Preparation and Properties of Pyridine-Analogue of TCNQ Dianion Salt

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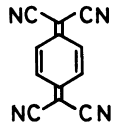
Bis(tetrapropyl- and tetrabutylammonium) 1,1′-(2,5-pyridinediyl)bis[dicyanomethanide] (**4a** and **4b**) were prepared in order to investigate the properties of pyridine-analogue **3** of TCNQ as a new electron acceptor and its complexation with TTF. Although **3** was not isolated, the cyclic voltammetry of the salt **4** indicated that **3** was a stronger electron acceptor than TCNQ. The charge-transfer complex of TTF and **3** was prepared by mixing TTF with **3** which was generated in situ from the electrolytic oxidation of **4** or from the oxidation of 2,5-bis(dicyanomethyl)pyridine, a precursor of **4**, with hydrogen peroxide. It consisted of 1:1 composition of donor and acceptor and showed a high electrical conductivity of 19 S cm^{-1}. The 2:1 complex was prepared by metathesis of $(TTF)_3(BF_4)_2$ and **4**, and also highly conductive.

The pyridine analogue of 7,7,8,8-tetracyanoquinodimethane (TCNQ) (**1**) attracts much attention as a modified electron acceptor with an enhanced electron affinity due to a large electronegativity of the pyridinoid nitrogen. 1-AzoniaTCNQ (**2**) has so far been studied as one example, but exists as an anionic form involving a $\overset{+}{C}$–$\overset{-}{N}$ ylide bond.[1] 2,5-Bis(dicyanomethylene)-2,5-dihydropyridine, so-called 2-azaTCNQ (**3**) is an intriguing candidate for the real pyridine-analogue of TCNQ. We have undertaken the synthesis of **3**, which is, however, not isolated in a neutral state but as its dianion salts **4**. The electrochemical study of **4** provides an information on the acceptor character of neutral **3**. Here we would like to report the preparation and properties of bis(tetrapropyl- and tetrabutylammonium) 1,1′-(2,5-pyridinediyl)bis[dicyanomethanide] (**4a** and **4b**) as well as charge-transfer complexation of **3** and tetrathiafulvalene (TTF).



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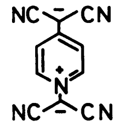

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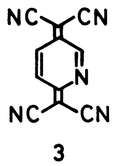

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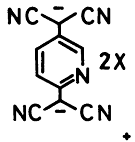
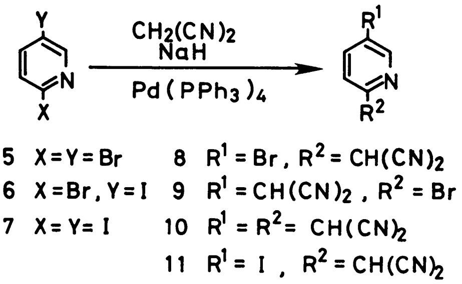


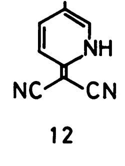
4a, X = $Pr_4\overset{+}{N}$
4b, X = $Bu_4\overset{+}{N}$

Results and Discussion

Recently Takahashi et al. developed a direct synthetic method of 2,2′-(*p*-phenylene)bis[malononitrile] from dihalobenzene and malononitrile anion.[2] We have applied a similar method for the present pyridine case (Scheme 1). First, commercially available 2,5-dibromopyridine (**5**) was treated with malononitrile anion in the presence of tetrakis(triphenylphosphine)palladium(0) as a catalyst in refluxing tetrahydrofuran (THF), giving 5-bromo-2-(dicyanomethyl)pyridine (**8**) as a sole product in 94% yield. Neither 2-bromo-5-(dicyanomethyl)pyridine (**9**) nor 2,5-bis(dicyanomethyl)pyridine (**10**) was detected. When the reaction was carried out at a higher temperature of refluxing 1,2-dimethoxyethane (DME) for a prolonged time of 24 h, a trace of the desired 2,5-disubstituted product **10** was formed together with **8** as main product (73%). In contrast to a preliminary experiment in which 3-bromopyridine was readily convertible into 3-(dicyanomethyl)pyridine,[3] an attempted conversion of **8** into **10** failed. This suggests that **10** must have been formed via 5-substituted isomer **9**. The inertness of **8** to further substitution is probably related to its structure which exists as a tautomeric form **12** as indicated by absorptions due to N-H at around 3200 cm^{-1} and conjugated C≡N at 2210 and 2186 cm^{-1} in the infrared absorption bands.[4]



Scheme 1.



