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Reaction of a Thioaminyl Diradical with 7,7,8,8-Tetracyanoquinodimethane (TCNQ). The Formation of a Cyclophane Compound[1)]

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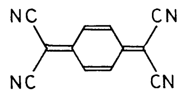
Synopsis. The reactions of thioaminyl mono- (MONOR) and diradicals (DIR) with 7,7,8,8-tetracyanoquinodimethane (TCNQ) have been investigated. The reactions of TCNQ with MONOR gave 1:2 adducts of TCNQ and MONOR in 85—88% yields, while the reaction with DIR afforded either a cyclophane compound (77%), or an alternating polymer of TCNQ and DIR (59 wt%), dependent on the structures of DIR.

7,7,8,8-Tetracyanoquinodimethane (TCNQ), which is a well-known strong electron acceptor, is also subject to free radical addition giving 1,6-adducts. A typical example is provided by the reaction of TCNQ with azobis(isobutyronitrile) yielding a 1:2 adduct of TCNQ and 1-cyano-1-methylethyl radical.[2)]

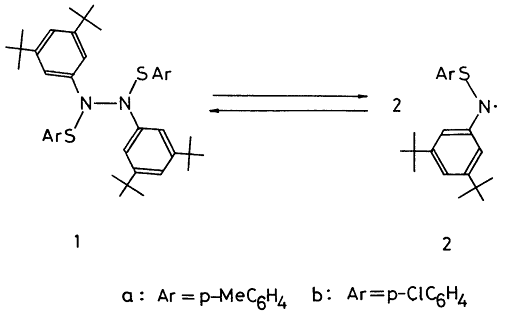


TCNQ

In the course of a study of the reaction of TCNQ with persistent thioaminyl mono- and diradicals, we found that the reaction of TCNQ with a thioaminyl diradical gives a cyclophane compound in a high yield. To our knowledge this is the first example of a cyclophane synthesis by the reaction of TCNQ with diradical, and we thought that such a reaction might be potentially useful as a convenient method for cyclophane syntheses. Herein we wish to report the reaction of TCNQ with thioaminyl diradicals.

Results and Discussion

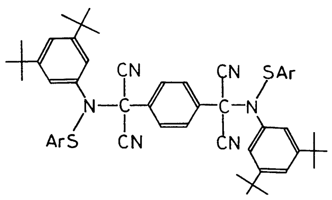
First, the reaction of TCNQ with thioaminyl monoradicals **2** was examined. As previously reported,[3)] **2** can be isolated as the hydrazine-like dimers **1**, which, upon dissolution, dissociate into **2** already at room temperature. Thus, we used **1** as the source of **2**.



1 2

a: Ar = p-MeC$_6$H$_4$ b: Ar=p-ClC$_6$H$_4$

When TCNQ was added to a stirred suspension of **1** in acetonitrile and the stirring was continued under nitrogen, the suspension turned almost homogeneous, and colorless microcrystals of **3** began to deposite. After 4 h stirring, the microcrystals were obtained in 85—87% yields. In the IR spectra of **3** an absorption due to C≡N (very weak) was found at 2200 cm^{-1}. The ^{1}H and ^{13}C NMR spectra, as well as the elemental analyses, established that the compounds are a 1:2 adduct of TCNQ and **1**, represented as **3**.



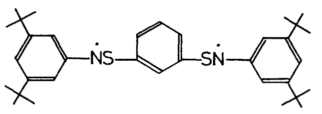
3

a: Ar=p-MeC$_6$H$_4$ b: Ar=p-ClC$_6$H$_4$

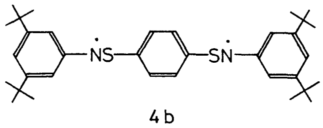
Compounds **3** were found to dissociate into **2** and TCNQ at high temperatures. For example, when a colorless solution of **3a** in benzene was heated to 50 °C, the solution immediately turned blue and the UV and visible spectrum gave $\lambda_{\max}$'s at 603, 400, and 355 nm. An independent experiment showed that the $\lambda_{\max}$'s at 603 and 355 nm are due to **2a** and that at 400 nm due to TCNQ itself. This dissociation was further confirmed by the high temperature ESR measurement of solutions of **3**. When a solution of **3** in benzene was heated to 50 °C, the solution gave a relatively weak and somewhat broad ESR signal whose hyperfine splitting constants (hfsc) were a_N=0.95, a_H=0.36 and 0.42 mT (for the spectrum from a solution of **3a**) and a_N=0.96, a_H=0.37 and 0.44 mT (for the spectrum from a solution of **3b**). On the basis of these hfsc's the spectra were assigned to **2a** and **2b** (for the reported hfsc's for **2a** and **2b**, see: Ref. 3).

