Studies on Heteropentalenes. IV.[1] Heteroannelations to Pyrrolo-[2,1-*b*]benzothiazole and Pyrrolo[2,1-*b*]thiazoles

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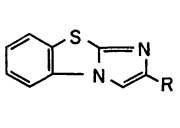
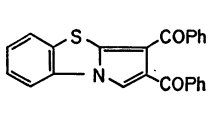
2,3-Dibenzoylpyrrolo[2,1-*b*]benzothiazole (**2**) and 6,7-dibenzoylpyrrolo[2,1-*b*]thiazoles (**5a**—**b**) have been synthesized by utilizing the cycloaddition reactions of imidazo[2,1-*b*]benzothiazole and imidazo[2,1-*b*]thiazoles, respectively, with dibenzoylacetylene followed by the elimination of a nitrile from each of the cycloadducts. Heteroannelations to **2** and **5** have been achieved by their reactions with hydrazine, aminoacetonitrile, ethyl glycinate, and phosphorus pentasulfide. The annelations by the second and third reagents proceed fairly regioselectively. Facile dimerizations of thieno[3′,4′:3,4]pyrrolo[2,1-*b*]benzothiazole and thieno[3′,4′:3,4]-pyrrolo[2,1-*b*]thiazoles to be produced by the reactions with the last reagent are also described.

We have recently disclosed that the cycloadditions of imidazo[2,1-*b*]benzothiazole (**1a**) and imidazo[2,1-*b*]thiazoles (**4a**—**c**), respectively, with dimethyl acetylenedicarboxylate (DMAD),[2] but not with methyl propiolate,[1] are accompanied by the elimination of a nitrile from the adduct to form pyrrolo[2,1-*b*]benzothiazole and pyrrolo[2,1-*b*]thiazole ring systems. It is now reported that the reactions of dibenzoylacetylene (DBA) with the above heteropentalenes are similar to those of DMAD and that the products thereof, like other 1,2-dibenzoly-substituted aromatics,[3–7] readily undergo heteroannelations.

2,3-Dibenzoylpyrrolo[2,1-*b*]benzothiazole (**2**) and 6,7-dibenzoylpyrrolo[2,1-b]thiazoles (**5a**—**b**) were obtained in moderate to good yields from the reactions of **1a**—**b** and **4a**—**c**, respectively, with DBA in xylene. Their structures were proved by elemental analyses, and ^{1}H NMR and IR spectral data, the latter of which, in common with the spectra of diaryl ketones, possessed a ν(C=O) band at 1630—1650 cm^{-1}. Reactions of **2** and **5a**, respectively, with hydrazine gave 1,4-diphenylpyridazino[4′,5′:3,4]pyrrolo[2,1-*b*]benzothiazole (**3**) and 3-methyl-6,9-diphenylthiazolo[3′,2′:1,2]pyrrolo[3,4-*d*]pyridine (**6**) in exellent yields.



1a: R = Me
1b: R = Ph



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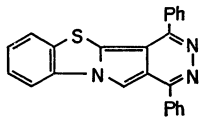
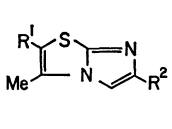
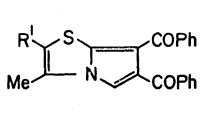


