### An Improved Synthetic Route to 11,11,12,12-Tetracyanonaphtho-2,6-quinodimethan<sup>1a,b</sup>

#### D. J. Sandman<sup>\*1c</sup> and A. F. Garito

Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19174

### Received November 1, 1973

11,11,12,12-Tetracyanonaphtho-2,6-quinodimethan (TNAP, 1) is an extended conjugated analog of 7,7,8,8-tetracyanoquinodimethan (TCNQ, 2), the acceptor molecule on which the highest conductivity organic solids are based. Indeed, giant conductivity maxima, attributed to superconducting fluctuations at high (60°K) temperatures, have been observed in charge-transfer salts where the donor is based on tetrathiafulvalene (TTF, 3) and the acceptor is  $2.^{2}$ 



At the molecular level, the features of 2 which are essential for these properties are clear. In the anion-radical salts of 2 the unpaired electron is largely localized on the terminal dicyanomethylene groups. In a solid in the event of an ionic fluctuation with two excess electrons a *single* molecule of 2, there is a clear tendency for the two electrons to localize at opposite ends of the molecule and correlate to stay apart in order to reduce their mutual Coulomb repulsion. This correlated structure may be described by a generalized Heitler-London-type wave function

$$\psi = \frac{1}{\sqrt{2}} \left[ \phi_{\rm A}(1)\phi_{\rm B}(2) + \phi_{\rm A}(2)\phi_{\rm B}(1) \right] \tag{1}$$

where  $\phi_A$  denotes the wave function for one dicyanomethylene group and  $\phi_B$  denotes the wave function at the opposite group (B).<sup>3</sup> It is the ability of 2 to accommodate two excess electrons in the manner described above which distinguishes 2 from other types of acceptor molecules. Other molecules which allow Heitler-London-type correlation, as in 2, and which might further reduce Coulomb interactions due to their extended conjugated systems are 1 and 13,13,14,14-tetracyanodiphenoquinodimethan (TCNDQ, 4). The crucial importance of a reduced effective Coulomb interaction for achieving and maintaining a metallic state in organic systems has been discussed earlier.<sup>3</sup>

Given the interest cited above in acceptors such as 1 and 4, the present work was stimulated by the disadvantages found in an earlier<sup>4,5</sup> synthesis of 1. 2,6-Naphthalenediacetonitrile (5), the second compound in a sixstep synthesis, is available in only 25% yield. 2,6-Naphthalenedimalononitrile (6), the immediate precursor to 1, was prepared from 5 via the classical<sup>7</sup> aryl malononitrile synthesis. In this synthesis diethyl 2,6-naphthalenedicyanoacetate is prepared from 5 as a mixture of diastereomers. The purification of this compound is essentially the separation of a mixture of diastereomers and the potential yield is therefore limited.

In the present work, the stereochemical problem in the earlier<sup>4</sup> synthesis of 1 was averted by the adoption of a novel synthesis of aryl malononitriles via arylenedicy-



anoacetates.<sup>8</sup> Further, a high yield preparation of 5 has been achieved.

Reaction of 2,6-bis(bromomethyl)naphthalene<sup>4</sup> with sodium cyanide in aqueous alcoholic dioxane at room temperature gives 5 in 70% yield. Reaction of 5 with sodium ethoxide and diethyl carbonate, followed by reaction of the resultant dianion with cyanogen chloride, leads to a 60% yield of diethyl 2,6-naphthalene  $\alpha, \alpha, \alpha', \alpha'$ -tetracyanodiacetate (7). Hydrolysis and decarboxylation of 7 leads to 6, and oxidation of this compound leads to a mixture of 1 and a highly insoluble substance previously described.<sup>4</sup> Separation and purification of 1 may be achieved by chromatography on Florisil and subsequent recrystallization from acetonitrile. The relevant chemistry is outlined in Scheme I.

In acetonitrile solution, 1 reacts with 3 to give the 1:1 complex TTF-TNAP. This complex has a resistivity (room temperature compaction) less than 0.2 ohm-cm and accordingly is the lowest resistivity TNAP complex prepared to date.<sup>4</sup> Although unsuccessful to date, further attempts to grow single crystals of TTF-TNAP and other TNAP salts are in progress.

