groups. Therefore both naphthalene systems are shifted by 0.65 Å against one another along the lateral direction (Figure 1b). Transannular repulsive contacts (contacts given in Figure 1b and C(11)···C(12) 3.061 (3) Å, C(4)···C(12) 3.192 (3) Å, C(6)···C(11) 3.190 (3) Å) give rise to considerable bond angle enlargements from 120° to 124.8° and 125.4° for the angles C(5)–C(4)–C(11) and C(5)–C(6)–C(12), respectively. The peri-substituents C(11) and C(12) deviate by 0.215 Å from the naphthalene plane in opposite directions because of repulsive forces. The corresponding value in a ten-membered ring with C≡C groups instead of the CH_2–CH_2 groups, and therefore without transannular H···H contacts, is 0.182 Å.[9] The naphthalene system itself is slightly twisted (C(4)–C(5)–C(10)–C(9), −175.9°, and C(1)–C-(10)–C(5)–C(6), −173.4°).

By the X-ray analysis of 3 the structure of a [1.1]-naphthalenophane was detected. It shows that the two dihydronaphthalene systems which are substituted by a (methylthio)methylene group in the 1-position, are linked twice by one CH_2 bridge from the 2- to the 8-position, resulting in a [1.1](2,8)naphthalenophane system (see Figure 2). The molecule lies on a crystallographic center of symmetry, therefore the numbering scheme of 3 given in Figure 2 does not correspond to the IUPAC rules. The bond lengths of 3 are given in Figure 2. The carbon atoms C(5) to C(10) deviate only by small amounts (0.007–0.035 Å) from their ring plane. The partially hydrogenated six-membered ring (C(1) to C(5), C(10)), however, is considerably twisted (Figure 2). Because of short transannular contacts (C(1)···C(9′) 2.956 (2) Å; C(1)···C(10′), 3.253 (2) Å; C(1)···C(1′) 3.461 (2) Å) the atom C(1) is pushed out of the ring plane. Therefore the double bond group C(1)=C(11) is tilted by 44.2° against the plane C(2) to C(10).

Discussion

The origin of the two species, 2 and 3, may be rationalized in two ways: by breaking two C–S bonds in the dianion, maintaining C_2 symmetry as indicated in 4, and by breaking one C–S bond in the monoanion, giving rise to 5. In the species 4 bond formation between centers a and b as well a′ and b′ ([1,2] shift)[1,4] gives rise to the Wittig product 2. A [1,4] shift,[5] i.e., bond formation between a and d as well as a′ and d′ yields 3. If 5 is an intermediate the bond breaking has to occur stepwise to yield the Wittig product 2 (two times a [1,2] shift) or 3 (two times a [1,4] shift).

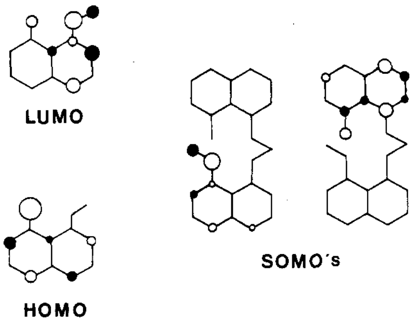
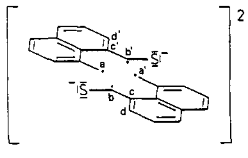
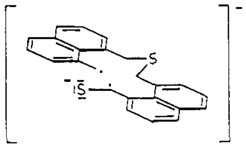
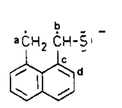


Figure 3. Schematic drawing of the HOMO and LUMO of 6 (left) and the two SOMO's of 5 (right) according to an EH calculation.


4


5


6

Both possibilities are supported by the results of extended Hückel[10] type calculations on either the fragment anion 6 or the anion 5. To estimate the regioselectivity of the ring closure of 4 and 5 we assume that the frontier orbitals determine the regioselectivity of the rearrangement.[11] This amounts to consider the HOMO and LUMO of the fragment orbitals of 6 and the singly occupied MO's (SOMO's) of the two radical fragments of 5. The corresponding frontier orbitals are shown in Figure 3.

Consideration of the HOMO of 6 reveals large coefficients for the atomic orbitals in the HOMO at a and in the LUMO at b and d. The same holds for the two SOMO's of 6. Thus, [1,2] and [1,4] shifts are most likely in both cases.

We tend to favor the intermediate 4 due to the fact that the products of an asymmetric [1,2] or [1,4] shift are missing.

To our knowledge, 3 is the first [1.1](2,8)-naphthalenophane tautomer described. The stability of the o-quinoid structure is due to the fact that any rearomatization means a planarization of both naphthalene moieties. This is, however, not possible due to the [1.1] bridges which require a strong bending of both substituents at positions 9 and 18.