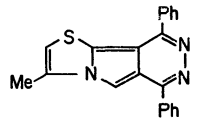
3



4a: R^1 = H, R^2 = Ph
4b: R^1 = H, R^2 = t-Bu
4c: R^1 = CO$_2$Et, R^2 = Ph



5a: R^1 = H
5b: R^1 = CO$_2$Et



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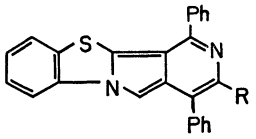
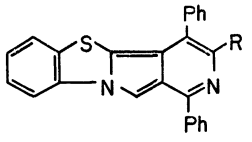
When **2** was heated under reflux with cyanomethylammonium hydrogensulfate in 1-butanol, a fluorescent yellow 5:1 mixture of **7a** and **8a** was obtained in almost quantitative yield, among which **7a** could be isolated by careful fractional crystallizations; separation of the products from the above mixture by means of chromatography was not successful and resulted in gradual discoloration on contact with silica gel or alumina. The structure of **7a** was assigned as 1,4-diphenylpyrido[3′,4′:3,4]pyrrolo[2,1-*b*]benzothiazole-3-carbonitrile on the basis of elemental analyses and spectral data. Whilst the ^{1}H NMR spectrum of **7a** displays a 1H singlet at δ 7.93 assignable to a H-5 proton, the spectrum of the above mixture has an additional singlet at δ 8.30 which we assign to an H-5 proton of **8a**. The H-5 proton of **7a** appears at higher field than that of **8a**; shielding by 4-Ph of **7a** will most probably result from the steric repulsion with the 3-CN group.

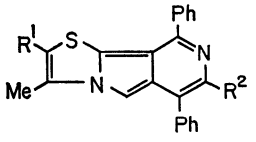
Likewise, **2** yielded **7b** upon reaction with ethyl glycinate hydrochloride, whose ^{1}H NMR spectrum exhibited an ester methyl singlet at δ 0.97, its higher field shift compared to that of common ethyl esters being also attributed to the shielding effect of the 4-Ph. The material before recrystallizations had a broad range of mp (140—152 °C), and its ^{1}H NMR spectral peaks were not satisfactorily integrated. Although there was only a singlet around δ 8.0, we tentatively conclude from the foregoing observations that **8b** may have been formed in addition to **7b** in the reaction.



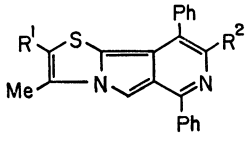
7a: R = CN
7b: R = CO$_2$Et



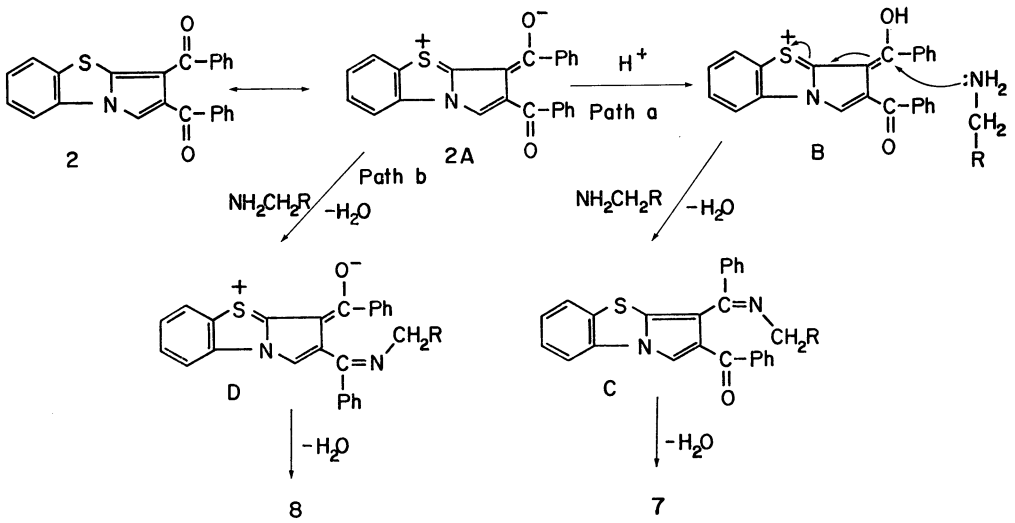
8a: R = CN
8b: R = CO$_2$Et



9a: R^1 = H, R^2 = CN
9b: R^1 = CO$_2$Et, R^2 = CN
9c: R^1 = H, R^2 = CO$_2$Et
9d: R^1 = R^2 = CO$_2$Et



10a: R^1 = H, R^2 = CN
10b: R^1 = CO$_2$Et, R^2 = CN
10c: R^1 = H, R^2 = CO$_2$Et
10d: R^1 = R^2 = CO$_2$Et

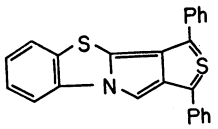


Scheme 1.

