

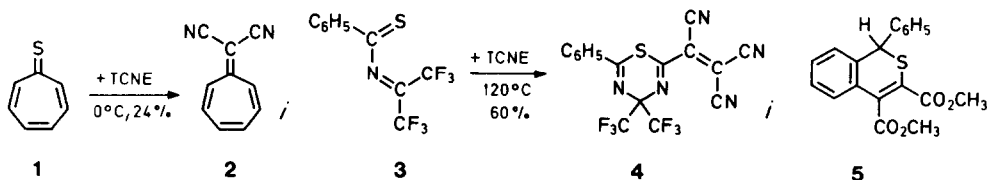
THIOBENZOPHENONE AND TETRACYANOETHYLENE

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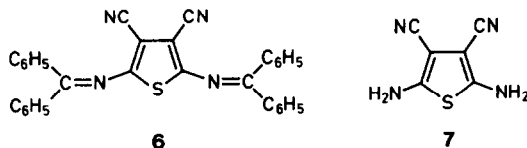
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Summary The title reaction furnished the yellow 3,4-dicyano-2,5-bis(diphenylmethyleneamino)-thiophene and a red precursor which contains one more sulfur atom; structures and mechanism are discussed.

The formation of 8,8-dicyanoheptafulvene (2) from 1 and tetracyanoethylene (TCNE) ¹ may be the result of a (2+2) cycloaddition and cycloreversion, whereas the *N*-thiobenzoyl azomethine 3 adds to the nitrile group of TCNE to give 4 in a Diels-Alder reaction. ² The adduct 5 emerges from thiobenzophenone and dimethyl acetylenedicarboxylate in a (4+2) cycloaddition involving the formal double bond of a phenyl group. ³ Should the interaction of thiobenzophenone with TCNE follow the same pattern ?



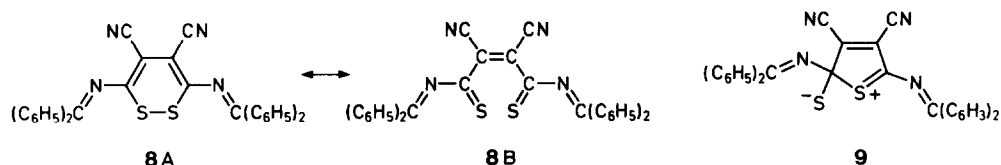
Thiobenzophenone (10 mmol) and TCNE (6.3 mmol) were refluxed in 150 ml chloroform for 8 h. After dilution with 150 ml CCl₄ the reaction mixture was cooled to -20°C: 2.24 mmol (45%) of the yellow 6. From the concentrated mother liquor 1.04 mmol (21%) of the red 8 was obtained. The reaction in refluxing benzene proceeded analogously: 45% 6, 23% 8.



The orange-yellow crystals of 6 (pyridine), mp 309-311°C, accord with C₃₂H₂₀N₄S, ⁴ *i.e.*, a 2:1 product minus S as confirmed by the base peak at *m/e* = 492. The IR spectrum (KBr) showed frequencies at 2228 (st, C≡N) and 1563 cm⁻¹ (st, C=N). The ¹H NMR spectrum (low solubility in CDCl₃) indicates only aromatic

protons. Treatment of 6 with 2,4-dinitrophenylhydrazine in boiling ethanolic sulfuric acid yielded 2.0 equiv of the benzophenone hydrazone. Thus, the two diphenylmethylene groups are still in the same oxidation state as in thiobenzophenone.

The supposed structure of a bis-azomethine 6 of 2,5-diamino-3,4-dicyanothiophene (7) with benzophenone was confirmed by the conversion of 7 into 6 (62% yield) with an excess of thiobenzophenone in refluxing DMF. Diamine 7 was obtained from TCNE and hydrogen sulfide in acetone/pyridine.⁵

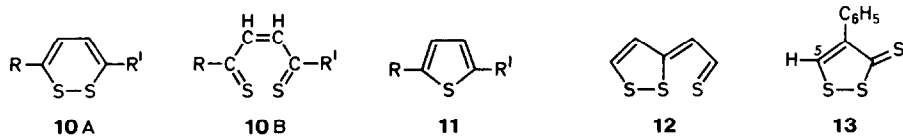


The second product, 8, crystallized from $\text{CH}_2\text{Cl}_2/\text{CCl}_4$ (1:1) in ruby-red prisms which correspond to $\text{C}_{32}\text{H}_{20}\text{N}_4\text{S}_2$, *i.e.*, a 2:1 product from thiobenzophenone and TCNE. The crystals give a dark-brown melt at 202–204°C which solidifies and melts again >290°C (impure 6); some S_8 sublimes. In solution, the conversion 8 → 6 is fast on exposure to sunlight, but slow in the dark at 80°C. The mass spectrum of 8 exhibits $m/e = 492$, *i.e.*, the thiophene 6, as the base peak, and the molecular ion (m/e 524) occurs with 11%.

The ^{13}C NMR spectrum (CDCl_3 , 32°C) of 8 reveals high symmetry: δ 114.5 for 2 $\text{C}\equiv\text{N}$, 156.9 for 2 $\text{C}=\text{N}$, s at 101.0 for 2 olefinic C-atoms, s at 136.6 and d at 132.2, 129.7, 128.7 for 4 C_6H_5 . $\delta_{\text{C}} = 172.7$ for 2 CS is not as high as is observed for thioamides (thiobenzpiperidide 199.6,⁶ thioacetamide 207.2⁷), much less for thioketones (thiobenzophenone 238.5, thiocamphor 269.0⁷).

