Tetracyano-4,7-indanoquinodimethanes: The First TCNQs with an Indan Nucleus

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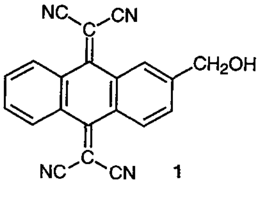
Received 2 August 1996; revised 14 February 1997

8,8,9,9-Tetracyano-4,7-indanoquinodimethane and 5-chloro-8,8,9,9-tetracyano-4,7-indanoquinodimethane, the first members of the hitherto unreported family of tetracyanoindanoquinodimethanes, have been synthesized from the corresponding 4,7-indandicarboxylic acids by the method of Yamaguchi. The indan-TCNQs are part of a series of polycyclic TCNQs which include 11,11,12,12-tetracyano-9,10-anthraquinodimethane and 9,9,10,10-tetracyano-1,4-naphthoquinodimethane, that have been prepared in our laboratory. A disadvantage found with the earlier polycyclic TCNQs was the non-coplanarity of their rings and the dicyanomethylene moities: a planar system is essential to efficient electrical conductivity of TCNQs in CT salts. X-ray analysis has shown 8,8,9,9-tetracyano-4,7-indanoquinodimethane to be more planar compared with tetracyanoanthraquinodimethanes and tetracyanonaphthoquinodimethanes. The half-wave potentials of the chlorotetracyanoindanoquinodimethane show it to be a stronger electron acceptor than several known TCNQs and its cyclic voltammogram indicate two single-electron reversible redox processes.

We have been interested in the synthesis of tetracyanoquinodimethanes (TCNQs) that will ultimately be incorporated into the acceptor portions of D-σ-A materials and charge-transfer complexes and/or be used in the surface modification of electrodes. D-σ-As are extended molecules in which the donor and acceptor moieties are connected through a non conjugated chain of C/N/O atoms (the sigma bridge).[1–3] Thus far, we have reported the syntheses of six alcohol-functionalized TCNQs: 2-(hydroxymethyl)-11,11,12,12-tetracyano-9,10-anthraquinodimethane (**1**),[4] 2-(2′-hydroxyethoxy)-7,7,8,8-tetracyano-4-quinodimethane and derivatives (**2**, R=H, Cl, Et, MeO),[5,6] and 6-(hydroxymethyl)-9,9,10,10-tetracyano-1,4-naphthoquinodimethane (**3**).[7,8]



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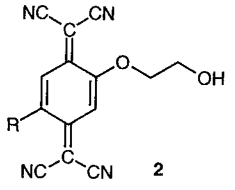

