Synthesis of New Sulfur Heteroaromatics Isoelectronic with Dibenzo[*g,p*]chrysene by Photocyclization of Thienyl- and Phenyl-Substituted Ethenes

Erik Fischer, Jan Larsen, Jørn B. Christensen, Marc Fourmigué,[†] Hans G. Madsen,[‡] and Niels Harrit*

Department of Chemistry, University of Copenhagen, Symbion, Fruebjergvej 3, DK-2100 Copenhagen, Denmark

Received January 2, 1996 (Revised Manuscript Received June 6, 1996[⊗])

A series of new sulfur heteroarenes, isoelectronic with dibenzo[*g,p*]chrysene, have been prepared by double photocyclization of the corresponding tetraaryl substituted ethenes. The first step proceeds efficiently in each case, and the corresponding intermediate sulfur heteroarenes, isoelectronic with phenanthrene, have been isolated. The second ring closure is only efficient when one of the participating aryl substituents is thienyl, which thus manifests a higher electron density on the carbon atom involved in the excited singlet state reaction. Most of the new compounds are of minimal solubility in common solvents and do not display improved electron donor properties otherwise commonly found among heteroaromatics.

Introduction

Two of the requirements to be met for the observation of electrical conductivity in solid charge transfer salts is high polarizability of the components and a strong intermolecular interaction between them.[1,2] Both properties may be achieved by the introduction of heteroatoms, and sulfur has been particularly popular for this purpose.[1−13] Introduction of sulfur frequently implies a reduction of the oxidation potential compared to the all-carbon analogue.[4−6,14] In other cases the effect may be negligible.[3,7]

Examples of fused sulfur heteroarenes are 3,4′:4,3′-bis-(benzo[*b*]thiophene)[7] and 3,3′:4,4′-bis(thieno[2,3-*b*]thiophene),[3] which are both isoelectronic with perylene and contain two and four sulfur atoms, respectively. Also like perylene, they both form complexes with molecular iodine with properties very similar to those of the known perylene-iodine solid. X-ray crystallographic analysis reveals that 3,3′:4,4′-bis(thieno[*2,3-b*]thiophene) is planar in spite of the considerable amount of strain that must be contained in the structure.[3] Dithieno[2,4-*d,e*:2′,4′-*i,j*]-naphthalene[5,6] is isoelectronic with pyrene but displays a lower oxidation potential and is also able to form CT-salts. The thiophene ring of quinoid structure can serve as both an acceptor and a donor[15] or as an acceptor only.[16]

Thia analogues of anthracene,[8,10] phenanthrene, and triphenylene[9,10] are examples of sulfur aromatics for which their enhanced donor properties have been verified by cyclic voltammetry. For tetrakis(1,4-benzodithiieno)-[2,3-*a*:2′,3′-*c*:2″,3″-*f*:2‴,3‴-*h*]naphthalene[4] the electrochemical determination of the oxidation potential is hampered by the low solubility of the compound, an obstacle which is frequently met with larger, unsubstituted heteroaromatics.

For these reasons, the work described herein is aimed to prepare a series of sulfur aromatics, isoelectronic with dibenzo[*g,p*]chrysene (**3**, Scheme 1),[17] containing two and four sulfur atoms (see below for structures), in order to relate donor properties with symmetry and substitutional patterns.

For our purposes, photocyclization of 6π-electron conjugated systems, as present in stilbenes and related compounds, represents a viable synthetic pathway since it is a major route to heteroaromatic molecules.[18] It is not a universal reaction though, and some 6π-systems fail to cyclize. For example, it was recognized early on,[19] that while photolysis of 1,1,2,2-tetraphenylethene (**1**) proceeds smoothly to form 9,10-diphenylphenanthrene (**2**) (Scheme 1), this compound resists further ring closure to the otherwise expected end product dibenzo[*g,p*]-chrysene (**3**).[20]

† Present address: Institut des Matériaux de Nantes, UMR-CNRS 110, 2 Rue de la Houssinière, F-44072 Nantes Cedex 03, France.
‡ Present address: Superfos, Packaging International, DK-4390 Vipperoed, Denmark.
⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1996.
(1) Saito, G.; Ferraris, J. P. *Bull. Chem. Soc. Jpn.* **1980,** *53,* 2141−2145.
(2) Williams, J. M. *Acc. Chem. Res.* **1985,** *18,* 261−267.
(3) Kono, Y.; Miyamoto, H.; Aso, Y.; Otsubo, T.; Ogura, F.; Tanaka, T.; Sawada, M. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 1222−1224.
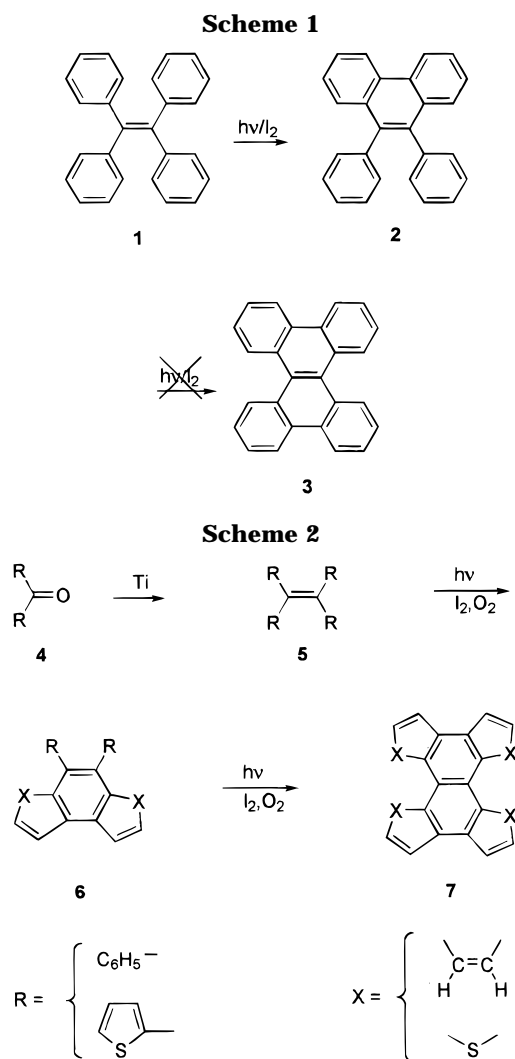(4) Bartl, A.; Fröhner, J.; Kniess, T.; Domschke, G.; Mayer, R.; Roth, S. *Synth. Met.* **1992,** *51,* 115−119.
(5) Moradpour, A. *J. Chem. Soc., Perkin Trans. 1* **1993,** 7−8.
(6) Watanabe, K.; Aso, Y.; Otsubo, T.; Ogura, F. *Chemistry Lett.* **1992,** 1233−1236.
(7) Wudl, F.; Haddon, R. C.; Zellers, E. T.; Bramwell, F. B. *J. Org. Chem.* **1979,** *44,* 2491−2493.
(8) Nabeshima, T.; Furukawa, N.; Ishizawa, T.; Morihashi, K.; Kikuchi, O. *Heterocycles* **1990,** *31,* 1575−1576.