Experimental Section

General. Melting points were measured on a Bock-Monoskop M and are uncorrected. The NMR spectra were taken with a Bruker WH 300 (^1H NMR at 300 MHz and ^{13}C NMR at 75.46 MHz) spectrometer using Me_4Si as internal standard (δ [ppm]; J, Hz). The mass spectra refer to data from a ZAB instrument from Vakuum Generators (EI, 70 eV), IR spectra were recorded with Perkin-Elmer 710 B and Bruker FT-IR IFS 85 instruments. UV light absorption data were recorded in CH_2Cl_2 by using a Varian Cary 17 D spectrometer. Chromatography was carried out by MPLC (middle-pressure liquid chromatography) using a

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[9] Irngartinger, H.; Jungk, A. E. *Chem. Ber.* **1977**, *110*, 749.

[10] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397 and subsequent papers.

[11] Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.

Table I. Crystallographic Data and Refinement Parameters of 2 and 3

	2	3
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
Z	2	2
a, Å	8.342 (3)	8.449 (2)
b, Å	15.270 (3)	16.352 (2)
c, Å	8.034 (2)	7.737 (2)
β, deg	101.69 (2)	107.46 (23)
crystal size, mm	0.55 × 0.50 × 0.25	0.14 × 0.17 × 0.27
max (sin θ)/λ	0.662	0.662
unique reflections	2426	2456
obsd reflections ($I > 3\sigma(I)$)	1859	1935
refinement: R factor	0.053	0.043

technical equipment from Fa. Latek and Labomatic.

X-ray Analysis. For the structure analyses colorless crystals of **2** (from toluene) and light yellow prisms of **3** (from methylene chloride) were used. The crystallographic data and the parameters of structure refinement are listed in Table I. The data were collected on an automatic diffractometer (CAD4-Enraf-Nonius, Mo Kα radiation, graphite monochromator, ω–2θ scan). Lorentz, polarization, and absorption corrections have been applied. The structures were solved by direct methods and refined by full-matrix least-squares procedure on F^2 with anisotropic thermal parameters for S and C atoms. The positions of the H atoms were calculated according to stereochemical requirements and were refined isotropically. Dispersion effects were corrected. The atomic coordinates are given as supplementary material. The SDP program system[12] was used on a PDP 11/44 computer.

***anti*-7,8,15,16-Tetrahydro-7,15-bis(methylthio)cyclodeca[1,2,3-*de*:6,7,8-*d′e′*]dinaphthalene and 8,9,17,18-Tetrahydro-9,18-bis[(methylthio)methylene][1.1](2,8)naphthalenophane (2 and 3).** To a suspension of 5 g (13.4 mmol) of 7*H*,9*H*,16*H*,18*H*-dinaphtho[1,8-*cd*:1′8′-*ij*][1,7]dithiacyclododecin (**1**)[2] in 400 mL of absolute THF was added within 10 min 3.43 g (53.6 mmol) of *n*-butyllithium (33.7 mL of a 15% solution of *n*-butyllithium in hexane) at 0 °C under Ar with stirring. The resulting dark brown solution was stirred for 2 h at room temperature. After the mixture was cooled to 0 °C, 15.22 g (107.2 mmol) of methyl iodide was added quickly. After the addition of 500 mL of H_2O, the organic phase was separated and washed twice with water. Addition of Et_2O to the organic phase yielded a precipitate. After filtration the residue was washed with Et_2O. It remained a white crystalline product, consisting of 12% **3** and 88% **2** (by ^1H NMR), with a total yield of 74%. **2** could be obtained by recrystallization from toluene or $CHCl_3$. A separation of both isomers could be achieved by MPLC with silica gel (Grace Kieselgel, 60 A-15 m, OR03). Separation conditions: column, 37 × 479 mm, 410 mL; flow 27 mL/min.; pressure, 9.6 bar; sample volume, 3 mL (c 4.5 mg/mL in toluene); elution with cyclohexane/toluene (both technical grade), 60/40 (v/v); detection by UV at 320 nm.

