Nonclassical Condensed Thiophenes. IV. Derivatives of Thieno[3,4-*c*]furan-S^{IV} and Thieno[3,4-*c*]pyrrole-S^{IV}

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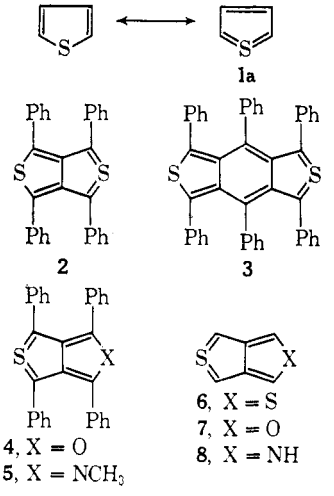
Abstract: Tetraphenyl[3,4-*c*]furan-S^{IV} (**4**) has been generated as a transient intermediate, which could be trapped efficiently by dimethyl acetylenedicarboxylate. In contrast, the red *N*-methyl-1,3,4,6-tetraphenyl[3,4-*c*]pyrrole (**5**) and pentaphenylthieno[3,4-*c*]pyrrole (**22**) have been synthesized and are stable in the solid state. Some simple reactions of the thienopyrrole system are discussed including catalytic reduction, oxidation, and cycloadditions. The results of CNDO/2 calculations for the parent heterocycles thieno[3,4-*c*]thiophene-S^{IV} (**6**), thieno[3,4-*c*]furan-S^{IV} (**7**), and thieno[3,4-*c*]pyrrole-S^{IV} (**8**) are presented and correlated with the observed chemistry of these systems.

Recent theoretical studies suggest that the resonance canonical **1a** does not contribute significantly to the structure of thiophene.[2] It does not necessarily follow, however, that related tetravalent sulfur forms, involving sulfur d orbital participation, may not contribute very significantly to the electronic structure of appropriately condensed thiophene heterocycles. Indeed, the very stable nonclassical thienothiophene **2** and the more reactive, but isolable, benzodithiophene **3** are examples of such systems.[3,4]

In a preliminary communication we reported some aspects of the chemistry of the thienofuran **4** and the thienopyrrole **5**, which are novel analogs of **2** in which



one of the two sulfur atoms is replaced by a nitrogen or an oxygen, respectively.[5,6] We now report details of this work, including new chemistry, as well as the results of a comparative theoretical study of the parent systems thieno[3,4-*c*]thiophene-S^{IV} (**6**), thieno[3,4-*c*]furan-S^{IV} (**7**), and thieno[3,4-*c*]pyrrole-S^{IV} (**8**).

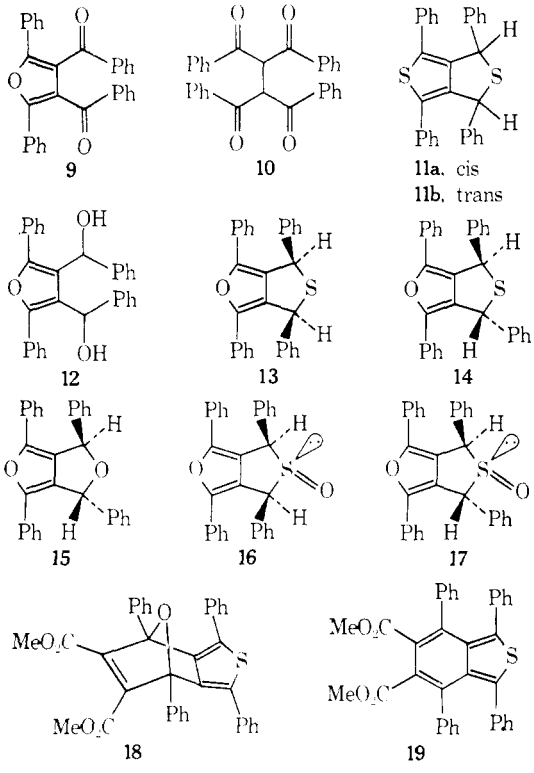
Results

A. Tetraphenylthieno[3,4-*c*]furan-S^{IV} (4). The reaction of phosphorus pentasulfide with 2,5-diphenyl-3,4-dibenzoylfuran (**9**), prepared from the dehydration of *sym*-tetrabenzoylethane (**10**),[7] seemed to offer a direct approach to the synthesis of **4**. However, the reaction of **9** with P_2S_5 in xylene yielded as the only isolable products a mixture of *cis*- and *trans*-dihydrothienothiophenes **11a** and **11b**, products earlier shown to result from the reduction of thienothiophene **2** under similar conditions.[3] Indeed the reaction of **9** with P_2S_5 in pyridine led directly to thienothiophene **2** in high yield.

Diketone **9** was reduced to the corresponding diol **12** which was converted to three products upon treatment with P_2S_5 in carbon disulfide;[8] these were the *cis*- and *trans*-1,3-dihydro-1,3,4,6-tetraphenylthieno[3,4-*c*]-furans (**13** and **14**, respectively) and 1,3-dihydro-1,3,4,6-tetraphenylfurano[3,4-*c*]furan (**15**). The configurations of **13** and **14** were assigned on the basis of the nmr spectra of their sulfoxides.[3,9] Thus, the cis sulfide, **13**, was oxidized by periodate[10] to give the corresponding cis sulfoxide, **16**. The equivalent benzylic protons of **16** appear as a singlet at δ 5.43. The more hindered trans sulfide **15** remained unchanged upon treatment with periodate, but was rapidly oxidized to the corresponding sulfoxide (**17**) by *m*-chloroperbenzoic acid. The trans sulfoxide, **17**, contains nonequivalent benzylic hydrogens which appear as two singlets at δ 5.20 and 5.60. The dihydrofuran, which is probably the trans isomer **15**, could also be obtained by direct acid dehydration of diol **12**.