The light absorption of 8 exhibits a bathochromic shift compared with 6. In CH_2Cl_2 values of λ_{max} (log ϵ) occur at 428 (4.36) and 256 nm (4.47) for 6 and at 509 (3.75), 376 (4.23), and 270 nm (4.46).

The degradation of 8 to 1.7 equiv of benzophenone 2,4-dinitrophenylhydrazone underlines the structural relation to 6. The unsaturated cyclic disulfide 8A and the dicyanomaleic bis(thioamide) 8B are reasonable candidates for the 2:1 product. In contrast to the corresponding *trans* compound with respect to the central CC bond, 8B provides a good pathway for the conversion 8 → 6. 1,5-Electro-

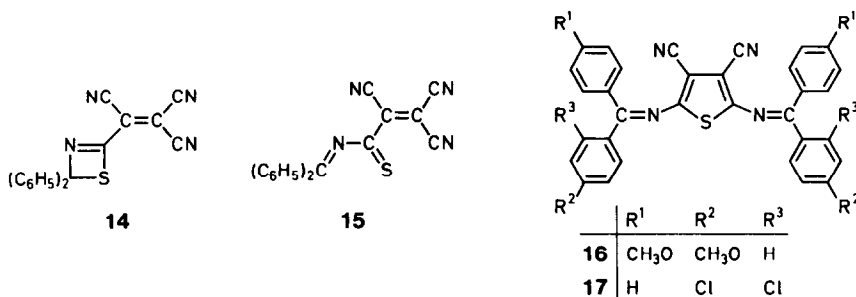


$\text{R} = \text{CH}_3(\text{C}\equiv\text{C})_n-$, $\text{R}' = (\text{C}\equiv\text{C})_m\text{CH}=\text{CH}_2$, $n, m = 1, 2$

cyclization of 8B gives rise to the zwitterion 9 which extrudes the exocyclic sulfur forming the aromatic thiophene 6. Such 1,5 electrocyclic ring closures are frequent among hetero-1,3,5-hexatriene systems as pointed out by George, Mitra and Sukumaran.⁸

The structural problem which we are facing with 8 has emerged in natural product chemistry, too. Among the polyacetylenic constituents of *Compositae*, Sørensen⁹ and Bohlmann¹⁰ found red S₂ compounds 10 which undergo thermal or photochemical conversion to the thiophenes 11. Bohlmann and Kleine¹⁰ discussed a tautomeric equilibrium, 10A \rightleftharpoons 10B, as well as a resonance hybrid, 10A \leftrightarrow 10B. The reference to the "no bond resonance" or "meribicyclo mesomerism" of thiathioptenes 12¹¹ is pertinent.

In our example $\delta_C = 172.7$ for CS is too low for 8B and too high for the dithiin 8A; e.g., δ 154.1 for C-5 of the aromatic dithiole-3-thione 13 was reported.¹² The long-wave light absorption would be improbable for the dithiin 8A. A resonance hybrid, 8A \leftrightarrow 8B, may be tentatively proposed.



How are 8 and 6 formed from thiobenzophenone and TCNE? A (2+2) cycloaddition to the activated nitrile group, probably step-wise, yields the 2H-1,3-thiazete derivative 14. The electrocyclic ring opening to give 15 finds a precedent in the formation of 3 from the corresponding 1,3-thiazete - the latter being the stable tautomer in the special case.² More difficult to interpret is the selection of the *cis-vic*-CN group of 14 for the second sequence of cycloaddition and ring-opening affording 8. It may be conceived that these steps are reversible and that the resonance energy of 8A \leftrightarrow 8B is responsible for the final stabilization of the *cis* 2:1 product. The desulfurization 8 \rightarrow 6 is the concluding step. When the thiobenzophenone has been consumed under the conditions described above, the larger portion of 8 has already undergone the sulfur extrusion, probably catalyzed by a constituent of the reaction system.

Analogous reactions of 4,4'-dimethoxythiobenzophenone and 2,4-dichlorothiobenzophenone with TCNE allowed the isolation of only the yellow thiophene derivatives: 16, mp 227-229°C, and 17, mp 298-300°C; xanthione and thioxanthione did not react with TCNE in boiling chloroform. The tetramethoxy compound 16 is better soluble than 6 and permitted the study of a dynamic process which makes the

four aryls equivalent. At 100°C , the ^1H NMR spectrum of 16 in $[\text{D}_6]\text{DMSO}$ shows one CH_3O singlet at δ 3.92 and one well resolved AA'BB' spectrum for four C_6H_4 at 7.03 and 7.35. At 34°C in CDCl_3 , the low-field branch of the AA'BB' system is in the state of coalescence. At -20°C , however, two C_6H_4 appear as AA'BB' at δ 6.89 and 7.74, and the other two C_6H_4 as 8H singlet at 6.96; the four CH_3O groups are represented by two singlets of equal intensity at δ 3.92 and 4.00. The dynamic process is either a rotation about the C=N bond or - more probable ¹³ - an inversion at the nitrogen atom.

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