(9) Nabeshima, T.; Iwata, S.; Furukawa, N.; Morihashi, K.; Kikuchi, O. *Chem. Lett.* **1988,** *1988,* 1325−1328.
(10) Morihashi, K.; Kikuchi, O.; Nabeshima, T.; Iwata, S.; Furukawa, N. *Chem. Lett.* **1989,** *1989,* 79−82.
(11) Ishii, A.; Nakayama, J.; Kazami, J.; Ida, Y.; Nakamura, T.; Hoshino, M. *J. Org. Chem.* **1991,** *56,* 78−82.
(12) Tsubouchi, A.; Matsumura, N.; Inoue, H. *J. Chem. Soc., Chem. Commun.* **1991,** 520−521.
(13) Kimura, T.; Ishikawa, Y.; Furukawa, N. *Heterocycles* **1993,** *35,* 53−56.
(14) Suzuki, T.; Shiohara, H.; Monobe, M.; Sakimura, T.; Tanaka, S.; Yamashita, Y.; Miyashi, T. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 455−458.
(15) Takahashi, K.; Suzuki, T.; Akiyama, K.; Ikegami, Y.; Fukazawa, Y. *J. Am. Chem. Soc.* **1991,** *113,* 4576−4583.
(16) Günther, E.; Hünig, S.; Peters, K.; Rieder, H.; Schnering, H. G.; Schütz, J.-U.; Söderholm, S.; Werner, H.-P.; Wolf, H. C. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 204−205.
(17) Heeres, G. J.; Wynberg, H. *Synth. Commun.* **1972,** *2,* 335−344.
(18) Mallory, F. B.; Mallory, C. W. In *Organic Reactions*; Wiley & Sons: New York, 1984; Vol. 30, p 1.
(19) Mallory, F. B.; Wood, C. S.; Gordon, J. T. *J. Am. Chem. Soc.* **1964,** *86,* 3094−3402.
(20) Olsen, R. J.; Buckles, R. E. *J. Photochem.* **1979,** *10,* 215−220.
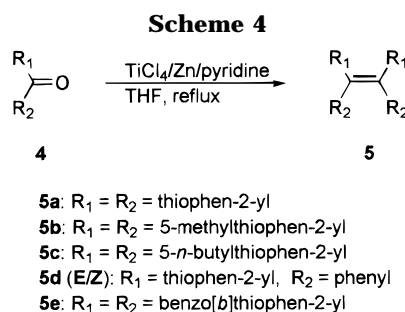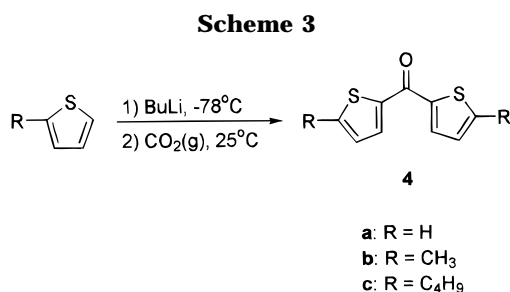
Scheme 1

Scheme 2

Therefore, in addition to preparing series of sulfur aromatics isoelectronic with dibenzo[g,p]chrysene as mentioned above, an additional objective of this work was to compare the reactivity of the photoinduced two-step ring closure of these various thienyl- and phenyl-substituted ethenes with those of compounds **1** and **2**.

Results

Heteroaromatic compounds isoelectronic with dibenzo-[g,p]chrysene have been synthesized by means of oxidative photocyclization from the corresponding tetraaryl-substituted ethenes. In most cases, the synthetic procedures follow the generalized (and simplified) pathway outlined in Scheme 2.

Phenyl- and thienyl-substituted ketones (**4**) were prepared by standard methods (see Experimental Section). When ethene (**5**) was symmetrically substituted, its preparation was most conveniently accomplished by a McMurry coupling.[21,22] Irradiation of **5** under oxidative conditions could, in most cases, be controlled by proper selection of wavelength to produce first the single-cyclization product **6**, and subsequently the double-cyclization product **7**.

In additional cases, not included in Scheme 2, the thiophene group carries an alkyl substituent or is fused to a benzene ring as a benzothiophene unit.

Scheme 3

a: R = H
b: R = CH₃
c: R = C₄H₉

Scheme 4

5a: $R_1 = R_2$ = thiophen-2-yl
5b: $R_1 = R_2$ = 5-methylthiophen-2-yl
5c: $R_1 = R_2$ = 5-n-butylthiophen-2-yl
5d (**E/Z**): R_1 = thiophen-2-yl, R_2 = phenyl
5e: $R_1 = R_2$ = benzo[b]thiophen-2-yl

Preparation of Diarylketones 4. Bis(thiophene-2-yl) ketone (**4a**) and 2-benzoylthiophene (**4d**) were prepared by published procedures.[23,24] All other ketones were prepared by lithiation of the corresponding thiophene using n-butyllithium followed by reaction with carbon dioxide[25] (Scheme 3).

In the same manner, bis(benzo[b]thiophene-2-yl) ketone (**4e**) was prepared from benzo[b]thiophene and carbon dioxide.

McMurry Coupling of Diaryl Ketones. The reductive McMurry coupling takes place at the surface of freshly prepared Ti(0),[22] but preliminary experiments showed that the reactivity of the elemental titanium is crucial when thiophene units are present. We have experienced that reduction of $TiCl_3$ with alkali metals or magnesium caused polymerization or degradation in the subsequent reaction with thienyl ketones. $TiCl_4$ reduced with zinc was better, but still the yields were unacceptably low. Suzuki et al.[14] reported, however, that the yield is considerably improved when pyridine is added as mediator in an amount equivalent with titanium. In the standard procedure for implementation of the Mc-Murry coupling,[21,22] the product is isolated after quenching the reaction by adding aqueous potassiun carbonate followed by extraction with dichloromethane. At this point an emulsion is usually formed, which makes the workup tedious and time consuming. We have therefore developed a very easy and straightforward workup procedure as described in the Experimental Section.

Thus, the symmetrically substituted ethenes **5a–e** were prepared from the corresponding ketones **4a–e** as illustrated in Scheme 4.

HPLC analysis (with UV-vis detection of the products) of 1,2-diphenyl-1,2-bis(thiophene-2-yl)ethene (**5d**) revealed two peaks, indicating the production of E/Z-isomers. The absorption spectrum of the first fraction was red shifted (λ_{max} = 262 and 332 nm) from that of (Z)-1,2-bis(thiophene-2-yl)ethene (λ_{max} = 305 nm)[26] but otherwise showed the same profile and number of transi-

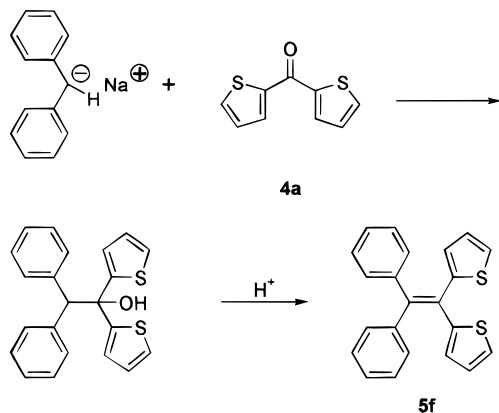(21) Lenoir, D. *Synthesis* **1977**, 553.
(22) Lai, Y.-H. *Org. Prep. Proc. Int.* **1980**, *12*, 363–390.
(23) Acheson, R. M.; MacPhee, K. E.; Philpot, P. G.; Barltrop, J. A. *J. Chem. Soc.* **1956**, 698–705.
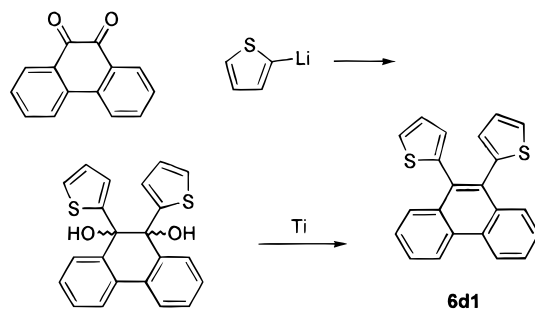(24) Minnis, W. *Organic Syntheses*; Wiley: New York, 1943; Coll. Vol. II, p 520.
(25) Jorgenson, M. J. In *Organic Reactions*; Dauben, W. G., Ed.; Wiley and Sons: New York, 1970; pp 1–98.

Scheme 5

Scheme 6

Figure 1. UV-vis spectra recorded at time intervals 0, 25, 40, 55, and 90 min, respectively, during photolysis ($\lambda > 380$ nm) of **5a** (7.1×10^{-5} M) in aerated cyclohexane with catalytic, nonabsorbing amounts of iodine.

Scheme 7

tions with no vibrational structure. Accordingly, the absorption spectrum of the second fraction ($\lambda_{max} = 253$ and 343 nm) resembled that of (*E*)-1,2-bis(thiophene-2-yl)ethene ($\lambda_{max} = 345$ nm)[26] with vibrational fine structure of long wavelength band. When the HPLC analysis was performed at 304 nm, where the two *E/Z*-isomers have identical absorption coefficients (*vide infra*), integration of the peaks revealed that the two isomers were formed in equimolar amounts (50:50). This implies that there is no preference for either configuration in the coupling of the two ketyl anion radicals in the product-forming step,[22] and that steric repulsion between the thienyl and phenyl substituents is the same as that between two thienyl and two phenyl groups, respectively.

Preparation of 1,1-Bis(thiophene-2-yl)-2,2-diphenylethene. The unsymmetrical 1,1-bis(thiophene-2-yl)-2,2-diphenylethene (**5f**) was prepared by the reaction between the ylide of diphenylmethane and bis(thiophene-2-yl) ketone, followed by acid-catalyzed elimination of water (Scheme 5).