When sulfoxide **16** was refluxed in acetic anhydride under nitrogen, a violet color appeared due to the development of a visible absorption band at 550 nm. The violet compound could not be identified due to its extreme sensitivity to air and light. The dehydration of **16** or **17** in the presence of dimethyl acetylenedicarboxylate afforded a single adduct **18**. The assigned structure of **18** is supported by its facile loss of oxygen in the

(1) National Institutes of Health Predoctoral Fellow.
(2) D. T. Clark, *Tetrahedron*, **24**, 2663 (1968).
(3) M. P. Cava, M. Behforouz, G. E. M. Husbands, and M. Srinivasan, *J. Amer. Chem. Soc.*, **95**, 2561 (1973).
(4) (a) K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **95**, 2750 (1973); (b) M. P. Cava and M. A. Sprecker, *J. Org. Chem.*, **38**, 3975 (1973).
(5) M. P. Cava and M. A. Sprecker, *J. Amer. Chem. Soc.*, **94**, 6214 (1972).
(6) For examples of other heterocycles containing tetravalent sulfur which have been reported in the literature, see (a) M. P. Cava, N. M. Pollack, and G. A. Dieterle, *J. Amer. Chem. Soc.*, **95**, 2558 (1973); (b) R. H. Schlessinger and I. S. Ponticello, *ibid.*, **89**, 3641 (1967); **90**, 4190 (1968); (c) J. M. Hoffman, Jr., and R. H. Schlessinger, *ibid.*, **91**, 3953 (1969); (d) J. D. Bower and R. H. Schlessinger, *ibid.*, **91**, 6891 (1969); (e) M. Carmack, R. W. Street, and R. Y. Wen, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN-54; (f) K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **94**, 6215 (1972).
(7) A. Andres, Dissertation Strassburg, 1911.
(8) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3073 (1965).
(9) C. Y. Meyers and A. M. Malte, *J. Amer. Chem. Soc.*, **91**, 2123 (1969).
(10) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

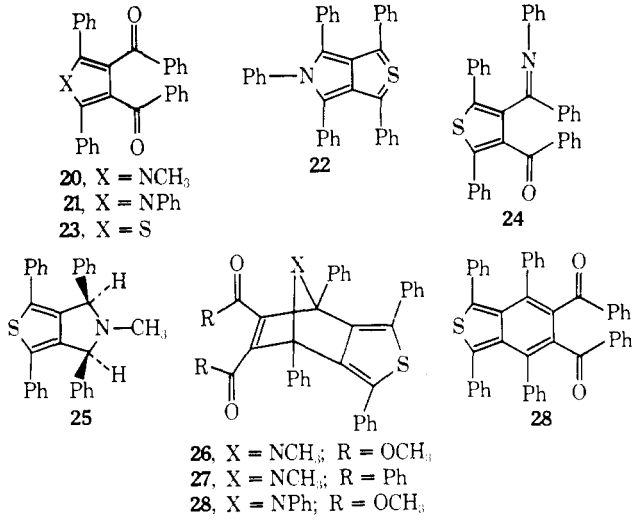


mass spectrometer ($M^+ - 16$, 33%), and was confirmed by the deoxygenation of **18** by hot triethyl phosphite to afford the known isothianaphthene diester **19**.[3] When sulfide **13** was heated in the presence of dimethyl acetylenedicarboxylate under identical conditions, starting material was recovered (90%), indicating that the furan ring of the analogous sulfoxide **16** is not reacting with dimethyl acetylenedicarboxylate as the first step in the formation of **18**. Thus, the formation of **18** from **16** is good evidence for the generation of the thienofuran **4** as a transient intermediate.

Derivatives of 1,3,4,6-Tetraphenylthieno[3,4-*c*]pyrrole (5 and 22). The reaction of tetrabenzoylethane (**10**) with methylamine in acetic acid readily afforded *N*-methyl-2,5-diphenyl-3,4-dibenzoylpyrrole (**20**). Treatment of pyrrole **20** with phosphorus pentasulfide in refluxing toluene gave a purple solution which gradually lost color with the appearance of an amorphous brown gum. Digestion of this material with aqueous sodium hydroxide yielded thienopyrrole **5** as bright red microcrystals, mp 210–214°.[11,12] Attempts to recrystallize this material failed due to its sensitivity to light and air in solution. Solid samples, however, remained stable at room temperature for many months. Unlike thienothiophene **2**,[3] thienopyrrole **5** is insoluble in nonpolar solvents such as hexane and benzene, but is slightly soluble in chloroform and more soluble in alcohol.

It was anticipated that substitution of a phenyl group for the methyl group in thienopyrrole **5** would lead to a less reactive compound which would be amenable to purification. Hence, 1,2,5-triphenyl-3,4-dibenzoylpyrrole (**21**) was prepared by the reaction of **12** with aniline in acetic acid containing a catalytic amount of *p*-toluenesulfonic acid. Diketone **21** reacted with P_2S_5 in xylene affording an amorphous gum, which was hydrolyzed to yield pentaphenylthieno[3,4-*c*]pyrrole-S^{IV} (**22**) as a fine, brick-red powder. This material was sufficiently stable to permit crystallization from hot acetic anhydride, from which it separated as long red needles, mp 212–214°. Compound **22** could be recovered unchanged by evaporation of freshly prepared chloroform solution; such solutions were, however, slowly bleached by air and light. Solutions of both **22** and **5** in aromatic solvents gave no esr signal, indicating singlet ground states for these compounds.