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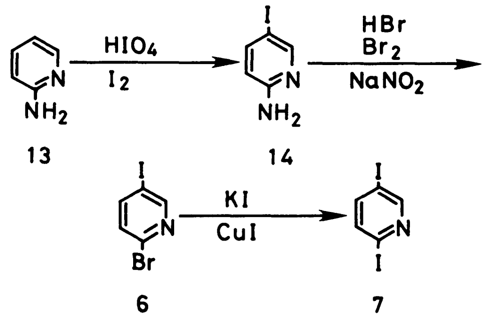
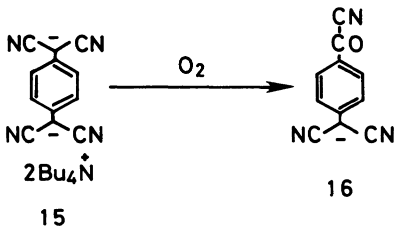
Since iodoarenes are more reactive to the palladium-catalyzed substitution,[5] we next examined 2-bromo-5-iodopyridine (**6**) and 2,5-diiodopyridine (**7**), both of



Scheme 2.



Scheme 3.

which were long known but accesible by an improved procedure as shown in Scheme 2. A similar reaction of **6** in refluxing THF gave a mixture of 5-substituted products **9** (45%) and **10** (12%), while that of **7** gave a mixture of 2-substituted products **11** (45%) and **10** (18%). Alternative treatment of either compound in refluxing DME gave a high yield of **10**. A shorter reaction time (8 h) and a somewhat higher yield (71%) for **6** than those (24 h, 64%) for **7** again support the advantage of the first substitution at 5-position for the 2,5-disubstitution.

Dehydrogenation of **10** to **3** with a common oxidizing agent, i.e., H_2O_2, chloranil, DDQ, Br_2, NBS, NCS, or $Pb(OAc)_4$ was attempted, giving only unidentified colored materials which were presumably derived from **3**. Treatment of **10** with tetrapropylammonium iodide in O_2-free aq. NaOH solution gave the ammonium salt **4a** of pyridine-analogue of TCNQ dianion in an excellent yield. The tetrabutylammonium salt **4b** was similarly obtained. They with hydrochloric acid returned to the precursor **10**. The electrolytic oxidation of **4** to **3** was furthermore attempted, but **3** was not isolated because of its air-sensitivity.

Both salts **4a** and **4b** are hydrated yellow crystals which gradually decompose on prolonged exposure to air, but are extremely sensitive to oxygen in solution, immediately turning orange. The electronic spectra of **4a** and **4b** are almost identical and have two strong absorptions at 238 and 325 nm together with a weak one at 403 nm as shown in Fig. 1. For comparison, bis(tetrabutylammonium) 7,7,8,8-tetracyanoquinodimethanide (**15**), prepared according to the literature,[6] absorbs light at 207, 244, and 326 nm. The close spectral resemblance of **4** and **15** reflects a similarity in their electronic structures. The light yellow solution of TCNQ dianion salt (**15**) turns orange in the presence of oxygen, too. Suchanski and Van Duyne assigned its decay product to be α,α-dicyano[*p*-(cyanocarbonyl)phenyl]methanide (**16**) (Scheme 3).[7] The considerable resemblance of both decay spectra (λ_{max} 276, 336, 458 nm from **4** and 282, 330, 480 nm from **15**) indicates that the same decay process is operative for **4**.

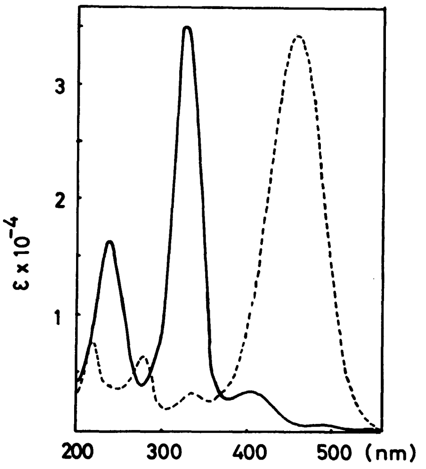


Fig. 1. Electronic absorption spectra of **4a** (——) and its decay product (------) in acetonitrile.