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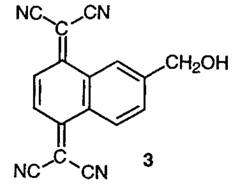
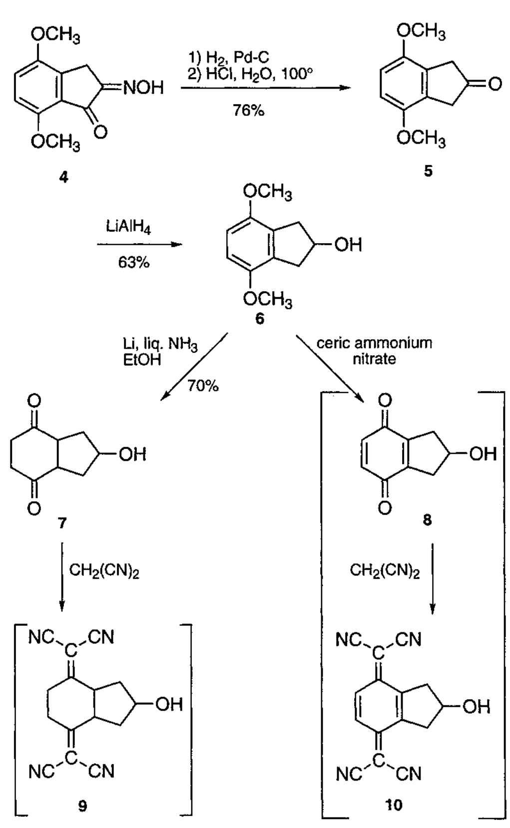
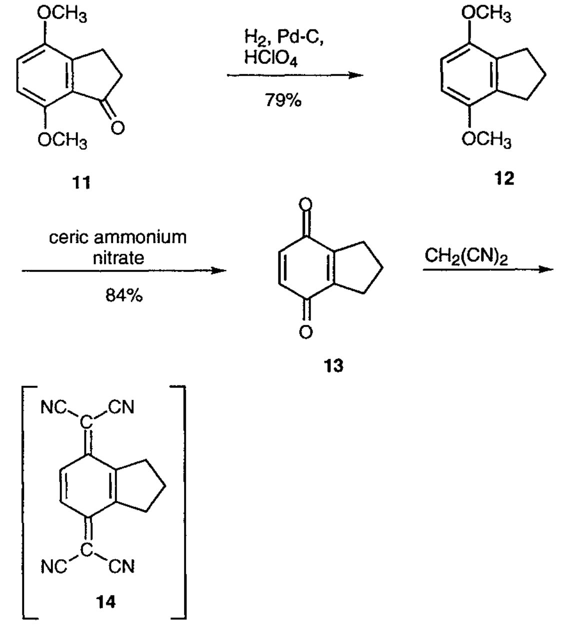


3

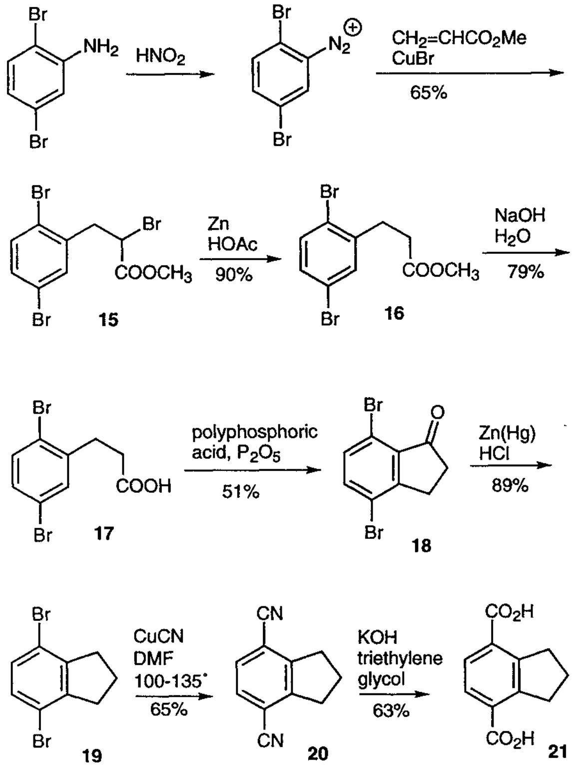
To complete this series, we attempted the first synthesis of the symmetrical 2-hydroxy-8,8,9,9-tetracyano-4,7-indanoquinodimethane (**10**), a member of the hitherto unreported family of tetracyanoindanoquinodimethanes. Since Knoevenagel-type condensations of malonitrile with quinones were successful in the syntheses of **1** and **3**, the 4,7-indanoquinone, **13**, and the tetrahydro-4,7-indanoquinone, **7**, were made with the intent of using a similar procedure. 4,7-Dimethoxy-2-isonitrosoindan-1-one (**4**)[9] was converted to the new compound, 4,7-dimethoxyindan-2-one (**5**), which, in turn, was reduced to the corresponding alcohol (**6**, Scheme 1).[8] Either the indan-2-one or the indan-2-ol was reduced using the Birch method to the 2-hydroxyhexahydroindan-4,7-dione (**7**).[8] Several attempts to condense **7** with malononitrile to produce the tetracyano derivative, **9**, were not successful. Another route began with the oxidation of **6** to what was assumed to be 6-hydroxyindanoquinone (**8**). However, **8** could not be obtained pure nor could a crude sample [^{1}H NMR ($CDCl_3$) $\delta = 6.70$ (s, 2H), 4.47 (m, 1H), 3.10 (dd, 2H), 2.82 (dd, 2H), 1.64 (s, 1H, exchangeable); IR ($CHCl_3$): $\nu = 3437$, 3048, 2933, 1650, 1559, 1326, 1271, 1012, 840 cm^{-1}] be converted to the tetracyano derivative, **10**. Attempts to condense malonitrile with the known 2-desoxy compound, **13**[17] (Scheme 2), were also unsuccessful.