Thienopyrrole **22** was rapidly oxidized by peracetic acid, attack taking place on the pyrrole nucleus to yield a mixture of the known[3,12] thiophene diketone **23** and its mono-*N*-phenylimine **24**. The structure of imine **24** was confirmed by its slow hydrolysis to diketone **23** under acidic conditions.



Compound **22** was surprisingly resistant to reduction by complex hydrides and was recovered unchanged after refluxing with a benzene solution of vitride. However, red solutions of either **5** or **22** were readily decolorized under conditions of catalytic reduction. Preparative hydrogenation of **5** in the presence of palladium led to a single crystalline dihydro derivative, assigned structure **25**. The nmr of **25** showed, in addition to a two proton benzylic singlet at δ 4.70, an aliphatic N–CH_3 signal at δ 2.28, indicating that selective reduction of the pyrrole ring had occurred. The cis stereochemistry of dihydropyrrole **25** is assigned by analogy with the exclusive formation of the cis dihydro derivative (**11a**) of thienothiophene **2** under similar conditions.[3]

Thienopyrrole **5** forms colorless 1:1 cycloadducts with dimethyl acetylenedicarboxylate and dibenzoylacetylene, respectively. Both of these adducts were identified as the substituted thiophenes **26** and **27** on the basis of their shielded nmr absorptions for the *N*-methyl groups and their facile conversion upon treatment with *m*-chloroperbenzoic acid to the known isothianaphthenes **19** and **28**.[13] Thienopyrrole **22** undergoes a more sluggish reaction with dimethyl acetylene-

(11) Subsequent to our original communication, in which **5** was described as a "bright red powder,"[5] other workers have reported a simplified preparation of **5** from **20** which gave **5** as "small brilliant red needles, mp 110–112°."[12] In our hands, material prepared by either procedure was microcrystalline and had mp 210–214°.

(12) K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, **95**, 2749 (1973).

(13) This reaction undoubtedly proceeds by formation of an intermediary *N*-oxide followed by the facile elimination of nitrosomethane or nitrosobenzene. For a closely related decomposition of an aziridine *N*-oxide to an olefin, see J. E. Baldwin, A. K. Bhatnager, Se Chun Choi, and T. J. Shortridge, *J. Amer. Chem. Soc.*, **93**, 4082 (1971).

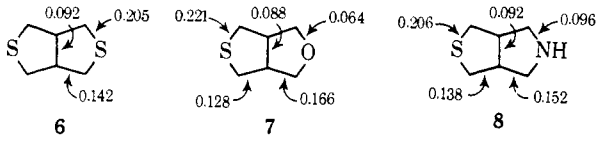


Figure 1. Relative π overlap.

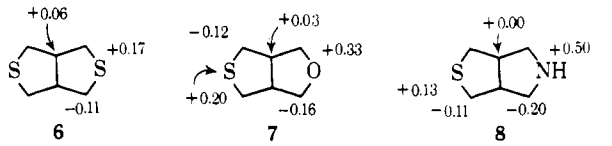
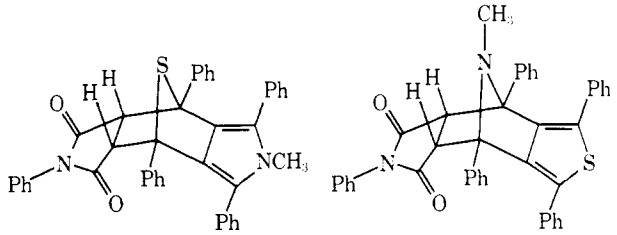
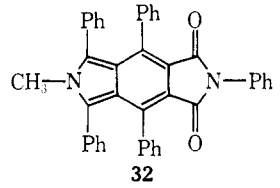


Figure 2. π-Charge densities.

dicarboxylate to afford an analogous product, **29**, which was likewise converted to **19**. Upon melting, these adducts turned red, suggesting that the cycloaddition was reversed at high temperatures.

Thienopyrrole **5** reacted rapidly with *N*-phenylmaleimide (NPM) in refluxing benzene to give, in high yield, a crystalline adduct which was assigned structure **30**. The nmr spectrum of this adduct indicated the presence of an aliphatic *N*-methyl group at δ 2.83, showing that addition had occurred to the pyrrole ring.[14] By contrast, the reaction of **5** with NPM at 180° (*o*-dichlorobenzene) afforded two new products. The minor product was the endo adduct **31** formed by





the addition of NPM to the thiophene nucleus of **5**. Its nmr showed a pyrrole *N*-methyl at δ 3.22 and protons α to the imide carbonyls at δ 5.15, a position indicative of the endo configuration for this type of adduct.[3] The major product, which formed yellow needles, corresponded in composition to the isoindole **32** which was evidently derived from **31** by loss of hydrogen sulfide.[15]

Discussion and Theoretical Results

There have been several earlier calculations reported for the isomeric thienothiophenes[16] and isomeric thienopyrroles.[17] These calculations, which neglect sulfur d orbital participation, predict the nonclassical compounds **6** and **8** to be far less stable than their classically bonded isomers; several of these calculations[16a,17] predict ground state triplet states for **6** and **8**. We decided to examine heterocycles **6–8**, which serve as models for the previously discussed derivatives **4**, **5**, and **22**, using a semiempirical molecular orbital approach, CNDO/2,[18] in which d orbital participation is included.