Two attempts to synthesize 4 have been reported. Oxidation of p,p'-biphenylenedimalononitrile (8) with N-iodosuccinimide led to a polymer of 4,<sup>9</sup> and thermal or photolytic decomposition of 3-diazo-6-dicyanomethylene-1,4cyclohexadiene also did not lead to 4.<sup>10</sup>

Since 8 prepared by the reported method<sup>9</sup> is quite difficult to purify, it was hoped that its preparation via the dicyanoacetate method<sup>8</sup> might lead to material of sufficiently improved purity<sup>11</sup> so as to allow isolation of 4. Accordingly, p,p'-bis(cyanomethyl)biphenyl<sup>12</sup> was converted into diethyl 1,12-biphenylene- $\alpha, \alpha, \alpha', \alpha'$ -tetracyanodiacetate as described above, and this compound was used to prepare 8. However, attempted preparation of 4 via 8 again led to polymer.<sup>9</sup>

## Experimental Section<sup>13</sup>

2,6-Naphthalenediacetonitrile (5). To a mixture of sodium cyanide (94.5 g, 1.93 mol) in water (114 ml), ethanol (227 ml), and dioxane (280 ml) stirred mechanically at room temperature was added 2,6-bis(bromomethyl)naphthalene (140 g, 0.446 mol). This mixture was stirred for 16 hr at room temperature and then was

filtered. The filter cake was washed with ca. 21. of water and airdried to give 5 as an off-white solid, 82 g (89%), mp 153-159°. This solid was recrystallized in four batches from 50:50 v/v acetone-absolute ethanol to give 5, 65.4 g (71%), mp 163-166, 164-167, 163-165, 162-165° (lit.4 mp 163.5-165.5°). The infrared spectrum of the product exhibited absorption due to a nonconjugated cyano group at 2275 cm<sup>-1</sup> (lit.<sup>4</sup> 2280 cm<sup>-1</sup>).

Diethyl 2,6-Naphthalene- $\alpha, \alpha, \alpha', \alpha'$ -tetracyanodiacetate (7). To sodium ethoxide [freshly prepared from sodium metal (22.6 g, 0.548 g-atom) and absolute ethanol (240 ml), followed by removal of excess alcohol at reduced pressure] was added diethyl carbonate (292 g, 2.48 mol), toluene (100 ml), and 5 (52.5 g, 0.25 mol). This mixture was stirred mechanically and distilled until the boiling point reached 111°. Toluene (100 ml) was added, and the mixture was cooled to  $0^{\circ}$ . Cyanogen chloride (36.9 g, 0.60 mol) was dis-tilled into the reaction mixture kept at  $0-5^{\circ}$ . After the completion of the cyanogen chloride addition (ca. 6 hr), the mixture was heated at 55-60° for 2 hr and then cooled to room temperature and filtered. The filter cake was washed with ice-water and recrystallized from benzene to give 7 as an off-white solid, 60 g (60%), mp 141.5-143.5°. Recrystallization from benzene gave mp 142-143.5°. This compound showed infrared absorption at 2270 (nonconjugated CN), 1750 (ester carbonyl), and 1240 cm<sup>-1</sup> (ester C-O). The nmr spectrum of 7 exhibited absorption at  $\delta$  1.20-1.45 (triplet, J = 7.5 Hz, 6 H,  $-CH_2CH_3$ ), 4.25-4.65 (quartet, J = 7.5 Hz, 4 H,  $-CH_2CH_3$ ) and 7.75-8.35 (multiplet, 6 aromatic protons).

Anal. Calcd for C<sub>22</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>: C, 66.00; H, 4.03; N, 13.99. Found: C, 65.68; H, 3.83; N, 14.12.