Scheme 1



Scheme 2



Scheme 3

We now report the successful syntheses of two TCNQs with an indan nucleus: 8,8,9,9-tetracyano-4,7-indanoquinodimethane (**27**) and its 5-chloro derivative, **28**. The tetracyanoquinodimethane groups were installed using the same method[10] that was successful in the preparation of the hydroxyethoxy-TCNQ, **2**: the diacid chlorides of the indan-4,7-dicarboxylic acids were treated with trimethylsilanecarbonitrile. The crucial intermediates for both syntheses were the indan-4,7-dicarboxylic acids (**21** and **26**[11]) and these two preparations are illustrated in Schemes 3 and 4. The first procedure introduces the carboxyl groups via a route that included the known 3-(2,5-dibromophenyl)propanoic acid (**17**),[12,13] 4,7-dibromoindan-1-one (**18**),[13] and the previously unreported 4,7-dibromoindan (**19**), 4,7-dicyanoindan (**20**), and indan-4,7-dicarboxylic acid (**21**). The second synthesis involved the cleavage of a Diels–Alder adduct, **22** and subsequent reactions to afford **26** via the method of Horner and Spietschka.[11]

The cyclic voltammetry of **28** (Figure 1) revealed two successive reduction waves each with an associated oxidation wave similar to those seen for **2**,**3**, and TCNQ itself. The peak potential separations of these two pairs of waves suggested that both pairs originated from one-electron reversible processes (the tetracyanoanthraquinodimethane, **1**, and similar structures have shown only two-electron redox processes). The peak current ratios for both pairs of waves were close to unity at the scan rate of 100 nV s^{-1}, indicating that the products of these reactions, presumably the radical anion and dianion, respectively, were stable on the time scale of voltammetry.

Comparison of the half-wave potentials of **28** with those of other TCNQs reported earlier,[8] have shown that the chloroindan-TCNQ was a stronger electron acceptor, mostly due to the electronegative substituent (Table 1).