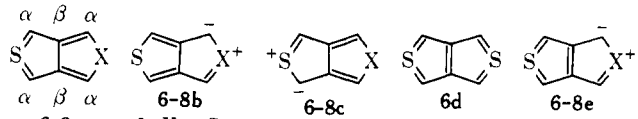
We varied both bond angles and bond lengths to obtain equilibrium geometries. The vertical ionization potentials (Table I), which were found to be comparable

Table I

	Total energy, au	Binding energy, au	First IP, eV	Second IP, eV	Dipole moment, D
6	−67.32	−6.30	9.85	10.67	0.00
7	−74.63	−6.30	8.98	10.82	0.15
8	−68.79	−6.76	8.83	11.46	3.21

to those of naphthalene, were determined by Koopmans' theorem.[19] The π-overlap values[20] (Figure 1) were used to assess relative bond orders. The calculated π-charge densities are shown in Figure 2.

The electronic structures of heterocycles **6–8** can be formally described by assessing the relative importance of uncharged resonance contributors containing tetravalent sulfur (**a**) and mesoionic resonance contributors (**b** and **c**). The contributions of extreme resonance forms (**e**) in which sulfur is tetravalent and the other heteroatom is positively charged, as well as the form **6d** containing two tetravalent sulfurs, are negligible as demonstrated by the low π-overlap values calculated for the β,β bonds in these systems (see Figure 1).



6, X = S
7, X = O
8, X = NH

Compounds **6–8** all exhibit considerable π-bonding between carbon and sulfur of which over half is attributable to $d\pi$–$p\pi$ overlap.

The unsymmetrical compounds **7** and **8** exhibit π-charge separations of greater magnitude than that of the thienothiophene **6**, indicating that dipolar canonicals of the type **b** and **c** contribute more to the electronic structure of **7** and **8** than to the electronic structure of **6**. Furthermore, the degree of charge separation is greater in the furan and pyrrole rings, indicating that the azomethine and carbonyl ylide forms **7b** and **8b** are energetically favored in contrast to the thiocarbonyl ylide

(14) This compound almost certainly has the endo configuration as drawn, by analogy with the almost exclusive formation of an endo adduct from thienothiophene **2** and NPM.[3]

(15) An analogous temperature dependent addition of fumaronitrile to either ring of **5** has been reported very recently.[12]

(16) (a) D. T. Clark, *Tetrahedron*, **24**, 2567 (1968); (b) M. J. S. Dewar and N. Trinajstić, *J. Amer. Chem. Soc.*, **92**, 1453 (1970).

(17) L. Klasinc and N. Trinajstić, *Tetrahedron*, **27**, 4045 (1971).

(18) For the semiempirical CNDO/2 calculation discussed below, we used the computor program CNINDO. This method considers only the valence electrons which are all treated explicitly. All two-electron integrals which depend on the overlap charges between different basis orbitals are neglected. This means that $(\mu\nu/\lambda\sigma)$ is zero unless $\mu = \nu$ and $\lambda = \sigma$. Some one electron integrals are calculated empirically while others are neglected. The zero-differential overlap approximation is adopted for the electron repulsion integrals and the remaining two-electron integrals are replaced by average values. The basis set is Slater-type orbitals with Slater exponents. For details and parameterization, see (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965); (c) D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).

(19) T. A. Koopmans, *Physica*, **1**, 104 (1933).

(20) J. J. Kaufman, *Int. J. Quant. Chem.*, 205 (1971).

forms **7c** and **8c**. The greater stability of the thienopyrroles **5** and **22** relative to thienofuran **4** is not unexpected in view of the greater stability of azomethine ylides as compared to carbonyl ylides.[21]

The relative importance of the canonicals **7b** and **8b** is reflected experimentally in the preferential addition of acetylenic dienophiles to the furan and pyrrole rings of heterocycles **4**, **5**, and **22**. In the case of the reaction of thienopyrrole **5** with NPM, addition to the pyrrole ring is observed at moderate temperatures. In this case, however, formation of the kinetically controlled adduct **30** is reversible at 180° to give rise to the isomeric adduct **31**, in which addition has taken place to the thiophene ring.[15] The reason for the thermodynamic stability of **31** over **30** is not obvious.

Experimental Section

General. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Elemental analyses were made available in the original manuscript and are consistent with the assigned formulas with the limits ±0.30% for compounds **13–17**, **20–22**, **24–27**, and **29–31** and within the limits ±0.40% for compounds **12**, **18**, and **32**. Spectra were recorded on a Perkin-Elmer Model 137 ir spectrophotometer, a Perkin-Elmer Model 202-uv-visible spectrophotometer, a Varian Model A-60A and a Model HA-100D nmr spectrometer, a Perkin-Elmer Model 270B mass spectrometer, and a Varian Model V-4502 esr spectrometer. All ir spectra were taken in KBr. All nmr spectra were taken in $CDCl_3$. All uv spectra were determined in dioxane unless otherwise stated. Recovered starting materials were identified (melting point, ir, and tlc) by comparison with authentic samples.

2,5-Diphenyl-3,4-dibenzoylfuran (9). This compound was made as described in the dissertation of Andres.[7] A dry stream of hydrogen chloride was passed through a hot, stirred solution of *sym*-tetrabenzoylethane (10.0 g) in acetic acid (250 ml) for 1 hr. Addition of water afforded bright yellow needles of **9** (9.1 g, 94%), mp 128° (lit.[7] mp 140°).