2,6-Naphthalenedimalononitrile (6).14 To a magnetically stirred 10% potassium hydroxide solution was added 7 (4.00 g, 10 mmol), and this mixture was stirred at room temperature until homogeneous. Hydrochloric acid (6 N, 11.2 ml) was added carefully, and a quantitative yield of 6, mp 233-240° dec, precipitat-ed.<sup>15</sup> The precipitate was recrystallized from acetonitrile<sup>4</sup> to give 6, 1.86 g (72%), mp 251–253° dec (lit.<sup>4</sup> mp 241–243° dec). The infrared spectrum of this material (Nujol and Fluorolube) is in accord with that previously reported.4

Anal. Calcd for C<sub>16</sub>H<sub>8</sub>N<sub>4</sub>: C, 74.99; H, 3.15; N, 21.86. Found: C, 74.98; H, 3.18; N, 21.80.

11,11,12,12-Tetracyano-2,6-naphthoquinodimethan (TNAP, 1). General Method of Preparation from 7.14 As described above, 7 (10.0 g, 25 mmol) and 10% potassium hydroxide (75 ml) were stirred until homogeneous. Hydrochloric acid (6 N, 28 ml) was added; a precipitate of 6 formed. To this suspension of 6 was added bromine (5.0 g, 31.2 mmol) in ice-water (250 ml), and a purple precipitate formed immediately. This precipitate was filtered and washed with ice-water, acetonitrile, and ether to give 6 g (100%) of crude 1. This material was purified in batches as follows. Crude 1 (ca. 500 mg) was suspended in boiling acetonitrile (2000 ml), the suspension was filtered, and a precipitate (300-400 mg) of 1 and its oligomer<sup>4</sup> formed. This precipitate was dissolved in acetonitrile and chromatographed on Florisil (60-100 mesh) and eluted with acetonitrile until no more 1 was eluted, as judged by the color of the column effluent. As much as 1 g of 1 and its oligomer could be chromatographed on 350-400 g of Florisil. The column effluent was concentrated by evaporation under reduced pressure, and the precipitated 1 was recrystallized from acetonitrile to give 1 as metallic purple plates, mp  $>\!365^\circ$  (lit.4 mp >420°). The recovery of 1 from the chromatographic experiment is ca. 50%. The infrared and uv-visible spectra of 1 are in accord with those previously reported.4

Anal. Calcd for C16H6N4: C, 75.58; H, 2.38; N, 22.04. Found: C, 75.57; H, 2.57; N, 21.98.

11,11,12,12-Tetracyanonaphtho-2,6-Tetrathiafulvalinium quinodimethanide (TTF-TNAP). To a hot solution of 1 (16 mg, 0.063 mmol) in acetonitrile (65 ml) was added a hot solution of 3 (14.2 mg, 0.069 mmol) in acetonitrile (5 ml). The mixture slowly cooled to room temperature, was filtered, and vacuum dried, 240-245° dec.

Anal. Calcd for  $C_{22}H_{10}N_4S_4$ : C, 57.62; H, 2.20; N, 12.22; S, 27.96. Found: C, 57.75; H, 2.35; N, 12.51; S, 27.97.

Diethyl 1,12-Biphenylene- $\alpha, \alpha, \alpha', \alpha'$ -tetracyanodiacetate. A mechanically stirred mixture of diethyl carbonate (146.1 g, 1.24 mol), sodium ethoxide (18.0 g, 0.265 mol), p,p'-bis(cyanomethyl)biphenyl (29.0 g, 0.125 mol), and toluene (100 ml) was distilled until a boiling point of 111° was reached. The mixture was cooled to  $0^\circ$ , and cyanogen chloride (18.45 g, 0.30 mol) was distilled into the mixture, which was kept at 0-5°. After cyanogen chloride addition was completed, the mixture was heated at 50°55° for 2 hr. Addition of hexane to the mixture formed a precipitate which was

washed with ice-water to give a gummy solid. The gummy solid was heated in benzene and filtered. Evaporation of the benzene solution gave an oil which slowly crystallized. Absolute ethanol was found to be a satisfactory recrystallization solvent, and three crystallizations from it gave 7.0 g (13%) of the desired compound, mp 125-127.5°. This compound showed infrared absorption at 2270 (nonconjugated CN), 1760 (ester carbonyl), and 1230 cm<sup>-1</sup> (ester C-O). The nmr spectrum exhibited resonances at  $\delta$  1.20-1.50 (triplet, J = 7.5 Hz, 6 H,  $-CH_2CH_3$ ), 4.20-4.65 (quartet, J =7.5 Hz, 4 H, -CH<sub>2</sub>CH<sub>3</sub>), and 7.65-8.00 (complex, 8 H, aromatic protons).