The reaction of **5a** with cyanomethylammonium hydrogensulfate gave a 6:1 mixture of 3-methyl-6,9-diphenylthiazolo[3′,2′:1,2]pyrrolo[3,4-*c*]pyridine-7-carbonitrile (**9a**) and its isomer (**10a**), as evidenced by the presence of two singlets at δ 7.93 and 8.47 in the ^{1}H NMR spectrum of the product before recrystallizations. However, the H-9 proton of each of **10b—d** was not discerned probably due to the overlap with aromatic protons in each of the ^{1}H NMR spectra of the products derived from **5b** and aminoacetonitrile or from **5a—b** and ethyl glycinate.

It may be concluded that heterocyclizations of **2** or **5** are fairly regioselective. Plausible mechanisms leading to **7** or **9** are shown in Scheme 1. Preferential attack of a proton on the carbonyl group at C-3 takes place by virtue of conjugation involving the sulfur 3d orbital (**2A**) to give an intermediate **B**, which undergoes a nucleophilic attack by an amine to form a Schiff base **C** followed by loss of water to produce **7** (Path a). Alternatively, if the amine directly attacks the carbonyl group at C-2 of **2A**, dehydration of a Schiff base **D** thereby produced would lead to **8** (Path b). Under the acidic conditions, the Path a is obviously favored and, in fact, when the reaction was effected in the presence of a base (NaOEt or DBU), an inseparable mixture of products was obtained.

Annelation of thiophene ring to **2** was achieved by its reaction in short period with phosphorus pentasulfide in pyridine followed by the rapid quenching of the reaction mixture with water. 1,3-Diphenylthieno[3′,4′:3,4]pyrrolo[2,1-*b*]benzothiazole (**11**) thus



11

prepared, though not analyzed because of its hygroscopic property, showed an M^+ ion at *m/e* 381 (rel intensity 63%, base peak *m/e* 175) and M^{2+} ion at *m/e* 190.5 (6%), and had a λ_{max} absorption at 620 nm (log ε 2.11). IR and ^{1}H NMR spectra of **11** are also in keeping with the structure proposed.[8] The compound **11**, when heated in acetone or xylene, readily changed to a dimer **12**,[8,9] which is independently obtained from the reaction of **2** with phosphorus pentasulfide in boiling xylene. It has an M^+ ion at *m/e* 762 in its mass spectrum and displays a 2H singlet at δ 5.78 and a multiplet at δ 7.25—8.25 corresponding to 28 aromatic protons in its ^{1}H NMR spectrum. The reactions of **5a** and **5b**, respectively, with phosphorus pentasulfide in pyridine produced dimers alone, whose ^{1}H NMR spectra were very simple in keeping with their symmetrical structures.

Experimental

Melting points were uncorrected. IR spectra were recorded for Nujol mulls and ^{1}H NMR spectra with either of a Hitachi R-24B spectrometer at 60 MHz or a JEOL FX-100 spectrometer at 100 MHz (Me_4Si as internal standard). Mass spectra were determined with a Hitachi M-80 instrument by means of electron impact or field desorption ionization methods. Chromatography was performed on Kieselgel 60. Yields are based on consumed starting materials. Imidazo[2,1-*b*]benzothiazole (**1a**) and imidazo[2,1-*b*]thiazoles (**4a—c**) were prepared as described in the previous paper[2] and imidazo[2,1-*b*]benzothiazole (**1b**) was prepared according to the literature.[10]

*Reactions of **1a—b** and **4a—c** with DBA. General Procedure*: A mixture of **1** or **4** (0.005 mol) and DBA (0.015 mol) in xylene (30 ml) was heated under reflux for 5—24 h and then evaporated to dryness under reduced pressure. The residue was chromatographed with benzene. Thus, **1a** and **1b** gave **2** (47 and 81% yield respectively), **4a** and **4b** gave **5a** (47 and 52% yield, respectively), and **4c** gave **5b** (90% yield), respectively.