Reaction of 9 with Phosphorus Pentasulfide (11a and 11b). A slurry of P_2S_5 (3.0 g) and **9** (3.0 g) in 160 ml of xylene was refluxed with stirring for 2.5 hr. The mixture was filtered and the solution was reduced to a small volume. Column chromatography (neutral I alumina) yielded sulfur (25 mg), mp 111–114°, upon elution with hexane and 1,3-dihydro-1,3,4,6-tetraphenylthieno[3,4-*c*]thiophene (1.607 g, 53%) upon elution with benzene. Fractional crystallization (cyclohexane) yielded the less soluble cis sulfide **11a** as the major component (1.05 g, 35%), mp 197–198°, and the trans sulfide **11b** (0.43 g, 14%), mp 155–156° (lit.[3] mp 153–154°).

1,3,4,6-Tetraphenylthieno[3,4-*c*]thiophene-S^{IV} (2). A solution of **9** (100 mg) and P_2S_5 (300 mg) in dry pyridine (8 ml) was refluxed (N_2) for 4 hr. The deep violet solution was poured into 10% sodium hydroxide solution yielding **2** as violet crystals (100 mg, 96%), mp 225–240° (lit.[3] mp 257–258°).

2,5-Diphenyl-3,4-bis(hydroxybenzyl)furan (12). A solution of sodium borohydride (0.30 g) and 2,5-diphenyl-3,4-dibenzoylfuran (**9**, 1.00 g) in 30 ml of 95% ethanol was digested on the steam bath for 45 min. A solution of 5% sodium hydroxide (150 ml) was added and the resulting slurry was heated for an additional hour. Filtration followed by washing several times with water yielded **12** as a white amorphous powder (0.98 g, 98%), mp 156–160°. The powder could not be crystallized, but was purified by reprecipitation from ethanol and water: ir 3.1 μ (O–H); uv λ_{max} 235 nm (log ε 3.84) and 300 (4.12). *Anal.* Calcd for $C_{30}H_{29}O_3$: C, 83.30; H, 5.60. Found: C, 82.94; H, 5.67.

Treatment of 12 with Phosphorus Pentasulfide (13, 14, and 15). A solution of **12** (3.00 g) and phosphorus pentasulfide (3.0 g) in carbon disulfide (800 ml) was stirred at room temperature for 2 days. The solvent was evaporated and the residues were extracted with two portions of hot chloroform (50 ml). The chloroform extracts were reduced in volume and chromatographed (300 g of neutral I alumina, hexane) to yield three fractions on elution with solutions of increasing concentrations of benzene in hexane. Fraction A yielded *trans*-1,3-dihydro-1,3,4,6-tetraphenylthieno[3,4-*c*]furan (**14**) as fluffy white crystals upon crystallization from cyclohexane (0.74 g, 24%): mp 202–203°; nmr δ 5.89 (s, 2 H) and 7.05–7.50 (m, 20 H); mass spectrum 430 (M^+, 100), 398 (30), 353 (13), 325 (36), 290 (25), 247 (25). *Anal.* Calcd for $C_{30}H_{22}SO$: C, 83.70; H, 5.15; S, 7.43. Found: C, 83.76; H, 5.33; S, 7.16.

Fraction B yielded *cis*-1,3-dihydro-1,3,4,6-tetraphenylthieno-[3,4-*c*]furan (**13**) as white needles from cyclohexane (0.51 g, 19%): mp 244–246°; nmr δ 5.95 (s, 2 H) and 7.18–7.62 (m, 20 H); mass spectrum was identical with that of **14**; uv λ_{max} 241 nm (log ε 4.39), 317 (4.37), 330 (4.42), 347 (4.32). *Anal.* Calcd for $C_{30}H_{22}SO$: C, 83.70; H, 5.15; S, 7.43. Found: C, 83.72; H, 5.09; S, 7.73.

Fraction C yielded 1,3-dihydro-1,3,4,6-tetraphenylfurano[3,4-*c*]-furan (**15**) as white crystals from benzene and hexane (0.835 g, 37%): mp 252–256°; nmr δ 6.21 (s 2 H) and 7.1–7.5 (m, 20 H); mass spectrum 414 (M^+, 100), 337 (17), 309 (66); uv λ_{max} 242 nm (log ε 4.32), 247 sh (4.21), 316 (4.40), 330 (4.48), 347 (4.37). *Anal.* Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.85; H, 5.36.

Compound **15** was also prepared by treating a solution of **12** (100 mg) in tetrahydrofuran (10 ml) with two drops of concentrated H_2SO_4. After heating 5 min on a steam bath, water was added and crystals of **15** were recovered (85 mg, 85%), mp 250–258°.

***cis*-1,3-Dihydro-1,3,4,6-tetraphenylfurano[3,4-*c*]thiophene 2-Oxide (16).** To a solution of **13** (90 mg, 0.2 mmol) in benzene (15 ml) and chloroform (15 ml) was added 1 ml (0.27 mmol) of an aqueous solution of sodium periodate (343 mg dissolved in 5 ml). After stirring and refluxing the two phase solution overnight, the reaction was filtered and evaporated to dryness. The resulting white powder was heated in 20 ml of water on the steam bath. The precipitated powder was filtered and dried. Recrystallization from benzene yielded white crystals of **16** (86 mg, 92%): mp 244–245°; nmr δ 5.43 (s, 2 H) and 7.1–7.5 (m, 20 H); ir 9.5 μ (S=O); mass spectrum 446 (M^+, 12), 430 (21), 398 (100), 321 (39); uv λ_{max} 242 nm (log ε 4.29), 315 (4.33), 330 (4.38), 347 (4.25). *Anal.* Calcd for $C_{30}H_{22}SO_2$: C, 80.70; H, 4.97; S, 7.17. Found: C, 80.57; H, 5.15; S, 7.36.