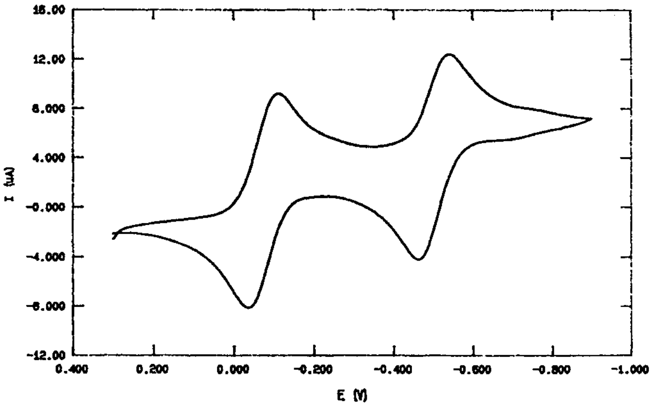


Figure 1. The Cyclic Voltammogram of Product **28**

Since the planarity of a TCNQ is vital to its ability to serve as an organic conductor in C–T salts, an X-ray crystal structure was determined on **27** (Figure 2). In the past, polycyclic TCNQs have been found to be mostly nonplanar. For example, the dihedral angle between the planes defined by the two aromatic rings in **1** was 37.3°.[14] For **3**, the angle between the quinone ring and the dicyanomethylene groups was 10.5°[7] and for **3** without the hydroxymethyl side chain, the angle was 26.4°.[15] This angle in **27** was shown to be approximately 8° making it the most planar of the polycyclic TCNQs in this series. Therefore, 8,8,9,9-tetracyano-4,7-indanoquinodimethane (**27**) was almost as planar as expected since there should be less steric interference between the cyano

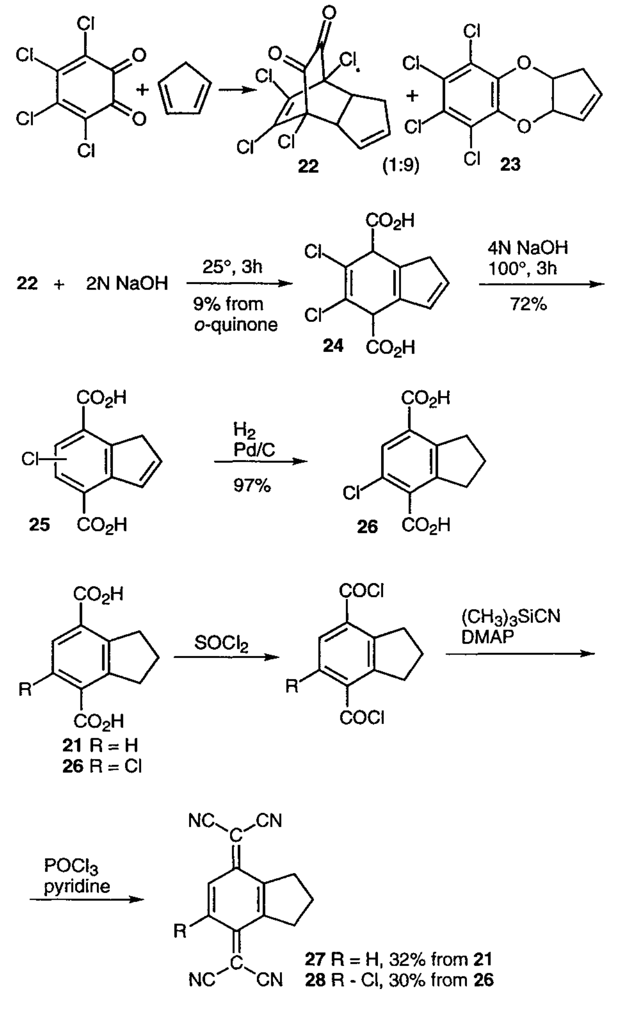
Table 1. Cyclic Voltammetric Half-Wave Potentials of TCNQs (in Volts)[a]

Compound	$E_{1/2}$ (first wave)	$E_{1/2}$ (second wave)
TCNQ[b]	−0.136	−0.693
2, R = H[b]	−0.189	−0.690
2, R = Cl[c]	−0.086	−0.580
2, R = Et[c]	−0.244	−0.717
2, R = MeO[c]	−0.312	−0.779
3[b]	−0.315	−0.781
27	−0.218	−0.742
28	−0.074	−0.501

[a] vs Ag/AgNO$_3$ (0.01–0.1 M), electrolyte $Bu_4N \cdot PF_6$ (0.1 M), in MeCN.

[b] reference[8]

[c] reference[6]



Scheme 4

groups and the α-hydrogen atoms on the adjacent ring compared with those of the tetracyanoanthraquinodimethane, **1**, and tetracyanonaphthoquinodimethane, **3**.