Anal. Calcd for C24H18N4O4: C, 67.60; H, 4.25; N, 13.14. Found: C, 67.59; H, 4.22; N, 13.15.

Acknowledgments. The technical assistance of P. J. Nigrey, S. Goldberg, and Mrs. C. Folk is gratefully acknowledged.

Registry No.-1, 6251-01-0; 3, 31366-25-3; 5, 4949-02-4; 6, 4948-93-0; 7, 50764-74-4; TTF-TNAP, 50764-75-5; 2,6-bis(bromomethyl)naphthalene, 4542-77-2; p,p'-bis(cyanomethyl)biphenyl, 7255diethyl 83-6: 1,12-biphenylene- $\alpha, \alpha, \alpha', \alpha'$ -tetracyanodiacetate, 50764-76-6.

#### **References and Notes**

- (1) (a) This work was supported by the National Science Foundation through the Laboratory for Research on the Structure of Matter and Grant No. GP-29583 and by the Advanced Research Projects Agency through DAHC-15-72C-0174. (b) Portions of this paper were presented at the 166th National Meeting of the American Chemical Society, Chicago, III., Aug. 26–31, 1973, Abstracts of Pa-pers, ORGN 145. (c) Correspondence should be directed to this author at Xerox Corporation, Webster Research Center, W-114, Webster New York 14580.
- Webster, New York 14580. L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973). A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heeger, *Phys. Rev.* (2)
- (3)B, 5, 952 (1972)
- (4)J. Diekmann, W. R. Hertler, and R. E. Benson, J. Org. Chem., 28, 2719 (1963).
- (5) This earlier publication<sup>4</sup> also reports the preparation of several anion-radical salts of 1 and a study of their resistivities as room temperature compactions. In all cases reported, the salts of 1 have resistivities comparable to, and in some cases lower than, those reported<sup>6</sup> for salts of **2**. Neither single crystal conductivity nor crys-tai structure data are available as yet for **1** and its anion-radical salts. Accordingly, it is not feasible at present to attempt a detailed discussion of the properties of 1 and its salts. However, the close resemblance of the resistivities observed for the salts of 1 to those of analogous salts of 2 makes it reasonable to assume that the to-pographical features to be found in crystal structures of the salts of
- pographical features to be found in crystal structures of the salts of 1 may be generally analogous to those found in salts of 2.
  (6) L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, J. Amer. Chem. Soc., 84, 3374 (1962).
  (7) J. C. Hessler, Amer. Chem. J., 32, 119 (1904).
  (8) E. L. Martin, U. S. Patent 3, 504,001.
  (9) W. R. Hertler, U. S. Patent 3, 153,658.
  (10) H. D. Hartzler, J. Amer. Chem. Soc., 86, 2174 (1964).
  (11) See preparation of 6 in Experimental Section, for example.
  (12) D. D. Pavnolds and K. B. Dunham, U. S. Patent 2, 789,971.

- D. D. Reynolds and K. R. Dunham, U. S. Patent 2,789,971.
   Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., or Midwest Microlab, Ltd., Indianapolis, Ind. Infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 700 spectrophotometer. Proton magnetic resonance spectra were recorded on a Varian A-60 spectrometer in 10% CDCl<sub>3</sub> solution. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane
- (14) This experiment is best carried out in a glove box under an inert atmosphere
- (15) Material of this quality may be used for the preparation of 1; in-deed, 7 may be converted to 1 in one flask.<sup>8</sup>

### Antimetabolites Produced by Microorganisms. IX. Chemical Synthesis of $N^5$ -Hydroxyornithine and N<sup>5</sup>-Hydroxyarginine<sup>1</sup>

Hubert Maehr\* and Michael Leach

Chemical Research Department, Hoffmann-La Roche Inc., Nutley, New Jersey 07110

# Received October 16, 1973

 $N^5$ -Hydroxyornithine (1), isolated as a degradation product of a host of naturally occurring hydroxamic