Preparation of 9,10-Bis(thiophene-2-yl)phenanthrene. Since this compound could not be obtained by photolysis of 1,2-bis(thiophene-2-yl)-1,2-diphenylethene (**5d**) (*vide supra*), a thermal synthetic pathway was developed. 9,10-Phenanthroquinone was reacted with thiophene-2-yllithium, and the intermediate diol was reduced with elemental titanium (from $TiCl_3$ + K) (Scheme 6).

Photolytic Reactions Monitored by UV-vis Spectroscopy. The photolytic reactions of the ethenes **5** were all investigated in dilute solutions by means of absorption spectroscopy before implementation of the preparative photolysis. In all cases it was possible, by proper selection of excitation wavelengths, to effectuate the individual steps sequentially and record the spectra of
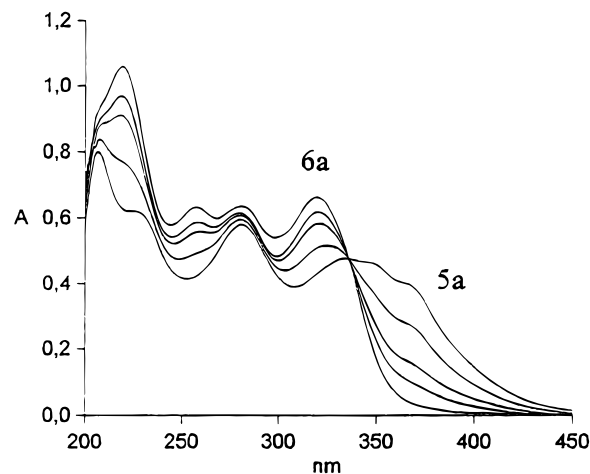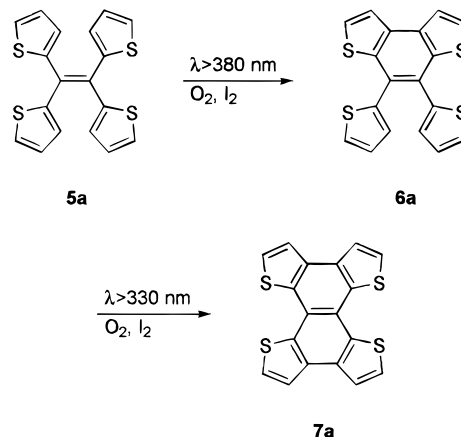
(26) Zimmerman, A. A.; Orlando, C. M.; Gianni, M. H. *J. Org. Chem.* **1969**, *34*, 73–77.

the singly cyclized structures **6**. The photolysis of the parent tetrakis(thiophene-2-yl)ethene (**5a**), according to Scheme 7, will serve as an illustration. The superimposed spectra of the transformation of **5a** displays an isosbestic point at 336 nm (Figure 1). This observation makes the final spectrum (curve 6a) assignable to 4,5-bis(thiophene-2-yl)thieno[3,2-*e*]benzo[*b*]thiophene (**6a**). Likewise, the subsequent course of photolysis (Figure 2) displayed isosbestic points at 233, 280, 311, 333, 339, and 357 nm making the final spectrum assignable to tetrathieno[2,3-*a*:3′,2′-*c*:2″,3″-*f*:3‴,2‴-*h*]naphthalene (**7a**).

Even though light intensities are not directly comparable in the two experiments shown in Figures 1 and 2, the much shorter irradiation times cited in the legend of Figure 2 undoubtedly reflect a greater relative quantum yield of the second photolytic step. Thus, when the solution of **5a** was exposed to the lamp equipped with an acetone filter ($\lambda > 330$ nm), an isosbestic point was observed (323 nm) for the direct conversion to **7a**, *i.e.* there was no trace of the intermediate **6a**. This implies that **6a** reacts much more efficiently than **5a**, a difference that might be due to competing processes from the exciting singlet state of **5a**, *e.g.* twisting around the double bond.

The photolytic transformation ($\lambda > 380$ nm) of **5f** into 5-phenyl-4-(thiophene-2-yl)thieno[3,2-*a*]naphthalene (**6f**) (Scheme 8) also proceeded smoothly and displayed an isosbestic point at 327 nm. Irradiation with $\lambda > 330$ nm
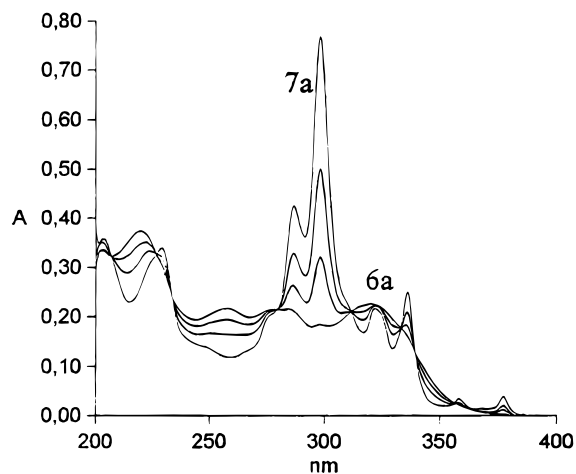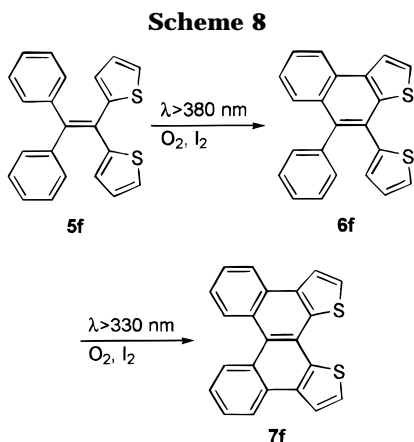
Figure 2. UV-vis spectra recorded at time intervals 0, 1, 2, 3, and 6 min, respectively, during photolysis ($\lambda > 330$ nm) of **6a** (2.0×10^{-5} M) in aerated cyclohexane with catalytic amounts of iodine.

Scheme 8

Scheme 9

Scheme 10

produced the absorption spectrum of dibenzo[*a;h*]dithieno-[3,2-*c*:2′,3′-*f*]naphthalene (**7f**), and isosbestic points were observed at 264 and 234 nm.

Contrary to all other reactions investigated, the spectra recorded during the photolytic transformation ($\lambda > 450$ nm) of tetrakis(benzo[*b*]thiophene-2-yl)ethene (**5e**) into 6,7-bis(benzo[*b*]thiophene-2-yl)bis(benzo[*b*]thiopheno)-[2,3-*a*:3′,2′-*c*]benzene (**6e**) (Scheme 9) failed to produce sharp isosbestic points. This is believed to be due to the ability of **5e** to exist as different rotamers, with high interconversional barriers by analogy to 9,10-bis(1-naphthyl)phenanthrene.[27] The second step from **6e** to tetra-(benzo[*b*]thiopheno)[2,3-*a*:3′,2′-*c*:2″,3″-*f*:3‴,2‴-*h*]naphthalene (**7e**) proceeded smoothly by means of the low-intensity light from a 60 W incandescent lamp. Isosbestic points were observed at 304, 368, 377, and 406 nm.