2: Colorless prisms (from EtOH), mp 209—210 °C, λ_{max} (EtOH) 250 nm (log ε 4.49), 285^{sh} (4.21), 335 (4.06). IR 1640 and 1630 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$) δ= 7.1—8.0 (14H, m, phenyl and H-5,6,7,8), 7.95 (1H, s, H-1). Found: C, 75.34; H, 3.98; N, 3.82; S, 8.58%. Calcd for $C_{24}H_{15}NO_2S$: C, 75.57; H, 3.96; N, 3.67; S, 8.40%.

5a: Colorless prisms (from EtOH), mp 137—138 °C,

λ_{max} ($CHCl_3$) 254 nm (log ε 4.49), 344 (4.08). IR 1650 and 1640 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ=2.74 (3H, d, J=1 Hz, Me), 6.62 (1H, q, J=1 Hz, H-2), 7.0—7.7 (10H, m, phenyl), 7.47 (1H, s, H-5). Found: C, 73.27; H, 4.25; N, 4.20; S, 9.21%. Calcd for $C_{21}H_{15}NO_2S$: C, 73.02; H, 4.38; N, 4.06; S, 9.28%.

5b: Colorless needles (from EtOH), mp 157—158 °C, λ_{max} (EtOH) 252^{sh} nm (log ε 4.42), 262 (4.42), 335 (4.11). IR 1710 and 1640 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ=1.45 (3H, t, J=7 Hz, Me), 2.85 (3H, s, Me), 4.45 (2H, q, J=7 Hz, CH_2), 7.1—7.75 (10H, m, phenyl), 7.60 (1H, s, H-5). Found: C, 68.94; H, 4.56; N, 3.36; S, 7.83%. Calcd for $C_{24}H_{19}NO_4S$: C, 69.05; H, 4.59; N, 3.36; S, 7.68%.

Reaction of ***2*** *with Hydrazine Hydrate.* A mixture of **2** (0.20 g) and 100% hydrazine hydrate (10 ml) in EtOH (30 ml) was heated under reflux for 2 h and then diluted with water to precipitate pyridazine **3** (0.189 g, 96% yield).

3: Yellow needles (from aq EtOH), mp 252—253 °C, λ_{max} ($CHCl_3$) 272 nm (log ε 4.62), 403 (3.87). IR 700 cm^{-1} (phenyl). ^1H NMR (DMSO-d_6) δ=7.4—8.2 (12H, m, phenyl and H-7,8), 8.4—8.6 (2H, m, H-6,9), 8.97 (1H, s, H-11). Found: C, 76.56; H, 3.79; N, 11.07; S, 8.63%. Calcd for $C_{24}H_{15}N_3S$: C, 76.37; H, 4.01; N, 11.13; S, 8.49%.

Reaction of ***5a*** *with Hydrazine Hydrate.* **6a** was prepared in 91% yield by the reaction of **5a** (0.20 g) and 100% hydrazine hydrate (10 ml) in EtOH (10 ml) as described for **2**.

6a: Yellow needles (from aq EtOH), mp 220—222 °C, λ_{max} ($CHCl_3$) 272 nm (log ε 4.53), 400 (3.92). IR 700 cm^{-1} (phenyl). ^1H NMR (DMSO-d_6) δ=2.62 (3H, d, J=0.5 Hz, Me), 7.38 (1H, q, J=0.5 Hz, H-2), 7.4—7.7 (6H, m, phenyl), 7.8—8.25 (4H, m, phenyl) 8.25 (1H, s, H-5). Found: C, 73.73; H, 4.35; N, 12.31; S, 9.36%. Calcd for $C_{21}H_{15}N_3S$: C, 73.87; H, 4.43; N, 12.31; S, 9.39%.