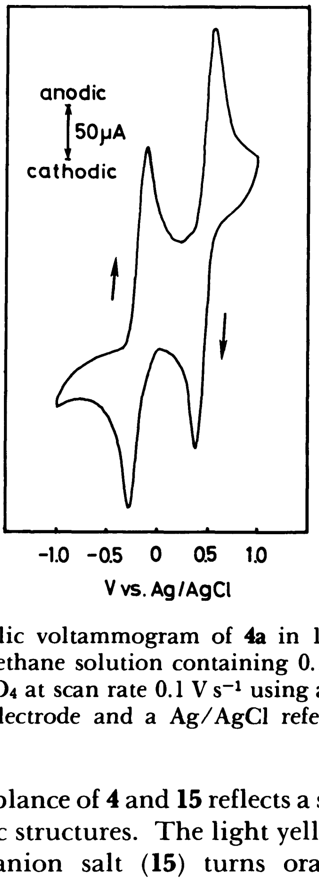


Fig. 2. Cyclic voltammogram of **4a** in 1.6 mol m^{-3} dichloromethane solution containing 0.1 mol dm^{-3} n-Bu_4NClO_4 at scan rate 0.1 V s^{-1} using a platinum working electrode and a Ag/AgCl reference electrode.

The cyclic voltammetry of **4** exhibits two reversible redox waves corresponding to two steps of one-electron oxidations (Fig. 2). The half-wave potentials are +0.48, −0.18 V, indicating that the neutral species

3 is a stronger electron acceptor than TCNQ ($E_{1/2}$+0.25, −0.35 V), as was expected. The charge-transfer complex of TTF and 3 was prepared by the following two methods. One used the mixing of TTF and 3 generated in situ from the electrolytic oxidation of 4 or from the dehydrogenation of 10 with hydrogen peroxide. The resulting complex consisted of 1:1 composition of donor and acceptor, and showed a high electrical conductivity of 19 S cm^{-1} which was measured on a compressed pellet at r.t. by a four probe method. Another used the metathesis of the dianion salt 4 and $(TTF)_3(BF_4)_2$.[8] In this case, the complex followed the 2:1 stoichiometry rich in donor and was also highly conductive (5.9 S cm^{-1}).

Experimental

General. Melting points are uncorrected. NMR measurements were made on a JEOL PMX-60 (60 MHz) using TMS as an internal standard. IR spectra were taken on a Hitachi 260-30 spectrophotometer, MS spectra on a Shimadzu QP-1000 spectrometer at 70 eV using a direct insertion technique, and electronic spectra on a Shimadzu UV-160 spectrophotometer.

2-Amino-5-iodopyridine (14). A mixture of 2-aminopyridine (**13**) (47.02 g, 0.50 mol), periodic acid dihydrate (22.82 g, 0.10 mol), and iodine (51.0 g, 0.20 mol) was heated in a mixed solution of acetic acid (300 cm^3), water (60 cm^3) and sulfuric acid (9 cm^3) at 80 °C for 4 h. It was then poured into aq. dil. $Na_2S_2O_3$ to remove unreacted iodine and extracted with ether. The extract was washed with aq. dil. NaOH, dried (K_2CO_3), and concentrated in vacuo. The residue was purified by column chromatography on silica gel with ethyl acetate as eluent and then recrystallization from ethanol to give colorless prisms of **14** (74.15 g, 67%): mp 132.0—132.7 °C (lit,[9] mp 129 °C).

2-Bromo-5-iodopyridine (6). Bromine (10 cm^3) and aq. solution (50 cm^3) of $NaNO_2$ (11.22 g, 0.163 mol) were succesively added into a stirred solution of 2-amino-5-iodopyridine (**14**) (13.79 g, 0.063 mol) in 47% hydrobromic acid (100 cm^3), the temperature being kept below 0 °C during the addition. The reaction was then continued for 2 h at 5—10 °C and quenched by addition of aq. solution (300 cm^3) of NaOH (36 g). The mixture was poured into aq. dil. $Na_2S_2O_3$ to remove unreacted bromine and extracted with ether. The extract was washed with water, dried (K_2CO_3), and concentrated in vacuo. The residue was purified by column chromatography on silica gel with chloroform as eluent and then recrystallization from ethanol to give colorless plates of **6** (11.65 g, 65%): mp 125—126 °C (lit,[10] mp 122.5 °C).

2,5-Diiodopyridine (7). A mixture of 2-bromo-5-iodopyridine (**6**) (2.27 g, 8.0 mmol), copper(I) iodide (7.75 g, 40.7 mmol), and potassium iodide (13.1 g, 78.5 mmol) in dry hexamethylphosphoric triamide (25 cm^3) was heated at 140—145 °C for 18 h under nitrogen. The reaction was quenched by addition of 10% HCl until the solution became neutral. Benzene (30 cm^3) was added and the insoluble copper salt was filtered off. The organic phase was separated, washed with water, dried (K_2CO_3), and evaporated. The residue was purified by column chromatography on silica gel with chloroform and then recrystallization from the same solvent to give colorless plates of **7** (1.96 g, 74%): mp 148—149.7 °C (lit,[10] mp 154 °C).