The photolysis of 1,2-bis(thiophene-2-yl)-1,2-diphenylethene (**5d**) (Scheme 10) represents a special case, since this starting material was a 50:50 mixture of *E/Z*-isomers obtained from the McMurry coupling (*vide supra*). When this was dissolved in cyclohexane and nitrogen bubbled through the solution during light exposure ($\lambda > 380$ nm), the stationary state shifted while an isosbestic point became observable at 304 nm, which consequently served as the wavelength of detection in the HPLC evaluation of the preparation (*vide supra*). Once the photostationary
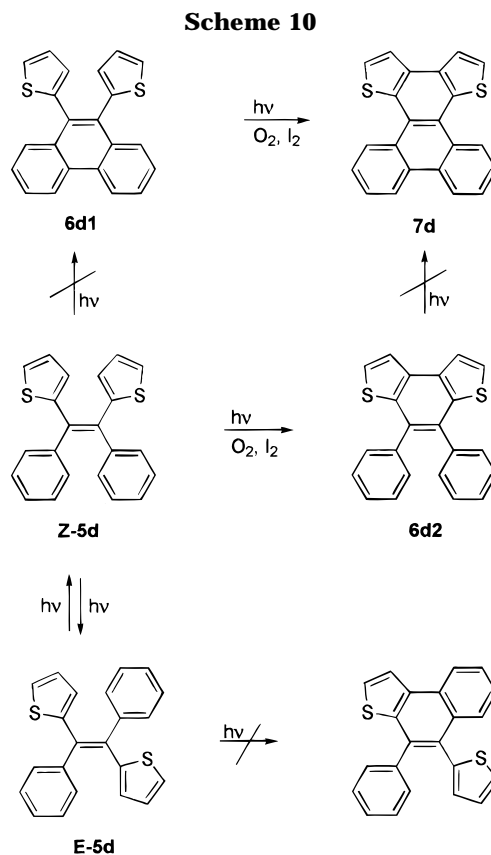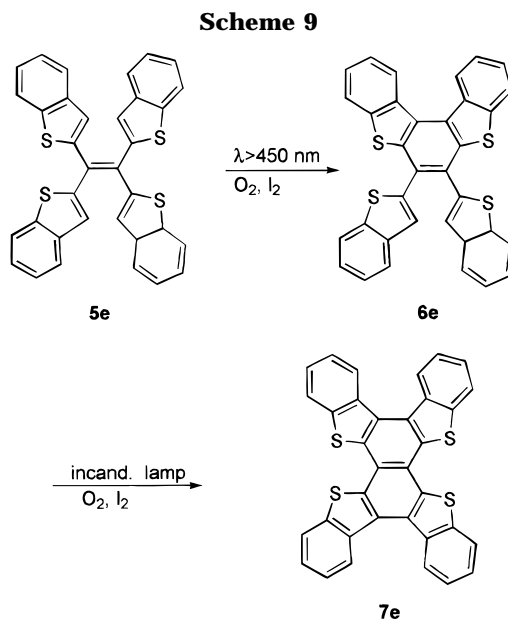
state was established, air was admitted into the cell and a photolytic transformation (isosbestic point 321 nm) into an absorption spectrum without any vibrational fine structure was observed. As was revealed by the preparative experiments, the corresponding product was 4,5-diphenylthieno[3,2-*e*]benzo[*b*]thiophene (**6d2**) (Scheme 10). Removing the filter and exposing **6d2** to the full spectrum of the lamp did not create a change, *i.e.* the photolytic transformation into **7d** could *not* be effectuated.

Small-scale photolysis ($\lambda > 330$ nm) of 9,10-bis-(thiophene-2-yl)phenanthrene (**6d1**) (Scheme 10) proceeded smoothly in the UV-cell under observation of an isosbestic point at 270 nm and appearance of the highly structured spectrum of **7d**.

(27) Gundermann, K.-D.; Romahn, E.; Zander, M. *Z. Naturforsch.* **1992**, *47b*, 1764−1774.

Preparative Photolysis. In a typical run, the ethene **5** (*ca.* 1.2 g) was dissolved in toluene (1.2 l) and irradiated through Pyrex in an immersion well equipped with a 700 W medium pressure Hg-lamp. Although oxygen acted cleanly as an oxidant in the diluted solutions (*vide supra),* it resulted in low yields of impure products, when used in more concentrated solutions. This problem may stem from unwanted reactions of the accumulated hydrogen peroxide or the higher concentration of singlet molecular oxygen. A better yield was obtained by flushing the solution with nitrogen during irradiation and adding an equimolar amount of iodine. The reactions were monitored by means of thin layer chromatography and stopped when all the starting material had been consumed.

During the subsequent workup, advantage was often taken of the fact that the double cyclized product **7** is generally less soluble than the singly cyclized **6**. By fractional crystallization and chromatography, substantial amounts of **6** could be obtained. This achievement appears less surprising, when one considers the spectral shifts accompanying the steps **5** to **6** and **6** to **7** described in the previous section. The starting materials and the end products have absorption maxima in the spectral range of maximum intensity delivered from the medium pressure Hg-arc (366 nm). The intermediate **6** has a weaker absorption in the same range and is therefore screened and protected throughout the photolysis.

Compound **7e** represents a special case since its resistance to dissolve in any solvent (not even in bromobenzene-*d*$_5$ at 130 °C) prevented spectral characterisation by means of NMR spectroscopy. A weak mass spectrum was obtained (inlet temperature 400 °C) showing the correct molecular mass. However, since **6e** can undergo alternative electrocyclic ring closure analogous to the formation of benzo[*g,h,i*]perylene from dibenzo[*c,g*]-phenanthrene (pentahelicene),[28] an X-ray structural analysis was required. This confirmed that the consecutive photoreactions did indeed lead to the symmetrical structure **7e** as shown in Scheme 9. Details of the crystal structure of **7e** and all coordinates will be reported elsewhere.[29]

Donor Properties. The oxidation potentials of the prepared heterocyclic donors were measured by cyclic voltammetry. The anodic processes were irreversible, probably due to chemical reactions at the free 2- and 3-positions in the thiophene moieties of the radical cations. The measurements were further complicated by adsorbtion phenomena on the electrode. The following peak values (E_p, V vs SCE, Pt-bottom electrode, 400 mV/s, CH$_2$Cl$_2$, (*n*-Bu)$_4$NPF$_6$ (0.1 M)) were obtained: **6d1** 1,40, **6f** 1,05, **6d2** 1,20, **7a** 1,10, **7b** 1,00, **7c** 1,08, **7d** 1,10, **7e** 1,08, **7f** 1,05. Electrochemical data on dibenzo[*g,p*]-chrysene were not obtainable when investigated under the same conditions. The first potential notwithstanding, the oxidation potentials are all within the range 1.0 to 1.2 V, indicating that the new sulfur heterocycles are not particularly strong donors. Similar values have been found for other large thiophene-annelated compounds such as the heterohelicenes.[36]

Compound **7a** forms a 1:1 complex with tetracyano-*p*-quinodimethane (TCNQ), which was obtained by slow cooling of a boiling *o*-xylene solution, saturated with **7a**
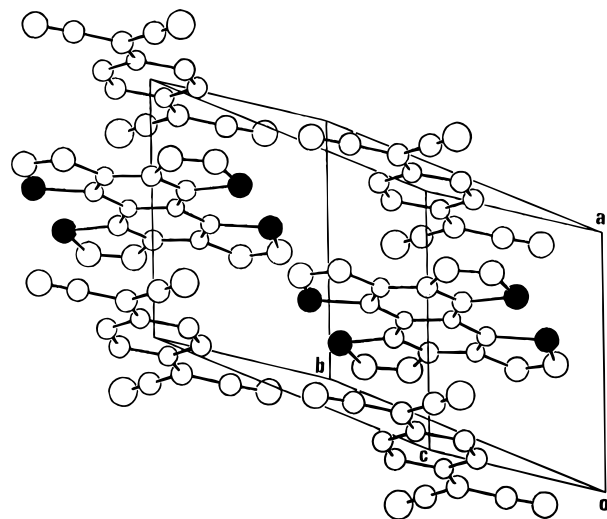

Figure 3. ORTEP view of the unit cell of **7a**−TCNQ. Thermal ellipsoids are drawn at the 50% probability level. The sulfur atoms have been darkened.

and containing an equimolar amount of TCNQ. The CT-complex precipitated as small, black crystals. X-ray crystal structure determination confirms the molecular structure of **7a**[47] and reveals a one-dimensional structure with columns of alternating donor (D) and acceptor (A) moieties (Figure 3). The flat molecules stack on top of each other with a plane-to-plane D−A distance of 3.32(2) Å. As a consequence of this structure, the material is fully insulating as confirmed by a compressed pellet conductivity measurement.

The molecule **7a** is located on an inversion center and appears to be essentially planar, the dihedral angle between the two independant thiophene rings amounting to 2.5(5)°. One interesting feature is the short intramolecular S(1)−S(2) distance (3.066(5)Å) when compared with the Van der Waals distance (S−S 3.7 Å), indicating a degree of delocalization between the two sulfur atoms, as already postulated in various molecules with the same 1,5-sulfur−sulfur interaction where S−S distances around 3 Å were observed.[30−32] The TCNQ molecule also lies on an inversion center. From the bond lengths, we can estimate the degree of charge transfer[33−35] which is found to be zero, *i.e.* we have a neutral D−A complex, as recently reported for a thiahelicene/TCNQ complex.[36]

Discussion

The lack of reactivity of 9,10-diphenylphenanthrene (**2**) (Scheme 1) and other systems has been attributed to both electronic and steric factors. Thus, Mallory *et al.*[19] recognized that the absorption spectrum of **2** resembles that of unsubstituted phenanthrene to such an extent that the phenyl groups are considered not to play a role in the electronic excitation. Consequently, the "electron

(28) Laarhoven, W. H. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1989; Vol. 10, pp 163−287.