***trans*-1,3-Dihydro-1,3,4,6-tetraphenylfurano[3,4-*c*]thiophene 2-Oxide (17).** A solution of *m*-chloroperbenzoic acid (47.4 mg, 0.22 mmol (based on 80% purity)) in 2 ml of chloroform was added dropwise to a cooled, stirred solution of **14** (100 mg, 0.22 mmol) in chloroform (10 ml). The reaction was instantaneous (tlc monitoring). The solution was twice extracted with dilute aqueous sodium bicarbonate and dried over sodium sulfate. Evaporation of the solvent yielded a foam which was crystallized from benzene and hexane to yield compact white crystals of **17** (85 mg, 80%): mp 209°; nmr δ 5.21 (s, 1 H), 5.65 (s 1 H), 7.1–7.5 (m, 20 H); ir 9.5 μ (S=O); uv λ_{max} 243 nm (log ε 4.32), 315 (4.34), 329 (4.41), 346 (4.23). *Anal.* Calcd for $C_{30}H_{22}SO_2$: C, 80.70; H, 4.97; S, 7.17. Found: C, 81.00; H, 5.11; S, 7.06.

Adduct with Dimethyl Acetylenedicarboxylate (18). A solution of cis sulfoxide **16** (110 mg, 0.25 mmol) and dimethyl acetylenedicarboxylate (150 mg) was refluxed in 3 ml of acetic anhydride (N_2) for 4 hr. Upon cooling, white needles of **18** separated (41 mg), mp 224–226°. A second crop was recovered by diluting the mother liquor with a small amount of acetic acid (61 mg). Recrystallization from benzene and hexane yielded granular white crystals of **18** (93 mg, 68%): mp 228–230°; nmr δ 3.88 (s, 6 H) and 7.12–7.68 (m, 20 H); ir 5.8 and 5.9 μ (C=O); mass spectrum 570 (M^+, 35), 429 (21), 427 (40), 402 (49), 398 (21), 320 (40); uv λ_{max} 257 nm (log ε 4.19), 296 (4.33), 303 sh (4.30). *Anal.* Calcd for $C_{36}H_{26}SO_5$: C, 75.78; H, 4.59. Found: C, 75.41. H, 4.60.

A solution of trans sulfoxide **17** (50 mg, 0.112 mmol) and dimethyl acetylenedicarboxylate (60 mg), refluxed in 1 ml of acetic anhydride (N_2) for 4 hr, afforded 38 mg (60%) of **18**, mp 228–230°.

Attempted Reaction of 13 with Dimethyl Acetylenedicarboxylate. A solution of **13** (100 mg) and dimethyl acetylenedicarboxylate (150 mg) was refluxed in 3 ml of acetic anhydride (N_2) for 4 hr. No color change was observed. Upon standing overnight, white needles of **13** were recovered (88 mg, 88%).

***N*-Methyl-2,5-diphenyl-3,4-dibenzoylpyrrole (20).** A slurry of tetrabenzoylethane (10.0 g) in 150 ml of a solution of 2% methylamine in acetic acid was refluxed with stirring for 1.5 hr. Upon addition of water to the clean solution, white needles of **20** were recovered in two crops (9.0 g, 90%): mp 198–200°; δ 3.38 (s, 3 H) and 7.1–7.65 (m, 20 H); ir 6.05 and 6.15 μ (C=O); uv λ_{max}^{EtOH} 256 nm (log ε 4.46) and 320 (3.65). *Anal.* Calcd for $C_{31}H_{23}NO_2$: C, 84.33; H, 5.25; N, 3.17. Found: C, 84.13; H, 5.60; N, 3.22.

***N*-Methyl-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole-S^{IV} (5).** A slurry of P_2S_5 (7.0 g) and **20** (7.0 g) was refluxed in toluene for 2 hr. The solvent was evaporated leaving a brown gum. Aqueous sodium hydroxide was added (250 ml, 10% solution) and the slurry was stirred and refluxed for 1 hr. Red microcrystals of **5** were re-

(21) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 2, 565 (1963).

covered by filtering through a sintered glass funnel and washing with water (6.2 g, 88%): mp 210–214°, nmr δ 3.28 (s, 2 H) and 7.0–7.6 (m, 20 H); mass spectrum *m/e* 441 (M^+, 100) and 426 (11); uv λ_{max} 526 nm.

A sample of **5** was also prepared according to the procedure of Potts and McKeough;[12] this material was identical with the material prepared by the method above, and the two samples appeared to be of similar purity and crystallinity.

A benzene solution of **5** exhibited no esr signal at room temperature or at −178°.

1,2,5-Triphenyl-3,4-dibenzoylpyrrole (21). A mixture of tetrabenzoylethane (5 g, 12 mmol), aniline (3 ml), and *p*-toluenesulfonic acid (100 mg) was refluxed in 150 ml of acetic acid for 3 hr. Addition of water yielded pale yellow needles of **21** (3.57 g, 63%). Recrystallization of **21** from benzene yielded colorless needles: mp 252–253°; ir 6.05 and 6.15 μ (C=O); uv λ_{max}^{EtOH} 254 nm (log ε 4.50) and 318 (3.74). *Anal.* Calcd for $C_{36}H_{25}NO_2$: C, 85.86; H, 5.00; N, 2.78. Found: C, 86.03; H, 5.07; N, 3.00.