The high yield formation of **3** from **2** and TCNQ prompted us to try the reaction of TCNQ with thioaminyl diradicals **4** since that was promisingly expected to give structurally interesting cyclophane or macrocyclic compounds consisting of **4** and TCNQ. As previously reported,[4)] **4** can be isolated as cyclic compounds **5**, which, upon dissolution, dissociate into diradical oligomers already at room temperature. Thus, we used **5** as the source of **4**.

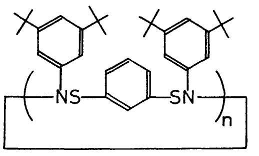
When a mixture of TCNQ and an equiv (in monomer units) of **5a** in benzene was stirred at room temperature for 3 h under nitrogen, cyclophane **7** was obtained in 77% yield. The structure was determined on the basis of the FAB-mass spectrum, the ^{1}H and ^{13}C NMR spectra, and the elemental analyses. The ^{1}H and



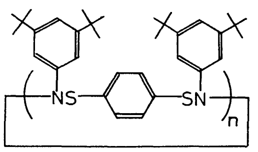
4a



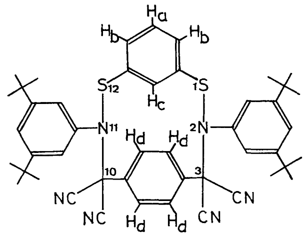
4b



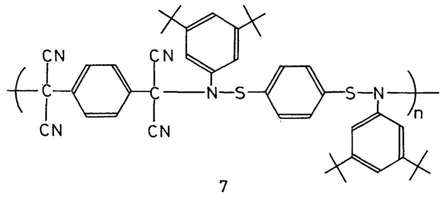
5a



5b



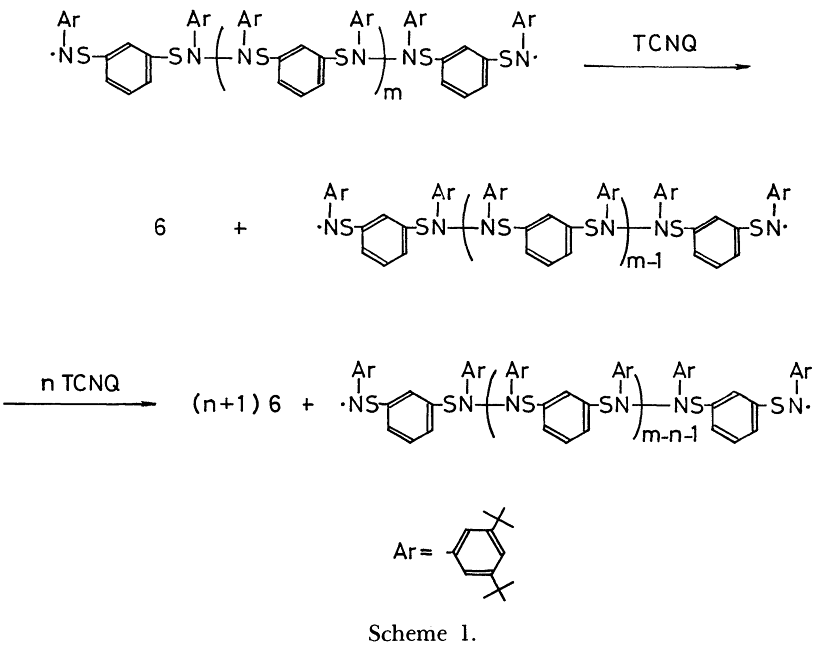
6



7

^{13}C NMR spectra, as well as the elemental analyses, indicated that the molecule is a 1:1 adduct of TCNQ and **4a**, and the FAB-mass spectrum gave an M^{+}+H peak at 751 with a relative intensity of 3%.[5] Accordingly, the compound was identified as cyclophane **6** consisting of one molecule of TCNQ and one molecule of **4a**. We assume that **6** was formed by the mechanism shown in Scheme 1. Cyclophane **6** is relatively unstable in an acidic medium such as $CHCl_3$ and MeOH containing HCl and slowly decomposes.