Reactions of ***2*** *and* ***5*** *with Cyanomethylammonium Hydrogensulfate.* A mixture of **2** (0.20 g) and cyanomethylammonium hydrogensulfate (0.807 g) in 1-butanol (10 ml) was heated under reflux for 6 h and poured into water. The mixture was extracted with $CHCl_3$, washed with dil HCl followed by water, and dried (Na_2SO_4). The extracts were evaporated to dryness and the residue was triturated with ligroine to give a mixture (0.205 g, 97% yield) of **7a** and **8a**, from which **7a** (0.120 g, 57% yield) was obtained by careful fractional crystallizations from EtOH.

7a: Yellow needles (from EtOH), mp 180 °C (dec), λ_{max} ($CHCl_3$) 275 nm (log ε 4.46), 326 (4.08), 420 (3.59), 430^{sh} (3.54). IR 2200 cm^{-1} (CN). ^1H NMR ($CDCl_3$) δ=7.2—8.1 (14H, m, phenyl and H-7,8,9,10), 7.93 (1H, s, H-5). Found: C, 77.83; H, 3.98; N, 10.17; S, 7.75%. Calcd for $C_{26}H_{15}N_3S$: C, 77.78; H, 3.77; N, 10.47; S, 7.99%.

Similarly, **5a** gave a mixture (97% yield) of **9a** and **10a** and **5b** a mixture (84% yield) of **9b** and **10b**. **9a** and **9b**, respectively, were isolated by recrystallizations of the mixture from EtOH.

9a: Yellow needles, mp 242—243 °C, λ_{max} ($CHCl_3$) 285 nm (log ε 4.45), 324 (3.81), 416 (3.86), 430^{sh} (3.80). IR 2200 cm^{-1} (CN). ^1H NMR (DMSO-d_6) δ=2.59 (3H, d, J=1 Hz, Me), 7.45 (1H, q, J=1 Hz, H-2), 7.6—8.1 (10H, m, phenyl), 7.93 (1H, s, H-5). Found: C, 75.69; H, 4.07; N, 11.35; S, 8.86%. Calcd for $C_{23}H_{15}N_3S$: C, 75.59; H, 4.14; N, 11.50; S, 8.77%.

9b: Yellow needles, mp 250—253 °C, λ_{max} ($CHCl_3$), 268^{sh} nm (log ε 4.52), 288 (4.57), 325^{sh} (3.99), 420^{sh} (3.68), 439 (3.78), 461 (3.66). IR 2200 (CN) and 1710 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ=1.39 (3H, t, J=7 Hz, Me), 2.88 (3H, s, Me), 4.38 (2H, q, J=7 Hz, CH_2), 7.4—7.8 (11H, m, phenyl and H-5), 7.85—8.0 (2H, m, phenyl). Found: C, 71.29; H, 4.66; N, 9.63; S, 7.54%. Calcd for $C_{26}H_{19}N_3O_2S$: C, 71.38; H, 4.38; N, 9.60; S, 7.33%.

Reactions of ***2*** *and* ***5*** *with Ethyl Glycinate Hydrochloride.* A mixture of **2** (0.20 g) and ethyl glycinate hydrochloride (0.731 g) in 1-butanol (10 ml) was heated under reflux for 24 h and then poured into water. The organic matter was extracted with ether, and washed with dil HCl followed by water. The dried (Na_2SO_4) extracts were evaporated to dryness. Trituration of the residue with ligroine afforded a mixture (0.220 g, 94% yield) of **7b** and **8b**, from which **7b** (0.138 g, 59% yield) was obtained by careful fractional crystallizations from ligroine.