2: mp 260–261.5 °C (from toluene); t_R (MPLC) 28.0 min; IR (KBr) 3065 m, 2930 m, 2900 m, 1615 m, 845 s, 788 s, 778 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.24 (dd, $J_{ig} = 1.3$, $J_{if} = 7.5$, 2 H, H_i), 7.86 (d, $J_{he} = 0$, $J_{hd} = 7.9$, 2 H, H_h), 7.85 (dd, $J_{gi} = 1.3$, $J_{gf} = 7.5$, 2 H, H_g), 7.59 (t, $J_{fg} = J_{fi} = 7.5$, 2 H, H_f), 7.51 (d, $J_{eh} = 0$, $J_{ed} = 7.9$, 2 H, H_e), 7.41 (t, $J_{de} = J_{dh} = 7.9$, 2 H, H_d), 5.58 (d, $J_{ca} = 10$, 2 H, H_c), 4.44 (d, $J_{ba} = 16.4$, 2 H, H_b), 3.49 (dd, $J_{ac} = 10$, $J_{ab} = 16.4$, 2 H, H_a), 1.54 (s, 6H, 2 SCH_3); ^{13}C NMR ($CDCl_3$) δ 15.14, 48.11, 51.01, 124.83, 125.67, 128.29, 129.53, 129.84, 130.13, 131.67, 135.01, 135.73, 140.97; MS (220 °C) m/z (relative intensity) 400.1312 (16.43, $C_{26}H_{24}S_2$, calcd 400.1319; M^+), 385 (3.76, $M^+ - CH_3$), 353 (11.20, $M^+ - SCH_3$), 352 (9.06, $M^+ - HSCH_3$), 337 (10.61, $M^+ - (HSCH_3 + CH_3)$), 307 (9.36), 306 (43.36, $M^+ - 2SCH_3$), 305 (80.77, $M^+ - (HSCH_3 + SCH_3)$), 304 (38.91, $M^+ - 2HSCH_3$), 303 (31.83), 289 (32.42), 185 (29.77), 155 (100.00), 152 (45.98), 151 (25.57); UV (λ_{max}, nm (log ϵ)) 224 (4.92), 274 (3.78) sh, 306 (4.13), 313 (4.09) sh. Anal. Calcd for $C_{26}H_{24}S_2$ (400.61): C, 77.95; H, 6.04; S, 16.01. Found: C, 77.71; H, 6.19; S, 16.10.

3: mp 311–313 °C (from CH_2Cl_2); t_R (MPLC) 24.4 min; IR (KBr) 3024 w, 2919 m, 1593 w, 1579 w, 1438 m, 1434 m, 1314 w, 1261 w, 1162 w, 1096 w, 1012 w, 894 w, 855 w, 804 m, 752 m, 736 s, 631 m cm^{-1}; ^1H NMR (CD_2Cl_2) δ 7.25 (dd, $J_{ih} = 7.5$, $J_{ig} = 1.3$, 2 H, H_i), 7.10 (t (dd), $J_{hi} = J_{hg} = 7.5$, 2 H, H_h), 6.90 (dd, $J_{gh} = 7.5$, $J_{gi} = 1.3$, 2 H, H_g), 6.45 (d, $J_{fe} = 9.3$, 2 H, H_f), 6.21 (dd, $J_{ef} = 9.3$, $J_{ec} = 5.8$, 2 H, H_e), 5.67 (s, 2 H, H_d), 3.60 (m, $J_{ce} = 5.8$, $J_{ca} = 4.9$, $J_{cb} = 12.4$, 2 H, H_c), 3.25 (t (dd), $J_{bc} = J_{ba} = 12.4$, 2 H, H_b), 2.76 (dd, $J_{ac} = 4.9$, $J_{ab} = 12.4$, 2 H, H_a), 1.95 (s, 6 H, 2 SCH_3); ^{13}C NMR ($CDCl_3$) δ 17.48, 34.26, 43.44, 123.81, 126.99, 127.56, 129.94, 130.10, 132.20, 132.73, 134.64, 135.78; MS (220 °C) m/z (relative intensity) 400.1290 (6.99, $C_{26}H_{24}S_2$, calcd 400.1319; M^+), 385 (5.80, $M^+ - CH_3$), 353 (4.76, $M^+ - SCH_3$), 337 (10.42, $M^+ - (HSCH_3 + CH_3)$), 306 (12.65, $M^+ - 2SCH_3$), 305 (27.98, $M^+ - (HSCH_3 + SCH_3)$) 153 (100.00), 152 (33.93); UV (λ_{max}, nm (log ϵ)) 240 (4.53), 252 (4.48) sh, 270 (4.32) sh, 307 (4.14).

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF Aktiengesellschaft in Ludwigshafen for financial support.

Registry No. 1, 76727-31-6; 2, 109583-36-0; 3, 109530-06-5.

Supplementary Material Available: Tables of bond angles, torsional angles, atomic coordinates, and thermal parameters of **2** and **3** (2 pages). Ordering information is given on any current masthead page.

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[12] Frenz, B. A. and Ass., Inc., College Station, TX, and Enraf-Nonius, Delft, Holland, 1982.