Table 2. Bond Lengths (Å) and Angles (°) for Product **27**

N(1)–C(12)	1.143(4)	C(3)–C(2)–C(1)	122.4(3)
N(2)–C(13)	1.139(6)	C(3)–C(2)–C(7)	110.0(4)
N(3)–C(14)	1.149(7)	C(1)–C(2)–C(7)	127.6(4)
N(4)–C(15)	1.137(4)	C(2)–C(3)–C(4)	119.8(4)
C(1)–C(10)	1.380(5)	C(2)–C(3)–C(9)	112.6(3)
C(1)–C(2)	1.426(6)	C(4)–C(3)–C(9)	127.6(4)
C(1)–C(6)	1.458(4)	C(11)–C(4)–C(5)	119.6(4)
C(2)–C(3)	1.369(6)	C(11)–C(4)–C(3)	123.8(4)
C(2)–C(7)	1.517(4)	C(5)–C(4)–C(3)	116.6(4)
C(3)–C(4)	1.468(4)	C(6)–C(5)–C(4)	123.1(3)
C(3)–C(9)	1.484(5)	C(5)–C(6)–C(1)	120.7(4)
C(4)–C(11)	1.370(6)	C(8)–C(7)–C(2)	103.9(3)
C(4)–C(5)	1.435(6)	C(7)–C(8)–C(9)	110.3(4)
C(5)–C(6)	1.335(6)	C(3)–C(9)–C(8)	102.9(4)
C(7)–C(8)	1.479(7)	C(1)–C(10)–C(13)	121.7(3)
C(8)–C(9)	1.518(5)	C(1)–C(10)–C(12)	125.6(4)
C(10)–C(13)	1.422(6)	C(13)–C(10)–C(12)	112.6(4)
C(10)–C(12)	1.427(4)	C(4)–C(11)–C(14)	126.1(4)
C(11)–C(14)	1.414(8)	C(4)–C(11)–C(15)	119.6(4)
C(11)–C(15)	1.441(5)	C(14)–C(11)–C(15)	114.3(4)
		N(1)–C(12)–C(10)	174.8(4)
C(10)–C(1)–C(2)	125.2(3)	N(2)–C(13)–C(10)	179.0(4)
C(10)–C(1)–C(6)	117.6(4)	N(3)–C(14)–C(11)	177.6(5)
C(2)–C(1)–C(6)	117.2(4)	N(4)–C(15)–C(11)	179.3(3)

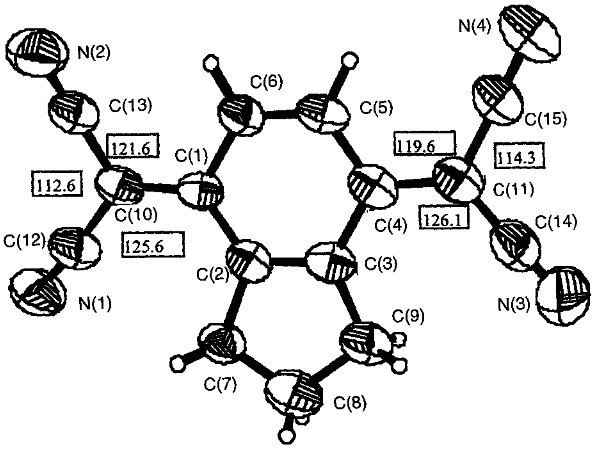


Figure 2. ORTEP presentation of 8,8,9,9-tetracyano-4,7-indanoquinodimethane (**27**).

Melting points were run on a Thomas-Hoover apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer Series 1600 FTIR and the NMR spectra on a Bruker AC300 instrument. TLC analyses were done on Analtech Silica Gel HLF plates and elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN and Atlantic Microlab, Inc., Norcross, AG. The HRMS was run at the Mass Spectrometry Laboratory at the University of Kansas, Lawrence, KS.