5-Bromo-2-(dicyanomethyl)pyridine (8). A solution of malononitrile (0.626 g, 9.48 mmol) in dry THF (10 cm^3) was mixed with a suspension of NaH (60% in oil, 0.667 g, 16.68 mmol) in dry THF (20 cm^3) and stirred at r.t. for 10 min in a nitrogen atmosphere. 2,5-Dibromopyridine (**5**) (0.911 g, 3.84 mmol) in dry THF (10 cm^3) and tetrakis(triphenylphosphine)palladium(0) (0.201 g, 0.174 mmol) were succesively added. The mixture was refluxed for 3 h and concentrated in vacuo. The residue was taken up with water (50 cm^3), washed with benzene, and acidified to pH 1 with 10% HCl. The resulting yellow precipitate was collected by filtration and dried. It was then purified by column chromatography on silica gel with chloroform and recrystallization from acetonitrile to give yellow prisms of **8** (0.80 g, 94%): decomp 216 °C; IR (KBr) 3200—2900 (N–H, C–H), 2210, 2186 cm^{-1} (C≡N); ^{1}H NMR (DMSO-d_6) δ=7.01 (d, J=9.6 Hz, 1H), 7.75 (dd, J=9.6 and 1.8 Hz, 1H), 7.89 (d, J=1.4 Hz, 1H); MS (70 eV) m/z 221, 223 (M$^+$). Anal. ($C_8H_4N_3Br$) C, H, N.

When the same reaction was conducted in refluxing DME for 24 h, a mixture of **8** (73%) and **10** (2%) was formed.

2-Bromo-5-(dicyanomethyl)pyridine (9), 2,5-Bis(dicyanomethyl)pyridine (10), and 2-(Dicyanomethyl)-5-iodopyridine (11). The same reaction as described in the preparation of **8** was carried out using either 2-bromo-5-iodopyridine (**6**) or 2,5-diiodopyridine (**7**) instead of **5**. The usual work-up gave a mixture of **9** (45%) and **10** (12%) from **6** and a mixture of **10** (18%) and **11** (45%) from **7**. The mixtures were separated by column chromatography on silica gel, which first eluted the monosubstituted product with chloroform and then the disubstituted one with 1:5 acetone–chloroform.

Recrystallization of **9** from acetonitrile afforded colorless prisms: decomp 142 °C; IR (KBr) 3100—3000, 2900 (C–H), 2273 cm^{-1} (C≡N); ^{1}H NMR (acetone-d_6) δ=6.17 (s, 1H), 7.80 (d, J=8.4 Hz, 1H), 8.03 (dd, J=8.4 and 3.4 Hz, 1H), 8.65 (d, J=2.6 Hz, 1H); MS (70 eV) m/z 221, 223 (M$^+$); Anal. ($C_8H_4N_3Br$) C, H, N.

Recrystallization of **10** from acetonitrile afforded yellow plates: decomp 204 °C; IR (KBr) 3100—2800 (N–H, C–H), 2214, 2188 cm^{-1} (C≡N); ^{1}H NMR (acetone-d_6) δ=5.98 (s, 1H), 7.28 (d, J=9.4 Hz, 1H), 7.85 (dd, J=8.6 and 3.0 Hz, 1H), 8.13 (d, J=2.6 Hz, 1H), 12.6—11.5 (bs, 1H); MS (70 eV) m/z 207 (M$^+$); Anal. ($C_{11}H_5N_5$) C, H, N.

Recrystallization of **11** from acetonitrile gave yellow needles: decomp. 245 °C; IR (KBr) 3200—2900 (N–H, C–H), 2222, 2198 cm^{-1} (C≡N); ^{1}H NMR (acetone-d_6+DMSO-d_6) δ=6.93 (d, J=8.6 Hz, 1H), 7.83 (dd, J=8.6 and 1.8 Hz, 1H), 7.91 (d, J=1.8 Hz, 1H); MS (70 eV) m/z 269 (M$^+$); Anal. ($C_8H_4N_3I$) C, H, N.