1,3,4,5,6-Pentaphenylthieno[3,4-*c*]thiophene-S^{IV} (22). A mixture of P_2S_5 (1.5 g) and **21** (1.35 g, 2.68 mmol) in 100 ml of xylene was refluxed with stirring for 2 hr. The solvent was evaporated and the resulting amorphous residue was hydrolyzed by refluxing in 100 ml of 10% sodium hydroxide solution for 1 hr. A brick-red powder (1.1 g, 82%) was collected by filtering through a sintered glass funnel followed by washing with water. The powder was crystallized from acetic anhydride (N_2) to yield red needles of **22** (400 mg, 37% recovery): mp 212–214°; mass spectrum 503 (M^+, 100) and 426 (5); uv $\lambda_{max}^{C_2H_4Cl_2}$ 247 (4.34), 260 (4.35), 345 sh (3.82), 526 (3.86); nmr δ 6.4–6.6, 6.7–7.4, 7.7–7.9 (m). *Anal.* Calcd for $C_{36}H_{25}NS$: C, 85.86; H, 5.17; N, 2.78; S, 6.35. Found: C, 85.79; H, 5.14; N, 2.80; S, 6.45.

A toluene solution of **22** exhibited no esr signal at room temperature or at −178°.

Oxidation of Pentaphenylthieno[3,4-*c*]pyrrole (23 and 24). To a solution of pentaphenylthieno[3,4-*c*]pyrrole (100 mg) in 15 ml of a 1:1 mixture of benzene and methanol was added 5 drops of peracetic acid (40%). The solution was stirred at room temperature for 2 hr. The solvent was evaporated to dryness. The residue was taken up in a small portion of chloroform and separated by ptlc (silica gel, chloroform) to give two major bands. Band 1 (R_f 0.48) afforded 2,5-diphenyl-3,4-dibenzoylthiophene (**23**, 15 mg, 18%).[3] Band 2 (R_f 0.30) afforded 2,5-diphenyl-3-benzoyl-4-(*N*-phenyliminobenzyl)thiophene (**24**, 41 mg, 41%): mp 152–153°; nmr δ 6.4–6.6, 6.8–7.4, 7.7–7.9 (m); uv λ_{max} 247 nm sh (log ε 4.28), 264 (4.30), 278 sh (4.26), 335 (3.88); ir 6.1 μ (C=O). *Anal.* Calcd for $C_{36}H_{25}NSO$: C, 83.21; H, 4.85; N, 2.70; S, 6.16. Found: C, 82.98; H, 4.87; N, 2.57; S, 6.18.

2,5-Diphenyl-3,4-dibenzoylthiophene (23). A solution of **24** (50 mg) in a mixture of acetic acid (5 ml), water (1 ml), and concentrated HCl (4 drops) was heated 3 days on a steam bath. The reaction mixture was cooled and partitioned between chloroform and aqueous sodium bicarbonate. The chloroform layer was twice extracted with water and dried over sodium sulfate. Ptlc (silica, chloroform) separation yielded **23** (22 mg, 39%), mp 134–139° (lit.[3] mp 142–143°).

4,6-Dihydro-1,3,4,6-tetraphenylthieno[3,4-*c*]pyrrole (25). A mixture of **5** (150 mg) and 10% Pd/C (750 mg) in 100 ml of 1:3 ethanol–benzene solution was hydrogenated at 25° (1 atm). Decolorization was rapid. Filtration and evaporation of the solvent followed by crystallization (benzene–hexane) yielded **25** as colorless prisms (65 mg, 43%): mp 219–220°; nmr δ 2.28 (s, 3 H), 4.70 (s, 2 H), 6.9–7.4 (20 H, m); uv λ_{max} 245 nm sh (log ε 5.24), 313 (5.27). *Anal.* Calcd for $C_{31}H_{25}NS$: C, 83.95; H, 5.68; N, 3.16. Found: C, 83.91; H, 5.83; N, 3.20.

Adduct of 5 with Dimethyl Acetylenedicarboxylate (26). A solution of **5** (4.20 g, 9.52 mmol) and dimethyl acetylenedicarboxylate (2 g, 14 mmol) in 200 ml of chloroform was heated on a steam bath for 30 min. The solution was slowly evaporated to dryness and the residues were triturated with methanol (50 ml). After heating for 5 min, the precipitated white powder was filtered, mp 246–248°. Recrystallization from a mixture of benzene and hexane yielded **26** as white crystals (5.15 g, 2 crops, 93%): mp 248°; nmr δ 1.74 (s, 3 H), 3.90 (s, 6 H), 7.1–7.5 (m, 20 H); mass spectrum 583 (M^+, 82), 554 (25), 523 (100), 465 (12), 441 (56), 426 (12); uv λ_{max} 246 nm (log ε 4.27), 295 (4.36), 302 sh (4.35); ir 5.85 μ (C=O). *Anal.* Calcd for $C_{37}H_{29}NSO_4$: C, 76.14; H, 5.01; N, 2.40; S, 5.48. Found: C, 76.04; H, 5.13; N, 2.38; S, 5.45.

Adduct of 5 with Dibenzoylacetylene (27). A solution of **5** (1.00 g, 2.33 mmol) and dibenzoylacetylene (590 mg, 2.50 mmol) in 110 ml of toluene was refluxed (N_2) for 3 hr. Evaporation of the solvent afforded a residue which yielded colorless crystals of **27** upon crystallization from benzene and hexane: mp 146–148°; nmr δ 2.1 (s, 3 H) and 7.0–7.1 (m, 20 H); ir 6.05 and 6.1 μ (C=O); uv λ_{max} 238 nm (log ε 4.63), 264 (4.40), 290 (4.30). *Anal.* Calcd for $C_{47}H_{33}NSO_2$: C, 83.53; H, 4.92; N 2.07; S, 4.74. Found: C, 83.29; H, 5.20; N, 1.83; S, 4.74.