4,7-Dimethoxy-2-isonitrosoindan-1-one (4):

To a solution of 4,7-dimethoxyindan-1-one (2.47 g, 14 mmol) in anhyd MeOH (10 mL) was added conc. HCl (2 mL). The reaction was warmed to 60–62 °C while stirring. Then, fresh isoamyl nitrile (6 mL, Aldrich Chemical Company) was added under N_2, and the mixture was stirred for 3 h at 50 °C, cooled, and the yellow solid collected by vacuum filtration. Recrystallization from EtOH gave 2.6 g (91 %) of **4**: mp 233–234 °C (lit.[9] mp 233–234.5 °C).

IR (KBr): ν = 3300, 1730, 1650, 1600, 1500, 1275, 815, 720 cm^{-1}.

4,7-Dimethoxyindan-2-one (5):

A solution of 4,7-dimethoxy-2-isonitrosoindan-1-one (**4**; 1.18 g, 5.3 mmol) in EtOH (15 mL), 10% aq NaOH (25 mL), and 10% Pd—C (0.3 g) was hydrogenated at r.t. under 50 psi of H_2 for 4.5 h. The catalyst was removed by suction filtration through Celite and was washed with EtOH. The EtOH was removed and the aqueous layer was extracted with $CHCl_3$ (5 × 100 mL). The solvent was removed, and to the residue was added conc. HCl (20 mL) and H_2O (10 mL). The solution was refluxed for 30 min, extracted with $CHCl_3$ (3 × 70 mL) and the solvent was removed to yield 0.81 g (79%, pure by TLC) of product which could be further purified by column chromatography (E. Merck Silica 9385, EtOAc/hexane, 50:50) in 76% yield. This product was recrystallized from EtOAc/hexane: mp 178–179 °C.

IR (KBr): $v = 2950, 1750, 1500, 1265, 810, 720\ cm^{-1}$.

^1HNMR ($CDCl_3$): $\delta = 3.45$ (4H, s), 3.8 (6H, s), 6.7 (2H, s).

$C_{11}H_{12}O_3$ (192.22)	calc.	C 68.74	H 6.29
	found	68.75	6.37

4,7-Dimethoxyindan-2-ol (6):

A solution of 4,7-dimethoxyindan-2-one (0.5 g, 2.6 mmol) dissolved in anhyd THF (100 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (0.65 g, 17 mmol) in anhyd THF (200 mL) under Ar. After the addition was completed, the reaction was warmed (~60 °C) for 45 min. The reaction vessel was cooled by an ice bath, and ice-water (~100 mL) was added very slowly into the flask. The THF was evaporated under reduced pressure and the aqueous residue was acidified with 10% HCl. Then Na_2CO_3 was added until neutral (pH paper), and the aqueous layer was extracted with $CHCl_3$ (3 × 200 mL). The $CHCl_3$ layer was dried ($MgSO_4$), and the solvent removed to yield 0.70 g of a crude product. Column chromatography (E. Merck Silica 9385, EtOAc/hexane, 50:50) gave 320 mg (63%) of pure (by TLC using the same solvent system as above and by NMR) product. This product could be recrystallized from EtOAc/hexane: mp 92–93 °C.

IR (KBr): $v = 3200, 2960, 1490, 1255, 800, 720\ cm^{-1}$.

^1HNMR ($CDCl_3$): $\delta = 1.9$ (1H, s), 2.85–3.2 (4H, m), 3.75 (6H, s), 4.7 (1H, s), 6.7 (2H, s).