7b: Yellow needles (from ligroine), mp 149—150 °C, λ_{max} ($CHCl_3$) 280 nm (log ε 4.59), 320^{sh} (4.11), 415 (3.82), 428^{sh} (3.78). IR 1720 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ=0.98 (3H, t, J=7 Hz, Me), 4.14 (2H, q, J=7 Hz, CH_2), 7.1—7.7 (12H, m, phenyl and H-7,8,9,10), 7.50 (1H, s, H-5), 7.8—8.05 (2H, m, phenyl). Found: C, 71.81; H, 4.55; N, 5.59; S, 6.92%; M^+, m/e 448. Calcd for $C_{28}H_{20}N_2O_2S \cdot H_2O$: C, 72.08; H, 4.75; N, 6.00; S, 6.89%. M, 448.

Similarly, **5a** gave a mixture (96% yield) of **9c** and **10c** and **5b** a mixture (76% yield) of **9d** and **10d**, respectively. **9c** and **9d**, respectively, were isolated by recrystallizations of the mixture from ligroine.

9c: Yellow needles (from ligroine), mp 145—148 °C (dec), λ_{max} ($CHCl_3$) 260 nm (log ε 4.33), 315^{sh} (3.88), 410 (3.25). IR 1720 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ=0.97 (3H, t, J=7 Hz, Me), 2.17 (3H, bs, Me), 4.07 (2H, q, J=7 Hz, CH_2), 6.83 (1H, bs, H-2), 7.1—7.6 (8H, m, phenyl), 7.37 (1H, s, H-5), 7.8—8.05 (2H, m, phenyl). Found: C, 69.52; H, 5.13; N, 6.59; S, 7.09%; M^+, m/e 412. Calcd for $C_{25}H_{20}N_2O_2S \cdot H_2O$: C, 69.68; H, 5.15; N, 6.50; S, 7.45%; M, 412.

9d: Yellow needles (from ligroine), mp 92—93 °C, λ_{max} ($CHCl_3$) 265 nm (log ε 4.39), 283^{sh} (4.37), 330^{sh} (3.98), 425^{sh} (3.38), 441 (3.41), 463 (3.31). IR 1720 and 1710 cm^{-1} (C=O). ^1H NMR ($CDCl_3$) δ=0.97 (3H, t, J=7 Hz, Me), 1.27 (3H, t, J=7 Hz, Me), 2.57 (3H, s, Me), 4.10 (2H, q, J=7 Hz, CH_2), 4.27 (2H, q, J=7 Hz, CH_2), 7.1—7.8 (11H, m, phenyl and H-5). Found: C, 66.89; H, 5.14; N, 5.61; S, 6.25%; M^+, m/e 484. Calcd for $C_{28}H_{24}N_2O_4S \cdot H_2O$: C, 66.92; H, 5.21; N, 5.57; S, 6.38%. M, 484.

Reaction of ***2*** *with Phosphorus Pentasulfide. (a)*: A mixture of **2** (0.40 g) and phosphorus pentasulfide (1.17 g) in pyridine (5 ml) was heated under reflux for 10 min under nitrogen and then poured into ice–water (200 ml) containing acetic acid (5 ml) to give green precipitates. They were collected by filtration and recrystallized for several times from pyridine–petroleum ether to give **11** (0.075 g, 19% yield).

11: Hygroscopic green amorphous crystals, mp 120—122 °C (dec), λ_{max} (pyridine) 415^{sh} nm (log ε 2.40), 620 (2.11). IR 760 and 690 cm^{-1} (phenyl). ^1H NMR (pyridine-d_5) δ=7.0—8.2 (15H, m). M^+, m/e 381. Calcd for $C_{24}H_{15}NS_2$: M, 381.

(b): A mixture of **2** (0.10 g) and phosphorus pentasulfide (0.058 g) in xylene (30 ml) was heated under reflux for 50 min under nitrogen and then evaporated to dryness under reduced pressure. The residue was chromatographed with benzene–$CHCl_3$ to give **12** (0.051 g, 51% yield).