Bis(tetrapropyl- and tetrabutylammonium) 1,1′-(2,5-Pyridinediyl)bis[dicyanomethanide] (4a) and (4b). 2,5-Bis(dicyanomethyl)pyridine (**10**) (0.105 g, 0.51 mmol) was dissolved in 1 mol dm^{-3} NaOH solution (10 cm^3) in a nitrogen atmosphere. As soon as a solution of tetrapropylammonium iodide (0.471 mg, 1.50 mmol) in water (8 cm^3) was added, the yellow plates of **4a** precipitated. It was collected by filtration and dried in vacuo (0.264 g, 89%): decomp 133 °C; IR (KBr) 3400 (H_2O), 2974, 2888 (C–H), 2165, 2127, 2118 cm^{-1} (C≡N); Found: C, 71.61; H, 10.02; N, 15.99%. Calcd for $C_{35}H_{59}N_7 \cdot 1/2H_2O$: C, 71.63; H, 10.30; N, 16.71%. The ^1H NMR spectrum of **4a** showed some dintinct absorptions due to the propyl protons at δ 0.7—1.3 (t, 24H), 1.3—2.4 (m, 16H), 2.9—3.7 (m, 16H) and a very broad absorption due to the pyridinyl protons at δ 6.7—7.9. The latter broadening suggests that the dianion is apt to become a radical species.

The tetrabutylammonium salt **4b** was similarly obtained as yellow plates (97%): decomp 111 °C; IR (KBr) 3400 (H_2O), 2974, 2888 (C–H), 2159, 2121, 2108 cm^{-1} (C≡N); Found: C, 71.04; H, 10.92; N, 13.26%. Calcd for $C_{43}H_{75}N_7 \cdot 2H_2O$: C, 71.13; H, 10.97; N, 13.50%.

Complexation of TTF and Pyridine-Analogue 3 of TCNQ. A) Mixing Method Using Bis(tetrapropylammonium) 1,1′-(2,5-Pyridinediyl)bis[dicyanomethanide] (4a). A 20 cm^3 of H-type glass cell with a fine frit dividing the anolyte and catholyte compartments was used for electrolyses. It was equipped with platinum plates (1 cm^2 in area) as electrodes for the potentiostatic experiment and with platinum needles (3 cm in length, 1 mm in diameter) for the galvanostatic experiment. A 0.1 mol dm^{-3} solution of tetrabutylammonium perchlorate in dry acetonitrile (20 cm^3) was placed in the cell and thoroughly saturated with nitrogen gas. TTF (20.8 mg, 0.1 mmol) and **4a** (57.5 mg, 0.1 mmol) were added in the anolyte compartment and electrolyzed at +0.45 V for 1.5 h. The resulting black powder was collected, washed with dichloromethane, and dried (23.1 mg): mp>300 °C; IR (KBr) broad nitrile absorptions at 2188, 2129 cm^{-1}; σ=18.8 S cm^{-1}; Found: C, 49.68; H, 1.70; N, 16.90%. Calcd for TTF·**3**: C, 49.86; H, 1.72; N, 17.10%.

The galvanostatic electrolysis was carried out under a constant current of 0.5 mA for 12 h, giving black fine needles (14.6 mg): mp>300 °C; IR (KBr) broad nitrile absorptions at 2194, 2160, 2128 cm^{-1}; σ=19.3 S cm^{-1}; Found: C, 49.26; H, 1.63; N, 16.34%.

B) Mixing Method Using 2,5-Bis(dicyanomethyl)pyridine (10). 30% Hydrogen peroxide (2 cm^3) was added into a stirred solution of **10** (50.2 mg, 0.24 mmol) and TTF (43.1 mg, 0.21 mmol) in dry acetonitrile (5 cm^3) in a nitrogen atmosphere. After stirring for 10 min at r.t., the resulting reddish black powder was collected by filtration, washed with a small amount of acetonitrile, and dried (8.6 mg): decomp>300 °C; IR (KBr) broad nitrile absorptions at 2154, 2122 cm^{-1}; σ=1.0 S cm^{-1}; Found: C, 50.17; H, 1.74; N, 17.16%. Calcd for TTF·**3**: C, 49.86; H, 1.72; N, 17.10%.

C) Metathesis Method. A hot solution of **4a** (56 mg, 0.1 mmol) in dry acetonitrile (1.5 cm^3) was mixed with a hot solution of $(TTF)_3(BF_4)_2$ (78 mg, 0.1 mmol) in dry acetonitrile (6 cm^3) in a nitrogen atmosphere. After cooling, the resulting black powder was obtained (26.9 mg): decomp> 300 °C: IR (KBr) broad nitrile absorptions at 2187, 2156 cm^{-1}; σ=5.9 S cm^{-1}; Found: C, 45.08; H, 1.66; N, 12.32%. Calcd for $(TTF)_2$·**3**: C, 45.00; H, 1.81; N, 11.41%.

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