The reaction of TCNQ with **5b** (at room temperature), however, did not give the corresponding cyclophane compound. Diradical **4a** has a 1,3-dithiabenzene structure, while **4b** has a 1,4-dithiabenzene structure. The TLC analysis of the reaction mixture indicated the formation of a few thermally labile products which readily converted to polymeric compounds during the separation processes. We assume that the thermally labile products are cyclic oligomers consisting of a few TCNQ and **4b** units. When the reaction was carried out at 70 °C, the reaction mixture afforded a yellow polymer in 59 wt% yield. The IR spectrum was similar to those of **3** and the elemental analyses indicated that the polymer consists of a 1:1 composition of TCNQ and **4b**. Thus, we concluded that the polymer is an alternating copolymer of TCNQ and **4b**, represented as **7**.



Scheme 1.

Structurally similar copolymers were reported to be formed by the reaction of *p*-xylene-α,α′-diyl with stable nitroxide diradicals.[6,7] Since **7** was insoluble in ordinary solvents such as benzene, THF, and acetonitrile, the molecular weight could not be determined.

In summary, we found that the reaction of TCNQ with a thioaminyl diradical gives a cyclophane compound in a high yield. The reactions of TCNQ with other persistent free diradicals are also interesting from the viewpoint of cyclophane syntheses. We think that such reactions may be useful as a convenient method for cyclophane syntheses.

Experimental

The melting points were taken on a Yanagimoto micro melting point apparatus and are uncorrected. The IR and UV-visible spectra were run on a JASCO A-202 or Shimadzu UV-240 spectrophotometer, respectively. The ^{1}H NMR spectra were recorded with a JEOL PS-100 (100 MHz) or JEOL GX-400 spectrometer (400 MHz) and the ^{13}C NMR spectra were measured with a JEOL FX-100 spectrometer (25.05 MHz). The chemical shifts are expressed in ppm values (δ) using TMS as an internal standard. The FAB-mass spectrum was taken on a JEOL JMS-HX100 instrument, equipped with the standard FAB source (xenon, 5 kV), using 3-mercapto-1,2-propanediol matrix. The ESR spectra were recorded on a JEOL JES-ME-3X spectrometer.

Dimers **1** and cyclic compounds **5** were prepared by our previously reported methods.[3,4] 7,7,8,8-Tetracyanoquinodimethane (TCNQ) was purified by crystallization (acetonitrile) and subsequent sublimation.

Reaction of 1 with TCNQ. A suspension of **1** (0.20 mmol) in acetonitrile (20 ml) was stirred at room temperature for 30 min under nitrogen. To the suspension (blue) were added crystals of TCNQ (49 mg, 0.24 mmol) in one portion, and the mixture was stirred at room temperature for 3 h under nitrogen. During this time the mixture became almost homogeneous and microcrystals began to deposite. The crystals were collected by filtration, washed with hexane, and dried in vacuo.

α,α′-Bis[*N*-(*p*-tolylthio)-3,5-di-*t*-butylanilino]-*p*-phenylenedimalononitrile (3a): Yield 87% (149 mg); colorless needles (from hexane); mp 181—183 °C (decomp); IR (KBr) 2950—2850 (*t*-Bu), 2200 cm^{-1} (CN); ^{1}H NMR (CDCl$_3$) δ=1.23 (s, *t*-Bu, 36H), 2.32 (s, Me, 6H), 6.98—7.51 (m, aromatic, 18H). ^{13}C NMR (CDCl$_3$) 21.4 (Me), 31.3 ($\underline{\mathrm{Me}}_3$C), 35.6 (Me$_3\underline{\mathrm{C}}$), 65.8 [(CN)$_2\underline{\mathrm{C}}$], 113.4 (CN), 121.9, 122.0, 128.6, 129.8, 130.9, 132.8, 135.0, 139.9, 145.7, 152.2. Found: C, 75.64; H, 7.30; N, 9.50%. Calcd for $C_{54}H_{60}N_6S_2$: C, 75.66; H, 7.05; N, 9.80%.