(29) Larsen, S.; Püschl, A.; Binau, K.; Jansen, K. K.; Lolck, R.; Fischer, E.; Harrit, N. In preparation.

(30) Wudl, F.; Srdanov, G.; Rosenau, B.; Wellman, D.; Williams, K.; Cox, S. D. *J. Am. Chem. Soc.* **1988**, *110*, 1316.

(31) Bryce, M. R.; Coffin, M. A.; Hursthouse, M. B.; Mazid, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 871.

(32) Sallé, M.; Jubault, M.; Gorgues, A.; Boubekeur, K.; Fourmugué, M.; Batail, P.; Canadell, E. *Chem. Mat.* **1993**, *5*, 1196.

(33) Flandrois, S.; Chasseau, D. *Acta Crystallogr. B* **1977**, *33B*, 2744.

(34) Kistenmacher, T. J.; Emge, T. J.; Bloch, A. N.; Cowan, D. O. *Acta Crystallogr. B* **1982**, *38B*, 1193.

(35) Umland, T. C.; Allie, S.; Kuhlman, T.; Coppens, P. *J. Phys. Chem.* **1988**, *92*, 6456.

(36) Larsen, J.; Dolbecq, A.; Bechgaard, K. *Acta Chem. Scand.* **1996**, *50*, 83−89.

availability" in the excited state on the two ortho carbons between which the new bond is expected to be formed, cannot be much different from the ground state. A more quantitative measure for the reactivity in electrocyclic reactions is the so-called sum of Free Valence Numbers, ΣF_r^*, which have been calculated for a series of systems.[28,37–40] Also, the reactivity can be related to the electronic overlap population of the pair of atoms between which the new bond is formed in the excited state.[41]

In the case of **2**, Laarhoven[28] has also pointed toward steric conditions as the "obvious" reason for the lack of reactivity; the two phenyl rings cannot acquire the proper conformation prerequisite for cyclization, due to interaction between the hydrogen atoms on C1 and C8 of the phenanthrene moiety. Recent investigations of the photoreactivity of 9,10-bis(1-naphthyl)phenanthrene show, however, that steric factors are not the consideration.[27] This compound exists as two rotational *E/Z*-isomers with the naphthalene molecular planes perpendicular to the phenanthrene plane as revealed by NMR spectroscopy. The two isomers are not interconvertible but can be separated and recrystallized. This result is supported by calculations revealing an insurmountable barrier to rotation. However, in contrast to the photostability of **2**, 9,10-bis(1-naphthyl)phenanthrene closes efficiently upon irradiation to form benzo[*e*]phenanthro[1,2,3,4-*ghi*]-perylene.[27] This result illustrates that photoinduced cyclization is possible from an almost perpendicular configuration, and planarity is reached in the course of the process, concomitantly with the rehybridization of the carbon atoms involved in bond formation.

4,5-Diphenylthieno[3,2-*e*]benzo[*b*]thiophene (**6d2**) resisted all attempts to implement 6π-electrocyclic ring closure, by analogy with 9,10-diphenylphenanthrene (**2**). In case of **6d2**, there are no hydrogen atoms preventing the phenyl groups from obtaining the proper configuration. Neither is this a general phenomenon characteristic for any two phenyl groups sitting adjacent to one another on an aromatic ring, since *ortho*-terphenyl undergoes photocyclization to triphenylene.[42] The origin of this inertness must be linked to the resemblance of the electronic structures of the phenanthrene and thieno[3,2-*e*]benzo[*b*]thiophene moieties of **2** and **6d2**, respectively.

The 3-position of the thienyl substituent still seems to be more inclined to participate in electrocyclic reactions than the 2-position of phenyl. This is revealed when one of the phenyl groups of **6d2** is exchanged with thienyl as in **6f**, in which case cyclization proceeds smoothly (Scheme 8). If two thienyl substituents participate, the process is very efficient (**6a** to **7a** (Scheme 7) and **6d1** to **7d** (Scheme 10)). When a competition between thienyl and phenyl occurs, as in the parallel reactions of (*Z*)-**5d** and (*E*)-**5d**, a thienyl-group is clearly preferred over a phenyl-group as partner in a cyclization reaction (Scheme 10).

In terms of electron density and free valence number, the enhanced reactivity of the thienyl substituent over that of phenyl can be viewed, rather naively, as a

reflection of the fact that only five atoms are sharing the π-electrons of the aromatic sextet.[43] Accordingly, the thiophene ring is an efficient partaker in other 6π-electrocyclic ring closures,[18] and quantitative yields of reaction are often observed, as in the case of the transformation of 1,2-bis(thiophene-2-yl)ethene into thieno[3,2-*e*]benzo[*b*]thiophene.[44]

The absence of vibrational fine stucture in the absorption spectrum can be due to several circumstances, *e.g.* conformational broadning and predissociation. The first phenomenon is found in the spectra of the semiclosed structures **6** compared to the fully closed structures **7**, as illustrated by **6a** and **7a** in Figures 1 and 2. Even though they have the same number of π-electrons, the spectrum of **7a** is shifted to the red and displays a rich fine structure of electronic and/or vibronic bands, while that of **6a** is diffuse. This is due to the aromaticity and rigidity of the **7a** molecule while the exocyclic thienyl groups in **6a** display a continuum of diedral angles with respect to the thieno[3,2-*e*]benzo[*b*]thiophene core, causing a blur of the vibrational structure. The same trends are observed when comparing the spectra of **2** and **3**.[19,45] By analogy, the absorption spectrum of thieno[3,2-*e*]-benzo[*b*]thiophene[44] is structured but otherwise qualitatively identical to that of **6a**.

Since steric repulsion between the phenyl and thiophene-2-yl substituents of **5d** is the same, there is no basis for explaining the difference in observable vibrational structure of the *E/Z*-pair as being due to conformational effects. Neither is there reason to believe that the quantum yield for photoisomerization $Z \rightarrow E$ is different from the $E \rightarrow Z$ value. Therefore, the absence of vibrational fine structure in the absorption spectrum of (*Z*)-**5d** could be due to coupling of the Frank−Condon excited state to a "dissociative" mode, representing a 6π-electrocyclic ring closure in accordance with the observation that (*Z*)-**5d** reacts far more efficiently than (*E*)-**5d**.

In the CT-complex formed between **7a** and TCNQ, the donor is found to be completely planar. Since the charge transfer is found to be negligible in the ground state, the isolated molecule of **7a** must also be planar and consequently belongs to the D_{2h} point group. This result illustrates a characteristic feature of thiaheterocycles compared to their isoelectronic all-carbon analogues. A recent study[45] of dibenzo[*g,p*]chrysene (**3**), which relates to **7a** in this manner, has revealed that it is nonplanar and possesses D_2 symmetry. The distortion from planarity is due to hydrogen crowding in the bay areas of **3** which is obviously not occurring in **7a**. Sterically, a sulfur atom represents a more compact means of introducing two π-electrons in an aromatic sextet compared to 1,2-vinylidene. However, the potential of **7a** for enhanced intermolecular interactions does not translate over to the electrical conductivity of the CT-complex with TCNQ, since very little conductivity was detectable from a compressed pellet conducting measurements of the crystals.

Experimental Section

General Methods. Melting points are uncorrected and were determined using a hot plate. HPLC measurements were performed using an RP-8 column and methanol as solvent (1

(37) Sato, T.; Morita, T. *Bull. Chem. Soc. Jap.* **1972**, *45*, 1548.
(38) Laarhoven, W. H.; Cuppen, T. J. H. M.; Niverd, R. J. F. *Recl. Trav. Chim., Pays-Bas* **1968**, 687.
(39) Orchin, M.; Jaffe, H. H. In *Symmetry, Orbitals, and Spectra*; Wiley-Interscience: New York, 1971; pp 279−281.
(40) Laarhoven, W. H.; Cuppen, J. H. M.; Nivard, R. J. F. *Tetrahedron* **1970**, *26*, 1069−1083.
(41) Muszkat, K. A.; Sharafi-Ozeri, S. *Chem. Phys. Lett.* **1973**, *20*, 397−399.
(42) Kharasch, N.; Alston, T. G.; Lewis, H. B.; Wolf, W. *J. Chem. Soc., Chem. Commun.* **1965**, 242−243.

