

TETRAHEDRON LETTERS

Preparation and Redox Properties of Longitudinally Twinned TCNQ: Hexacyanostilbenequinodimethane Dianion

Kazuyuki Takahashi and Keiji Kobayashi*

Department of Chemistry, Graduate School of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153-8902, Japan

Received 19 April 1999; revised 12 May 1999; accepted 14 May 1999

Abstract: A new extended π -conjugated TCNQ, hexacyanostilbenequinodimethane, was isolated as a dianion salt. Its cyclic voltammograms show that the dianion is reduced reversibly to a trianion radical, while the oxidized species, a monoradical anion, dimerizes to give the dimer dianion, which is further electrochemically oxidized to a neutral polymer. © 1999 Elsevier Science Ltd. All rights reserved.

Structural modification of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) has been extensively explored to obtain new materials with enhanced conducting properties. Extended TCNQ analogues bearing π -conjugated spacers between the dicyanomethylene moieties have been the focus of much recent attention because they possess a more reduced on-site Coulombic repulsion than TCNQ and thereby enhance the conductivities of their anion radical salts.¹ Tetracyanodiphenoquinodimethane 1 is a relevant example of such structural modification,² whereas the neutral species of 1 is unstable, probably owing to twisting about the central double bond due to the repulsion between the *ortho* hydrogens. As a new π -extended TCNQ derivative which possesses little steric interaction and high electron-accepting property, we have now designed a longitudinally twinned TCNQ derivative, hexacyanostilbenequinodimethane (2). We report here the preparation of 2 as the dianion salt and its multistage redox behavior.



Among several synthetic approaches, the one that incorporates a *t*-butyl group in the early step to protect the benzylic hydrogen gave the most satisfactory results (Scheme 1). Thus, compound **4** was obtained by the reaction of 4-fluoronitrobenzene **3** with *t*-butylmalononitrile,^{3,4} which was then reduced to the amine and subsequently converted to iodide **5** in 54% yield. The reaction of **5** with the ethyl cyanoacetate anion in the presence of copper(I) iodide in HMPA afforded ester **6**.⁵ To avoid destruction of the cyano groups, hydrolysis of the ethoxycarbonyl group and the subsequent decarboxylation were carried out under neutral conditions; **6** was heated at 130 °C together with NaCl in a DMSO-H₂O mixture to give benzyl cyanide **7** in 76% yield from **5**.⁶ The stilbene framework of **8** was constructed in 74% yield by oxidative coupling of **7**. The *t*-butyl groups was removed by heating **8** in diphenyl ether for 3 h,³ giving **9** as a precursor of **2**.



Compound 9 was treated with a variety of oxidizing agents including Br_2-H_2O , NBS, NBS-pyridine, NBS-Et₃N, DDQ, PbO₂, Pb(OAc)₄, and CAN; however, the desired transformation to 2 could not be achieved in any case. Then, our efforts were directed to the isolation of the dianion salt of 2 rather than the neutral species. Thus, compound 9 was added in a 5% NaHCO₃ aqueous solution. The resulting dark-blue solution was treated with Et₄NBr to afford the tetraethylammonium salt (10) as metallic lustered leaflets. The solid of 10 is stable under an inert atmosphere for several weeks, whereas in solution it decomposes gradually within a few days. The structure of 10 was established by the microanalysis and spectral data.^{7,8} The IR spectrum of 10 exhibits the stretching cyano band at 2214, 2163, and 2126 cm⁻¹, the latter two being attributed to the four terminal cyano groups which should be highly conjugated with the anionic center. The UV/Vis spectrum of 10 in CH₃CN shows λ_{max} at 590 nm (ε =41500). Oxidation of 10 with iodine in MeOH did not yield 2 but resulted in the formation of highly insoluble colorless solids which appeared to be polymeric materials.

The electrochemical properties of 10 were investigated by means of cyclicvoltammetry in DMF (0.1 M n-Bu₄NBF₄) at room temperature (Figure 1). The voltammograms show a reversible reduction wave (-1.26 V vs Ag/AgCl) and two irreversible oxidation waves (+0.53, +0.77 V vs Ag/AgCl); irreversibility of the oxidation waves is deduced from the absence of the corresponding reduction peaks upon reversing the direction of sweep. At the second sweep a new irreversible reduction wave appears at -1.0 V (Figure 1b). The current of this wave gradually increases with repetitive potential scans, indicating that 10 undergoes polymerization at the electrode surface.



Figure 1 Cyclic voltammograms of 10 in DMF. (a) First Sweep. (b) Second sweep.