$C_{11}H_{14}O_3$ (194.23)	calc.	C 68.02	H 7.27
	found	68.30	7.24

2-Hydroxyhexahydroindan-4,7-dione (7):

Li wire (5 g) in small pieces was added to liquid NH_3 (100 mL) in a three-neck flask. 4,7-Dimethoxyindan-2-one (**5**, 300 mg, 1.5 mmol) or 4,7-dimethoxyindan-2-ol (**6**, 300 mg, 1.5 mmol) dissolved in anhyd THF (60 mL) and absolute EtOH (60 mL) was added dropwise over 1 h to this bronze-colored Li solution. During this period, 4 g of Li (1 g every 15 min) was also added to keep the solution a deep bronze color. This mixture was stirred for 45–60 min while excess of liquid NH_3 (145 mL) was being collected in an attached three-neck round bottom flask. The excess NH_3 was added slowly to the reaction mixture over 50 min. During this time, absolute EtOH (110 mL) and an additional 4 g of Li (1 g every 15 min) was added. Fifteen minutes after these additions were completed, the color of the solution changed from bronze to blue to white. The NH_3 was allowed to evaporate overnight under a slow stream of Ar. Water (600 mL) was added, and the white solid was completely dissolved. This aqueous solution was extracted with $CHCl_3$ (3 × 500 mL). The organic layers were combined, and the solvent was removed under reduced pressure. The residue was acidified by refluxing in EtOH (25 mL) and conc. HCl (2.5 mL) for 1 h. The solution was allowed to cool, and the EtOH was removed under vacuum. An aqueous solution of 10% Na_2CO_3 (10 mL) was added and the result was extracted with $CHCl_3$ (3 × 10 mL) and butanol (3 × 10 mL). The organic phases were combined, dried (molecular sieves), and the solvents were removed. The residue was column chromatographed (E. Merck Silica 9385, EtOAc/hexane, 70:30) to yield 166 mg (70%) of pure (by TLC) **7**.

IR (neat): $v = 3400, 2910, 1700, 1440, 1300, 1140\ cm^{-1}$.

^1HNMR ($CDCl_3$): $\delta = 1.2$–2.8 (7H, m), 4.7 (1H, s), 4.1 (4H, t).

The characterization of this product was completed with the preparation of a dinitrophenylhydrazone derivative in the next procedure.

The Bis-2,4-dinitrophenylhydrazone of 2-Hydroxyhexahydroindan-4,7-dione:

A solution of 2,4-dinitrophenylhydrazine (0.2 g, 0.38 mmol) in conc. H_2SO_4 (1 mL) was freshly prepared. H_2O (0.75 mL) was added dropwise, with swirling and stirring until the solution was complete. To this solution was added 95% EtOH (5 mL), and the solution was filtered to remove any undissolved material. This 2,4-DNP solution was added to a solution containing 2-hydroxyhexahydroindan-4,7-dione (**7**; 30 mg, 15 mmol) in 95% EtOH (3 mL). Stirring was continued for 10 h. A solid formed and was filtered, washed with EtOH, and dried to yield 135 mg (68%) of orange product. It could be recrystallized from EtOH: mp 224–225 °C (dec).

IR (KBr): $v = 3450$ (OH), 3300 (—NH), 1580–1610 (—CN), 1500, 1330, 825, 740 cm^{-1}.

$C_{21}H_{20}N_8O_9$ (528.43)	calc.	C 47.73	H 3.82	N 21.80
	found	47.88	4.15	21.22

4,7-Dimethoxyindan (12):

A mixture of 4,7-dimethoxyindan-1-one (**11**)[9] (1 g, 5.2 mmol), $HClO_4$ (0.3 mL), and 10% Pd/C (0.4 g) in HOAc (15 mL) was hydrogenated under a pressure of 50 psi of H_2 for 2.5 h. The mixture was treated with excess NaOAc before removal of the catalyst by filtration through Celite. The filtrate was diluted with H_2O (60 mL) and then extracted with $CHCl_3$ (2 × 30 mL). The organic layer was separated, washed with H_2O and dried ($MgSO_4$). A yellow oil was obtained after the solvent was evaporated and solidified after storage at r.t. Recrystallization from Et_2O provided 723 mg (79%) of pure **12**: mp: 65–66 °C.[16]

^1HNMR ($CDCl_3$): $\delta = 6.62$ (s, 2H), 3.80 (s, 6H), 2.86 (t, 4H), 2.08 (m, 2H).