(43) Solony, N.; Birss, F. W. *Can. J. Chem.* **1965**, *43*, 1569−1576.
(44) Kellogg, R. M.; Groen, M. B.; Wynberg, H. *J. Org. Chem.* **1967**, *32*, 3093−3100.
(45) Thulstrup, E. W.; Spanget-Larsen, J.; Waluk, J. *Theor. Chim. Acta* **1994**, *89*, 301−309.

mL/min, rt). Mass spectra were obtained at 70 eV ionizing energy. THF was distilled from sodium benzophenone ketyl radical. Zinc dust was used without further purification. Column chromatographic purifications were performed with activated basic aluminum oxide. All reagents were purchased from commercial sources and used without further purification except where reported. Small scale photolysis was carried out in standard absorption cells (quartz) at room temperature using a high pressure mercury source (200 W), fitted with a filter cutting all wavelengths below 380 nm (glass filter) or 330 nm (1 cm acetone). Preparative photolysis was carried out in an immersion well as outlined below.

Bis(thiophene-2-yl) ketone (4a) was prepared by a published procedure.[23]

Bis(5-methylthiophene-2-yl) Ketone (4b). A three-necked 500 mL flask equipped with a reflux condenser and a thermometer was charged under dry nitrogen with 9.8 g (100 mmol) of 2-methylthiophene and 300 mL of dry THF. A solution of butyllithium (40 mL, 2.5 M in hexane, 100 mmol) was added at −78 °C. The reaction mixture was allowed to reach room temperature, whereupon carbon dioxide gas was introduced over a short period of time. This was repeated over a 30 min period until the temperature of the reaction mixture remained constant upon further addition of carbon dioxide. The reaction mixture was then cooled to −78 °C, and chlorotrimethylsilane (12.6 mL 10.8 g, 100 mmol) was added. The reaction mixture was taken to room temperature and poured into 500 mL of 0.5 M hydrochloric acid. The organic phase was separated and the water phase extracted twice with 100 mL of ether. The combined organic phases were washed with saturated sodium carbonate solution and dried (MgSO$_4$), and the solvent was evaporated *in vacuo*. Distillation of the crude product (145 °C/0.6 mbar) afforded 13.3 g (60%) of **4b** as light yellow flakes: mp 53−55 °C; ^{1}H-NMR (90 MHz, CDCl$_3$) δ 7.7 (d, J = 3.5 Hz, 2H), 6.8 (d, J = 3.5 Hz, 2H), 2.6 (s, 6H). Anal. Calcd for C$_{11}$H$_{10}$OS$_2$: C, 59.43; H, 4.53; S, 28.84. Found: C, 59.67; H, 4.46; S, 28.70.

Bis(5-butylthiophene-2-yl) ketone (4c) was prepared in 64% yield by a procedure analogous to the synthesis of **4b**. Pale yellow flakes from petroleum ether: mp 36−37.5 °C; ^{1}H-NMR (90 MHz, CDCl$_3$) δ 7.7 (d, J = 3.5 Hz, 2H), 6.8 (d, J = 3.5 Hz, 2H), 3−0.8 (m, 18H). Anal. Calcd for C$_{17}$H$_{22}$O S$_2$: C, 66.62; H, 7.24; S, 20.92. Found: C, 66.74; H, 7.28; S, 21.20.

2-Benzoylthiophene (4d) was prepared according to a published procedure.[24]

Bis(benzo[*b*]thiophene-2-yl) ketone (4e) was prepared in 60% yield by a procedure analogous to the synthesis of **4b**. Yellow needles from toluene: mp 172−174 °C; ^{1}H-NMR (250 MHz, CDCl$_3$) δ 8.2 (s, 2H), 7.9 (m, 4H), 7,4 (m, 4H). Anal. Calcd for C$_{17}$H$_{10}$O S$_2$: C, 69.36; H, 3.42. Found: C, 69.81; H, 3.64.

Tetrakis(thiophene-2-yl)ethene (5a). All tetrasubstituted ethenes except 1,1-bis(thiophene-2-yl)-2,2-diphenylethene were prepared by a McMurry coupling, using the procedure by Lenoir[21] as a guideline. Since the workup procedure described in that article is rather tedious, we have applied the following modification. After completion of the reaction between the ketone, pyridine, and low valent titanium, the solvent (THF) was evaporated *in vacuo* leaving a black viscous oil. Addition of 0.5 M hydrochloric acid to this oil resulted in removal of the titanium (oxide), zinc chloride, and zinc, leaving the crude product as either crystals or an oil. After decantation of the water phase, the organic residue was dissolved in toluene and dried (MgSO$_4$). The solution was passed through a short column (basic aluminum oxide) which was eluted with hot toluene. Removal of the solvent and recrystallization afforded the pure compound. Thus, **5a** was obtained in 40% yield as red flakes from ethanol: mp 196−198 °C, lit.: 196−198 °C.[14]

Tetrakis(5-methylthiophene-2-yl)ethene (5b). Yellow needles from ethanol (53%): mp 130−131 °C; ^{1}H-NMR (90 MHz, CDCl$_3$) δ 6.6 (m, 8H), 2.4 (d, J = 1 Hz, 12H); MS (70 eV): 512 (M$^+$, 100), 364 (15), 206 (M^{2+}, 13). UV-vis λ_{max} (nm) (log ϵ) (CH$_2$Cl$_2$): 382 (4.32), 296 (4.27). Anal. Calcd for C$_{22}$H$_{20}$S$_4$: C, 64.04; H, 4.89; S, 31.08. Found: C, 64.20; H, 4.95; S, 30.55.

Tetrakis(5-butylthiophene-2-yl)ethene (5c). Yellow needles from petroleum ether (35%): mp 93.5−94 °C; ^{1}H-NMR (90 MHz, CDCl$_3$) δ 6.7 (d, J = 3.5 Hz, 4H), 6.5 (d, J = 3.5 Hz, 4H), 2.8−0.8 (m, 36H); MS (70 eV): 580 (M$^+$, 100), 290 (M^{2+}, 12). UV-vis λ_{max} (nm) (log ϵ) (hexane): 239 (4.50), 295 (4.58), 363 (4.55), 381 (4.59). Anal. Calcd for C$_{34}$H$_{44}$S$_4$: C, 70.29; H, 7.63; S, 22.07. Found: C, 70.39; H, 7.68; S, 22.15.

1,2-Bis(thiophene-2-yl)-1,2-diphenylethene (5d). Orange needles from CH$_2$Cl$_2$ (40%): mp 219−221 °C; HPLC indicated a 50/50 mixture of *E* and *Z* (see results section). ^{1}H-NMR (250 MHz, CDCl$_3$) δ 7.4 (s, 10H), 7.0 (dd, 2H), 6.7 (dd, 2H), 6.3 (dd, 2H); MS (70 eV): 344 (M$^+$, 100), 266 (13). Anal. Calcd for C$_{22}$H$_{16}$S$_2$: C, 76.73; H, 4.65; S, 18.62. Found: C, 76.25; H, 4.63; S 18.39.

Tetrakis(benzo[*b*]thiophene-2-yl)ethene (5e). The crude product was not suitable for column chromatography since it has low solubility in toluene. The crude product was therefore recrystallized twice from *o*-xylene (activated charcoal). Yellow needles (40%): mp 218 °C dec. ^{1}H-NMR (90 MHz, CDCl$_3$) δ 7.7 (m, 2H), 7.4 (m, 3H). MS (70 eV): 556 (M$^+$, 100), 278 (M^{2+}, 13). UV-vis λ_{max} (nm) (log ϵ) (CH$_2$Cl$_2$): 397 (4.35), 377 (4.35), 306 (4.44). Anal. Calcd for C$_{34}$H$_{20}$S$_4$: C, 73.35; H, 3.62. Found: C, 72.42; H, 3.70.

1,1-Bis(thiophene-2-yl)-2,2-diphenylethanol. To 100 mL of dry liquid ammonia was added sodium (0.6 g, 26 mmol), and the suspension was left until it became grey (20 min). Diphenylmethane (5.04 g, 30 mmol) in 15 mL of dry ether was then added and the color changed to deep red. After 15 min, bis(thiophene-2-yl) ketone (5.0 g, 26 mmol) in 25 mL of dry THF was added to the suspension, and the reaction was left for another 15 min. The reaction was quenched by pouring it into 50 mL of liquid ammonia containing NH$_4$Cl (2.67 g, 50 mmol). The ammonia was allowed to evaporate, and the ether phase was poured into 100 mL of water. The organic phase was isolated and dried (MgSO$_4$) and the solvent evaporated *in vacuo* leaving 7.5 g of a yellow oil. Triturating with 100 mL of hexane resulted in 4.0 g of crystals which were recrystallized from ethanol leaving 2.5 g 1,1-bis(thiophene-2-yl)-2,2-diphenylethanol (34%) as colorless crystals: mp 179−181 °C; ^{1}H-NMR (250 MHz, CDCl$_3$) δ 7.3 (dd, J = 2 Hz, 4H), 7.1 (8H, m), 6.8 (m, 4H), 4.9 (s, 1H), 3.2 (s, 1H). MS (70 eV): 344 (M$^+$ − H$_2$O, 65), 195 (100), 111(60). Anal. Calcd for C$_{22}$H$_{18}$OS$_2$: C, 72.89; H, 5.00; S, 17.69. Found: C, 73.16; H, 5.03; S, 17.65.