Based on the above observation, the redox behavior of dianion A^{2-} can be summarized as shown in Scheme 2. Radical anion A^{-*} is generated at the first oxidation wave (i). The coupling of two radical ions A^{-*} would irreversibly produce dimer dianion $[A-A]^{2-}$, as observed frequently in electrochemical redox process. Dianion $[A-A]^{2-}$ has two independent electron pools linked via the σ bond and hence is converted to diradical $[^{*}A-A^{*}]$ at the second oxidation wave (ii).⁹ The diradical undergoes polymerization to give polymer A_n . The polymer thus formed is reduced to its radical anion A^{-*} at the reduction wave (iii), which deposits at the electrode surface increasingly with repetitive scans. The reversible redox waves (iv and v) are independent of the electropolymerization and attributed to the reversible redox reaction between dianion A^{2-} and trianion radical A^{3-*} .

Scheme 2



In summary, we have demonstrated that hexacyanostilbenequinodimethane 2 is an unstable compound, being isolated only as the dianion species. Judging from its ready polymerization, neutral 2 should be represented by the canonical structure of a diradical such as 11 rather than a quinonoid structure.

Acknowledgment: This work was supported by a Grant-in-Aid for Scientific Research (No. 10146102) from the Ministry of Education, Science, Sports and Culture, Japan.

References and Notes

- 1. For a recent review, see: N. Martín, J. L. Segura, and C. Seoane, J. Mater. Chem., 7, 1661 (1997).
- W. R. Hertler, U.S. Patent 3,153,658 (1964); D. J. Sandman and A. F. Garito, J. Org. Chem., 39, 1165 (1974); A. W.Addison, N. S. Dalal, Y. Hoyano, S. Huizinga, and L. Weiler, Can. J. Chem., 55, 4191 (1977); E. Aharon-Shalom, J. Y. Becker, and I. Agranat, Nouv. J. Chim., 3, 643 (1979); M. Morinaga, T. Nogami, and H. Mikawa, Bull. Chem. Soc. Jpn., 52, 3739 (1979).
- 3. R. C. Wheland and E. L. Martin, J. Org. Chem., 40, 3101 (1975).
- 4. M. J. Crossley, S. Gorjian, S. Sternhell, and K. M. Tansey, Aust. J. Chem., 47, 723 (1994).
- 5. H. Suzuki, T. Kobayashi, Y. Yoshida, and A. Osuka, Chem. Lett., 1983, 193.
- 6. A. P. Krapcho and A. J. Lovey, Tetrahedron Lett., 12, 957 (1973).
- 7. The crystal structure of 10 was not determined, since a single crystal suited for an X-ray analysis could not be obtained in spite of our all efforts.
- 8. Characteristic spectral data for 7, 8, 9 and 10 are as follows.

7: mp 121–122 °C; ¹H NMR (CDCl₃, 500 MHz) δ 7.577 (d, 2H, J = 8.3 Hz), 7.459 (d, 2H, J = 8.3 Hz), 3.822 (s, 2H), 1.204 (s, 9H); ¹³C NMR (CDCl₃, 126 MHz) δ 131.97, 129.41, 128.76, 128.27, 117.00, 114.68, 52.51, 41.22, 25.62, 23.22; IR (KBr) 2254 (C=N) cm⁻¹; MS *m/z* 237 (M⁺). Anal. Calcd for C₁₅H₁₅N₃: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.74; H, 6.40; N, 17.61.

8: mp > 255 °C (decomp.); ¹H NMR (CDCl₃, 500 MHz) δ 7.980 (d, 4H, J = 8.4 Hz), 7.770 (d, 4H, J = 8.4 Hz), 1.256 (s, 18H); ¹³C NMR (CDCl₃, 126 MHz) δ 133.40, 132.99, 129.10, 129.03, 125.21, 115.76, 114.28, 52.73, 41.73, 25.76; IR (KBr) 2253 (C=N), 2223 (C=N) cm⁻¹; MS *m/z* 470 (M⁺). UV-Vis (CH₂Cl₂) λ max 327 (ε=25000), 238 (ε=9500) nm; Anal. Calcd for C₃₀H₂₆N₆: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.28; H, 5.74; N, 17.62.

9: mp > 230 °C (decomp.); ¹H NMR (CDCl₃, 270 MHz) δ 8.01 (d, 4H, J = 8.2 Hz), 7.76 (d, 4H, J = 8.2 Hz), 5.20 (s, 2H); IR (KBr) 2266 (w, C=N), 2231 (m, C=N) 2177 (m, C=N) cm⁻¹; MS *m/z* 358 (M⁺). UV-Vis (CH₂Cl₂) λ max 320, 239 nm.

10: mp 231–236 °C; ¹H NMR (CD₃CN, 500 MHz) δ 7.6–6.7 (m, 8H), 3.15 (q, 16H, J = 7.3 Hz), 1.20 (t, 24H, J = 7.3 Hz); IR (KBr) 2214, 2163, 2126 cm⁻¹; UV-Vis (CH₃CN) λ max 590 (ϵ =41500), 307 (ϵ =25600) nm; Anal. Calcd for C₃₈H₄₈N₈: C, 73.99; H, 7.84; N, 18.17. Found: C, 73.80; H, 7.73; N, 18.21.

9. The peak profile of this wave corresponds to the one-electron transfer, since the dimerization reduces the concentration of its monomer precursor to one-half.