α,α′-Bis[*N*-(4-chlorophenylthio)-3,5-di-*t*-butylanilino]-*p*-phenylenedimalononitrile (3b): Yield 85% (153 mg); colorless prisms (from hexane); 189—192 °C (decomp); IR (KBr) 2950—2850 (*t*-Bu), 2200 cm^{-1} (CN); ^{1}H NMR (CDCl$_3$) δ=1.20 (s, *t*-Bu, 36H), 6.92—7.54 (m, aromatic, 18H). ^{13}C NMR (CDCl$_3$) δ=31.2 ($\underline{\mathrm{Me}}_3$C), 35.0 (Me$_3\underline{\mathrm{C}}$), 65.9[(CN)$_2\underline{\mathrm{C}}$], 113.1 (CN), 121.8, 128.6, 129.3, 130.7, 134.9, 135.3, 145.1, 152.4. Found: C, 69.78; H, 6.16; N, 9.08%. Calcd for $C_{52}H_{54}Cl_2N_6S_2$: C, 69.50; H, 6.06; N, 9.36%.

Reaction of 5a with TCNQ. A solution of **5a** (70.0 mg, 0.128 mmol of monomer units) in benzene (30 ml) was stirred at room temperature for 10 min under nitrogen. To the blue solution were added crystals of TCNQ (26.1 mg, 0.128 mmol) in one portion, and the resulting yellow suspension was stirred at room temperature for 3 h under nitrogen. During this time the reaction mixture became almost homogeneous. The reaction mixture was then evaporated under reduced pressure and the residual yellow solid was washed with small amounts of acetonitrile, giving **6** as a colorless crystalline solid.

3,3,10,10-Tetracyano-2,11-bis(3,5-di-*t*-butylphenyl)-1,12-dithia-2,11-diaza[3.3]metaparacyclophane (6): Yield 77% (74 mg); colorless prisms (from benzene–hexane); mp 205—207 °C (decomp); IR (KBr) 2950—2850 (*t*-Bu), 2200 cm^{-1} (CN); FAB-MS (relative intensity) 751 (M$^+$+1, 3), 546 [M$^+$ −C(CN)$_2$C$_6$H$_4$(CN)$_2$, 100], 344 (43), 205 (38), 57 (87); ^{1}H NMR (C$_6$D$_6$) δ=1.40 (s, *t*-Bu, 36H), 5.78 (t, *J*=1.7 Hz, H$_c$, 1H), 6.69 (*t*, *J*=7.8 Hz, H$_a$, 1H), 7.15 (s, H$_d$, 4H), 7.31 (dd, *J*=1.7 Hz and 7.8 Hz, H$_b$, 2H) 7.62 (t, *J*=1.7 Hz, *p*-H of the anilino group, 2H), 7.79 (d, *J*=1.7 Hz,*o*-H of the anilino group, 4H). ^{13}C NMR (C$_6$D$_6$)[8] δ=31.4 ($\underline{\mathrm{Me}}_3$C), 35.3 (Me$_3\underline{\mathrm{C}}$), 65.8 [(CN)$_2\underline{\mathrm{C}}$], 113.3 (CN), 121.9, 122.9, 133.4, 134.3, 138.2, 148.9, 153.2. Found: C, 73.77; H, 6.74; N, 10.84%. Calcd for $C_{46}H_{50}N_6S_2$: C, 73.56; H, 6.71; N, 11.19%.

Reaction of 5b with TCNQ. A mixture of **5b** (90.8 mg, 0.166 mmol of monomer units) and TCNQ (34 mg, 0.17 mmol) in benzene (10 ml) was degassed by three freeze-pump-thaw cycles, and sealed in a degassed glass tube. The mixture was then heated to 70 °C for 4 h with shaking. After evaporation under reduced pressure, ca. 20 ml of hexane were added to the residue and the polymeric product deposited was collected, washed with acetonitrile, and dried in vacuo. Yield 74 mg (59 wt%); IR (KBr) 2950—2850 (*t*-Bu), 2200 cm^{-1} (CN). Found: C, 73.30; H, 6.79; N, 11.02%. Calcd for $(C_{46}H_{50}N_6S_2)_n$: C, 73.56; H, 6.71; N, 11.19%.

References

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5) Although we also took an EI-mass spectrum of **6**, an M$^+$ peak could not be detected.

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8) Although, in the ^{13}C NMR spectrum 14 lines are expected to appear, unless some lines overlap, only 11 lines were found, except for intense 3 lines due to the C$_6$D$_6$ NMR solvent (δ 127.0, 127.9, 128.9). We assume that the remaining 3 lines are masked by the lines due to the solvent.