1,1-Bis(thiophene-2-yl)-2,2-diphenylethene (5f). 1,1-Bis(thiophene-2-yl)-2,2-diphenylethanol (2.0 g, 70 mmol) dissolved in 100 mL of dry benzene was refluxed with a catalytic amount of *p*-toluenesulfonic acid using a Dean−Stark water separator. When the expected amount of water was trapped the solvent was evaporated *in vacuo* whereafter the residue was passed through a short column (basic aluminum oxide, toluene). The first fraction was evaporated *in vacuo*, and the solid recrystallized from acetone giving 1.5 g of 1,1-bis-(thiophene-2-yl)-2,2-diphenylethene (75%) as colorless crystals: mp 165−167 °C; ^{1}H-NMR (250 MHz, CDCl$_3$) δ 7.1 (m, 12H), 6.8 (m, 4H); MS (70 eV): 344 (M$^+$, 100), 278 (10), 172 (M^{2+}, 4). Anal. Calcd for C$_{22}$H$_{16}$S$_2$: C, 76.71; H, 4.68; S, 18.61. Found: C, 76.86; H, 4.64; S, 18.65. UV-vis λ_{max} (nm) (log ϵ) (CH$_2$Cl$_2$): 337 (4.08), 237 (4.27).

(*erythro*/*threo*)-9,10-Bis(thiophene-2-yl)-9,10-dihydroxy-9,10-dihydrophenanthrene. To a stirred solution of thiophene (12.63 g, 0.15 mol) in 200 mL of dry THF was added butyllithium (60 mL 2.5 M in hexane, 0.15 mol) at −78 °C. The mixture was allowed to warm up to room temperature, and 9,10-phenanthroquinone (13.0 g, 0.0625 mol) was added in small portions during 30 min. The reaction mixture was left overnight and poured into 400 mL of water. The resulting suspension was filtered, leaving the crude product. Recrystallization from ethanol gave 4.5 g (19%) of the title compound as yellow crystals with mp 213−218 °C. Further recrystallization from toluene did not diminish the melting point range, and the rather chaotic NMR spectrum indicated an erythro/threo mixture: ^{1}H-NMR (90 MHz, CDCl$_3$) δ 7.7 (m, 4H), 7.4 (m, 5H), 7.1 (q, J = 5 Hz, J = 1 Hz, 2H), 6.6 (m, 4H). MS (70 eV): 376 (M+, 90), 263 (90), 247 (85), 181 (50), 111 (100). Anal.

Calcd for $C_{22}H_{16}O_2S_2$: C, 70.19; H, 4.28; S, 17.03. Found: C, 70.28; H, 4.48; S, 16.83.

9,10-Bis(thiophene-2-yl)phenanthrene (6d). $TiCl_3$ (1.08 g, 7 mmol) was slowly added to 75 mL of dry THF under dry nitrogen at room temperature. Thereafter potassium (0.79 g, 25 mmol) was added in small pieces under reflux. After refluxing for a further 2 h, (*erythro/threo*)-9,10-bis(thiophene-2-yl)-9,10-dihydroxy-9,10-dihydrophenanthrene (2.0 g, 5.3 mmol) in 15 mL of dry THF was added, and the suspension was refluxed for additional 20 h. The reaction mixture was quenched with ethanol and then poured into 200 mL of water. The phases were separated, and the water phase was extracted twice with 50 mL of $CHCl_3$. The combined organic phases were washed with water and dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The crude product was redissolved in boiling toluene and purified by column chromatography (basic aluminum oxide, hot toluene). The first fraction was collected, the solvent was evaporated *in vacuo*, and the residue was recrystallized from acetone leaving 0.298 g (16%) as yellow crystals: mp > 230 °C; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 8.8 (d, J = 8 Hz, 2H), 7.8 (dd, J = 8 Hz, J = 1 Hz, 2H), 7.7 (dt, J = 8, J = 1, 2H), 7.5 (dt, J = 8 Hz, J = 1 Hz, 2H), 7.35 (dd, J = 5 Hz, J = 1 Hz, 2H), 7.0 (dd, J = 5 Hz, J = 5 Hz, 2H), 7.95 (dd, J = 5 Hz, J = 1 Hz, 2H). MS (70 eV): 342 (M$^+$, 100), 308 (40), 296 (20), 171 (M^{2+}, 2). Anal. Calcd for $C_{22}H_{14}S_2$: C, 77.16; H, 4.12; S, 18.72. Found: C, 76.74; H, 4.18; S, 18.00.

Preparative Photolysis. In a typical run, 1.2 g of ethene (**5**) and 2 equiv of iodine was dissolved in 1.4 L of toluene. This solution was irradiated through Pyrex in an immersion well equipped with either a 700 W or 400 W medium pressure Hg-lamp. During photolysis the solution was flushed with nitrogen. Irradiation was stopped when the starting material was no longer detectable by means of either TLC or absorption spectrometry. In some cases, the product precipitated during photolysis, and the solution was filtered before further workup. Intermediate cleaning of the surface of the cooling mantle was sometimes necessary during preparative photolysis. The filtered solution was shaken with a solution of sodium dithionite in water in order to remove excess iodine. The phases were separated, and the organic phase was washed with water and the solvent evaporated *in vacuo* leaving the crude product. Recrystallization (or fractional recrystallization if two products arose from the photolysis) of the crude product and the filtrate afforded the pure compound(s).

4,5-Bis(thiophene-2-yl)thieno[3,2-e]benzo[b]thiophene (6a) and Tetrathieno[2,3-a:3′,2′-c:2″,3″-f:3‴,2‴-h]naphthalene (7a). Tetrakis(thiophene-2-yl)ethene (1.75 g, 4.9 mmol) was irradiated as described above and monitored by means of UV-spectroscopy. When the photolysis was finished, the solution was filtered and processed as in the general procedure. The solid from the filtrate (502 mg) and the precipitate (1.30 g) were combined and extracted with 40 mL of boiling toluene. After evaporation of the toluene *in vacuo* and recrystallization of the crude product twice from toluene/heptane 85/15 (active carbon), **6a** could be isolated as colorless crystals (243 mg, 14%); mp 147−149 °C; ^{1}H-NMR (250 MHz, DMSO-d_6) δ 8.1 (dd, J = 5,5 Hz, 4H), 7.8 (q, J = 5 Hz, J = 1 Hz, 2H), 7.3 (q, J = 5 Hz, J = 5 Hz, 2H), 7.2 (q, J = 5 Hz, J = 5 Hz, 2H). MS (70 eV): 354 (M$^+$, 100), 309 (20), 277 (M^{2+}, 4). Anal. Calcd for $C_{18}H_{10}S_4$: C, 61.00; H, 2.82; S, 36.18. Found: C, 61.02; H, 2.82; S, 36.36. UV-vis λ_{max} (nm) (log ϵ) (cyclohexane): 256 (4.60), 283 (4.59), 318 (4.59). The residue from the extraction was recrystallized twice from *o*-xylene (active carbon) leaving 503 mg (29%) of **7a** as yellow-orange needles: mp > 330 °C; ^{1}H-NMR (250 MHz, bromobenzene-d_5, 130 °C) 8.1 (dd, J = 5,0 Hz). MS (70 eV): 352 (M$^+$, 100), 307 (9), 276 (M^{2+}, 12). UV-vis λ_{max} (nm) (log ϵ) (benzene): 289 (4.66), 300 (4.95), 324 (4.39), 338 (4.46), 359 (3.55), 378 (3.62). Anal. Calcd for $C_{18}H_8S_4$: C, 61.34; H, 2.27; S, 36.38. Found: C, 61.36; H, 2.36; S, 36.58.