12: Yellow needles (from EtOH–$CHCl_3$), mp 182—183 °C, λ_{max} ($CHCl_3$) 287 nm (log ε 4.49). IR 775, 760, and 690 cm^{-1} (phenyl). ^1H NMR (CF_3CO_2D) δ=5.78 (2H, s), 7.25—8.25 (28H, m). Found: C, 75.30; H, 3.81; N, 3.73; S, 17.02%; M^+, m/e 762. Calcd for $C_{48}H_{30}N_2S_4$: C, 75.56; H, 3.96; H, 3.67; S, 16.81%; M, 762.

Dimerization of ***11***. A mixture of **11** (0.40 g) in xylene

(or acetone, 50 ml) was heated under reflux for 1 h under nitrogen and then evaporated to dryness under reduced pressure. The residue was chromatographed with benzene–$CHCl_3$ to give **12** (0.348 g, 87% yield).

Reaction of ***5a*** *with Phosphorus Pentasulfide.* A mixture of **5a** (0.40 g) and phosphorus pentasulfide (1.288 g) in pyridine (5 ml) was heated under reflux for 10 min under nitrogen and then poured into ice–water. Precipitates were collected by filtration, further heated in xylene under reflux for 1 h, and collected by filtration. Recrystallization from MeOH–$CHCl_3$ gave dimer **13a** (0.230 g, 57.5% yield).

13a: Yellow needles, mp 158—159.5 °C, λ_{max} ($CHCl_3$) 302 nm (log ε 4.41), IR 755 and 680 cm^{-1} (phenyl). ^1H NMR (CF_3CO_2D) δ=2.72 (6H, s), 5.57 (2H, s), 7.2—7.8 (22H, m). Found: C, 73.35; H, 4.62; N, 4.01; S, 18.21%; M^+, *m/e* 690. Calcd for $C_{42}H_{30}N_2S_4$: C, 73.43; H, 4.40; N, 4.09; S, 18.09%; M, 690.

Reaction of ***5b*** *with Phosphorus Pentasulfide.* A mixture of **5b** (0.40 g) and phosphorus pentasulfide (0.319 g) in pyridine (5 ml) was heated under reflux for 1 h under nitrogen and then poured into ice–water (200 ml) containing acetic acid 5 ml). Precipitates were collected by filtration, dried, and chromatographed with benzene–$CHCl_3$ to give dimer **13b** (0.262 g, 66% yield).

13b: Colorless micro needles (from benzene–$CHCl_3$), mp 256—257 °C, λ_{max} ($CHCl_3$) 285 nm (log ε 4.40). IR 1715 (C=O) and 770 and 700 cm^{-1} (phenyl). ^1H NMR δ=1.53 (6H, t, J=7 Hz), 2.68 (6H, s), 4.61 (4H, q, J=7 Hz), 6.37 (2H, s), 7.15—7.55 (20H, m). Found: C, 69.04; H, 4.41; N, 3.33; S, 15.20%; M^+, *m/e* 834. Calcd for $C_{48}H_{38}N_2O_4S_4$: C, 69.03; H, 4.59; N, 3.36; S, 15.20%; M, 834.

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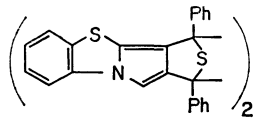
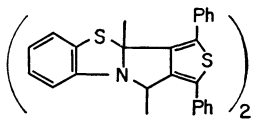
8) To obtain a further confirmative evidence for the structures of **11** and its dimer, each of them was allowed to react with a reactive acetylene (*e.g.* dimethyl acetylenedicarboxylate or dibenzoylacetylene). Unfortunately, an extremely complex mixture was formed from which no product was isolated.

9) Either of the structures **12A** or **12B** appears plausible from the spectral data at hand.



12A



12B

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