Adduct of 22 with Dimethyl Acetylenedicarboxylate (29). A solution of pentaphenylthieno[3,4-*c*]pyrrole (100 mg, 0.2 mmol) and dimethyl acetylenedicarboxylate (150 mg, 10 mmol) in 10 ml of toluene was refluxed (N_2) for 2 hr. The solution was evaporated to dryness and the residue yielded colorless prisms of **28** upon crystallization from a mixture of benzene and hexane (100 mg, 78%). An analytical sample was obtained from one further recrystallization: mp 221–222°, nmr δ 3.88 (s, 6 H) and 6.7–7.4 (m, 30 H); ir 5.9 μ (C=O); uv λ_{max} 255 nm (log ε 4.21) and 283 (4.26); mass spectrum 645 (M^+, 80), 615 (5), 588 (23), 554 (19), 527 (12), 503 (25), 483 (100). *Anal.* Calcd for $C_{42}H_{31}NSO_4$: C, 78.12; H, 4.84; N, 2.17; S, 4.96. Found: C, 78.25; H, 5.04; N, 1.90; S, 4.74.

Dimethyl-1,3,4,7-tetraphenylisothianaphthene-5,6-dicarboxylate (19). A. From Adduct 18. Thienofuran adduct **18** (15 mg) was heated with 0.5 ml of triethyl phosphite (N_2) at 140°. The triethyl phosphite was removed *in vacuo*. The residue was taken up in a small portion of chloroform and chromatographed (silica gel, ptlc, chloroform). A bright yellow fluorescent band yielded **19** as a yellow solid (7 mg, 42%), mp 257–260° (hot stage) (lit.[3] mp 255°).

B. From Adduct 26. A solution of *m*-chloroperbenzoic acid (72 mg, 0.35 mmol, 85% pure) in chloroform (2 ml) was added to a solution of *N*-methylthienopyrrole adduct **26** (220 mg, 0.34 mmol) in chloroform (25 ml). After heating on a steam bath for 15 min, the yellow fluorescent solution was washed twice with aqueous sodium bicarbonate, dried over sodium sulfate, and evaporated to dryness. Crystallization from benzene yielded fluorescent yellow needles of **19** (175 mg, 92.5%) in two crops, mp 254–255°.

C. From Adduct 29. A solution of *m*-chloroperbenzoic acid (6 mg, 0.33 mmol) in chloroform (1 ml) was added to a solution of *N*-phenylthienopyrrole adduct **29** (18 mg, 0.03 mmol) in 5 ml of chloroform. The reaction was worked up as above yielding **19** as a yellow solid (13 mg, 84%, mp 247–250°.

1,2,4,7-Tetraphenyl-5,6-dibenzoylisothianaphthene (28). A solution of adduct **27** (1.0 g, 1.5 mmol) and *m*-chloroperbenzoic acid (336 mg, 1.8 mmol) was dissolved in 20 ml of chloroform. The solution was heated on a steam bath for 15 min and then extracted twice with aqueous sodium bicarbonate, dried over sodium sulfate, and evaporated to dryness. Crystallization from benzene–hexane yielded yellow needles of **28** (0.86 g (3 crops), 90%), mp 296–297° (lit.[4b] mp 296–297°).

Adduct 30 from 5 and *N*-Phenylmaleimide at 80°. A solution of **5** (200 mg, 0.45 mmol) and NPM (80 mg, 0.45 mmol) in 10 ml of benzene was refluxed (N_2) 10 min. Evaporation of the solvent and crystallization of the residue yielded **30** as colorless plates (210 mg, 75%): mp 247–248°; nmr δ 2.83 (s, 3 H), 4.68 (s, 2 H), 6.8–7.3 (m, 20 H), 7.6–7.8 (m, 5 H); uv λ_{max} 235 nm sh (log ε 5.23) and 295 (5.22). *Anal.* Calcd for $C_{41}H_{30}N_2SO_2$: C, 80.10; H, 4.92; N, 4.56. Found: C, 80.03; H, 5.18; N, 4.43.

Adduct 31 and Compound 32 from *N*-Phenylmaleimide at 180° A solution of **5** (200 mg, 0.45 mmol) and NPM (80 mg, 0.45 mmol) in 8 ml of *o*-dichlorobenzene was refluxed (N_2) 6 hr. Distillation of the solvent under reduced pressure and chromatography of the resulting residue (silica gel, ptlc, chloroform) yielded two fractions. The minor fraction yielded **31** as colorless plates upon crystallization from benzene and hexane (20 mg, 7%): mp 233°; nmr δ 3.22 (s, 3 H), 5.15 (s, 2 H), 6.75–7.75 (m, 25 H); ir 5.9 μ (C=O); mass spectrum 614 (M^+, 10), 580 (29), 441 (100), 426 (13); uv λ_{max} 237 nm (log ε 5.26), 265 (4.24), 295 (5.35). *Anal.* Calcd for $C_{41}H_{30}N_2SO_2$: C, 80.10; H, 4.92; N, 4.56; S, 5.22. Found: C, 80.31; H, 5.13; N, 4.39; S, 4.99.

The major fraction yielded **32** as yellow needles from benzene and hexane (195 mg, 74%): mp >320°; ir 5.9 μ (C=O); nmr δ 3.44 (s, 3 H) and 6.9–7.4 (m, 25 H); uv λ_{max} 290 nm (log ε 5.33) and 390 (4.48); mass spectrum 580 (M^+). *Anal.* Calcd for $C_{41}H_{28}N_2O_2$: C, 84.84; H, 4.86. Found: C, 84.48; H, 5.16.

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