1,4,7,10-Tetramethyltetrathieno[2,3-a:3′,2′-c:2″,3″-f:3‴,2‴-h]naphthalene (7b). Tetrakis(5-methylthiophene-2-yl)ethene (**5b**) was photolyzed according to the standard procedure. The

only compound that could be isolated was the double ring closed compound **7b** in 42% yield as yellow needles from *o*-xylene: mp > 230 °C; ^{1}H-NMR (250 MHz, bromobenzene-d_5, 130 °C) 7.4 (q, J = 1.0 Hz, 1H), 2.7 (d, J = 1 Hz, 3H). MS (70 eV): 408 (M$^+$, 100), 204 (M^{2+}, 8). Anal. Calcd for $C_{22}H_{16}S_4$: C, 64.69; H, 3.92; S, 31.39. Found: C, 64.75; H, 3.99; S, 31.14.

1,4,7,10-Tetrabutyltetrathieno[2,3-a:3′,2′-c:2″,3″-f:3‴,2‴-h]naphthalene (7c). Tetrakis(5-butylthiophene-2-yl)ethene (**5c**) was photolyzed according to the standard procedure and **7c** isolated in 34% yield as yellow needles from hexane (active carbon): mp 160−162 °C; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 7.5 (s, 4H), 1−3 (m, 36H). Anal. Calcd for $C_{34}H_{40}S_4$: C, 70.82; H, 6.94; S, 22.24. Found: C, 70.63; H, 6.95; S, 22.07.

Dithieno[2,3-a:3′,2′-c]triphenylene (7d). 9,10-Bis(thiophene-2-yl)phenanthrene (**6d**) was photolyzed according to the standard procedure to give **7c** in 69% yield as yellow needles from toluene (active carbon): mp > 230 °C; ^{1}H-NMR (250 MHz, bromobenzene-d_5) δ 9.2 (dd, J = 1 Hz, J = 8 Hz, 2H), 8.4 (dd, J = 8 Hz, J = 1 Hz, 2H), 7.5 (d, J = 5 Hz, 2H), 7.4 (m, 2H), 7.3 (d, J = 5 Hz, 2H). MS (70 eV): 340 (M$^+$, 100), 295 (15), 170 (M^{2+}, 9). Anal. Calcd for $C_{22}H_{12}S_2$: C, 77.61; H, 3.55; S, 18.83. Found: C, 77.53; H, 3.59; S, 18.68. UV-vis λ_{max} (nm) (log ϵ) (CH_2Cl_2): 289 (4.72), 299 (4.75), 328 (4.30), 342 (4.23).

Tetrakis(benzo[b]thiophene-2-yl)[2,3-a:3′,2′-c:2″,3″-f:3‴,2‴-h]naphthalene (7e). Tetra(benzo[b]thiophene-2-yl)-ethene (**5e**) was photolyzed according to the standard procedure. Compound **7e** is extremely insoluble in toluene and precipitated during photolysis. Occasional cleaning of the cooling jacket was necessary. Compound **7e** was isolated by filtration and recrystallized from *o*-dichlorobenzene as yellow needles (81%): mp > 320 °C. The low solubility of **7e** prevented the use of NMR as a means of characterization. The X-ray structure was obtained (*vide supra*).

5-Phenyl-4-(thiophene-2-yl)-thieno[3,2-a]naphthalene (6f) and Dibenzo[a,h]dithieno[3,2-c:2′,3′-f]naphthalene (7f). 1,1-Dithienyl-2,2-diphenylethene (1.0 g, 2.9 mmol) was irradiated according to the standard procedure. Compound **7f** is rather soluble in toluene and did not precipitate. Instead, the solvent was evaporated *in vacuo*, and the remaining solid was dissolved in 50 mL of hot toluene and subjected to column chromatography (basic aluminum oxide, hot toluene). The first fraction was collected and the solvent evaporated *in vacuo*. Recrystallization from toluene (active carbon) afforded 423 mg (43%) of **7f** as pale yellow flakes: mp 260−262 °C; ^{1}H-NMR (250 MHz, DMSO-d_6) δ 9.1 (dd, J = 8 Hz, J = 2 Hz, 2H), δ 8.75 (dd, J = 8 Hz, J = 2 Hz, 2H), 8.5 (d, J = 5 Hz, 2 H), 8.2 (d, J = 5, 2H), 7.8 (m, 4H); MS (70 eV): 340 (M$^+$, 100), 395 (7), 170 (M^{2+}, 8). UV-vis λ_{max} (nm) (log ϵ) (CH_2Cl_2): 237 (4.46), 296 (4.69), 307 (4.81), 341 (4.22), 355 (4.16), 385 (3.54). Anal. Calcd for $C_{22}H_{12}S_2$: C, 77.61; H, 3.55; S, 18.83. Found: C, 77.83; H, 3.64; S, 18.93.

The filtrate was evaporated *in vacuo* and recrystallized from petroleum (bp 60−80 °C)/toluene (10:2) affording 184 mg (19%) of **6f** as colorless flakes: mp 196.5−198.5 °C; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 8.4 (d, J = 5 Hz, 1H), δ 8.1 (d, J = 5 Hz, 1H), 7.6 (t, 3H), 7.3 (m. 7H), 7.1 (d, 1H), 7.0 (t, 1H) MS (70 eV): 342 (M$^+$, 100), 308 (30), 171 (M^{2+}, 8). UV-vis λ_{max} (nm) (log ϵ) (CH_2Cl_2): 247 (4.66), 313 (4.16). Anal. Calcd for $C_{22}H_{14}S_2$: C, 77.15; H, 4.12; S, 18.73. Found: C, 77.19; H, 4.12; S, 18.01.

4,5-Diphenylthieno[3,2-e]benzo[b]thiophene (6d2). 1,2-Bis(thiophene-2-yl)-1,2-diphenylethene (*E/Z*) (**5d**) (1.02 g, 3.0 mmol) was irradiated according to the standard procedure. Evaporation of the solvent *in vacuo* and recrystallization from heptane afforded 678 mg (68%) of **6d2** as colorless needles: mp 190−192 °C; ^{1}H-NMR (250 MHz, $CDCl_3$) δ 7.8 (d, J = 5 Hz, 2H), δ 7.4 (d, J = 5 Hz, 2H), 7.3 (m, 10H). MS (70 eV): 342 (M$^+$, 100), 308 (35), 282 (10). UV-vis λ_{max} (nm) (log ϵ) (CH_2Cl_2): 254 (4.35), 307 (4.27). Anal. Calcd for $C_{22}H_{14}S_2$: C, 77.15; H, 4.12; S, 18.73. Found: C, 77.36; H, 4.11; S, 18.48.

(Z)-1,2-Bis(thiophene-2-yl)ethene was prepared according to Kumada *et al.*[46] using (thiophene-2-yl)magnesium

(46) Kumada, M.; Tamao, K.; Sumitani, K. *Organic Syntheses*; Wiley: New York, 1963; Coll. Vol. IV, p 407.

bromide, (*E*)-dichloroethene, and dichloro[1,2-bis(diphenylphosphino)ethane]nickel(II). Bp 105−109 °C/1.4 mbar. ^{1}H-NMR (90 MHz, CDCl$_3$) δ 6.6 (s, 2H), 6.95 (dd, J = 1 Hz, J = 5 Hz, 2H) 7.15 (dd, J = 5 Hz, J = 5 Hz, 2H) 7.25 (dd, J = 1 Hz, J = 5 Hz, 2H); MS (70 eV): 192 (M$^+$, 100), 147 (39), 115 (10).

Charge Transfer Complex between Tetrathieno[2,3-*a*:3′,2′-*c*:2″,3″-*f*:3‴,2‴-*h*]naphthalene and Tetracyano-*p*-quinodimethane (TCNQ). To a hot saturated solution of **7a** (50 mL) in *o*-xylene was added a hot saturated solution of TCNQ in *o*-xylene (50 mL). The mixture was left for slow cooling overnight. The crystals were collected by filtration and washed with small amounts of xylene and dried. IR (KBr) 2221 cm^{-1} (CN). Anal. Calcd for C$_{30}$H$_{12}$N$_4$S$_4$: C, 64.74; H, 2.16; N, 10.06; S, 23.04. Found: C, 64.80; H, 2.21; N, 10.04; S, 22.96.

JO960022X

(47) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallography Deposition Center. The coordinates, bond distances and angles, and thermal parameters can be obtained, on request, from the Director, Cambridge Crystallography Deposition Center, 12 Union Road, Cambridge CB2 1EZ, UK.