IR (KBr): $v = 3030, 2936, 2833, 1493, 1254, 1072, 961, 796, 709\ cm^{-1}$.

Indano-4,7-quinone (13):

4,7-Dimethoxy-2-indan (**12**; 672 mg, 4 mmol) was dissolved in MeCN (20 mL). Then, 5.5 g (10 mmol) of CAN in H_2O (5 mL) was added during a period of 5 min. During the addition, the color of the solution changed from colorless to brown, brownish-blue, and finally to yellow. The mixture was stirred for additional 25 min. After removal of most of the MeCN, the resultant mixture was diluted with H_2O (30 mL) and then extracted with EtOAc (30 mL and 2 × 20 mL). The organic portions were collected, combined, and dried ($MgSO_4$). Column chromatography (hexanes/EtOAc, 4:1) of the crude product afforded 350 mg (84%) of **13**: mp, 42–44 °C (from hexanes)(lit.[17] mp 42–43 °C).

^1HNMR ($CDCl_3$): $\delta = 6.67$ (s, 2H), 2.82 (t, 4H), 2.06 (m, 2H).

IR (KBr): $v = 3050, 2932, 2850, 1654, 1581, 1325, 1285, 1110, 850, 737\ cm^{-1}$.

4,7-Dibromoindan (19):

A mixture of Zn powder (9.0 g), 680 mg of $HgCl_2$, conc. HCl (0.6 mL) and H_2O (10 mL) was stirred for 5 min. The aqueous solution was decanted and the amalgamated Zn was covered with conc. HCl (30 mL) and H_2O (10 mL). As soon as 4,7-dibromoindan-1-one (2.6 g, 9 mmol) **(18)** (prepared from 2,5-dibromoaniline by the procedures of Bondinell, et al.[12] and Ishikawa, et al.[13]) was added, the reaction commenced. The mixture was refluxed until the starting material disappeared (about 8 h). The reaction was cooled to r.t., diluted with H_2O (30 mL) and then extracted with EtOAc (50 mL, 2 × 30 mL). The organic layers were separated, combined, washed with 10% aq NaOH solution, H_2O and brine, and dried ($MgSO_4$). Evaporation of the solvent gave 2.2 g (89%) of **19** (light yellow oil).

^1HNMR ($CDCl_3$): $\delta = 7.16$ (s, 2H), 3.04 (t, 4H), 2.10 (m, 2H).

IR ($CHCl_3$ film): $v = 3030, 2950, 1574, 1440, 1308, 1029, 845\ cm^{-1}$.

MS: m/z (%) = 278 (15), 276 (34), 274 (M^+, 22), 197 (10), 195 (28), 193 (17), 116 (100), 115 (51), 89 (11), 63 (21), 51 (8).

HRMS: m/z calcd. for $C_9H_8Br_2$ 273.8993, found 273.8987.

4,7-Dicyanoindan (20):
4,7-Dibromoindan (**19**, 828 mg, 3 mmol) and CuCN (810 mg, 9 mmol) were heated in anhyd DMF (5 mL) first at 100 °C for 4 h and then at 135 °C for 20 h. The mixture was poured into a solution of ammonia (40 mL, 15 weight %) in H_2O. The resulting mixture was extracted with CH_2Cl_2 (3 × 60 mL) and the impurities, which were insoluble in both phases, were removed by suction filtration through Celite. The organic portion was dried and concentrated. After column separation (hexanes/EtOAc, 4:1), 331 mg (66 %) of **20** was obtained: mp 157–158 °C (EtOAc).

^{1}H NMR ($CDCl_3$): $\delta = 7.52$ (s, 2 H), 3.20 (t, 4 H), 2.27 (m, 2 H).

IR (KBr): $\nu = 3084, 2919, 2848, 2226, 1610, 1467, 1409, 1309, 1252, 823$ cm^{-1}.

$C_{11}H_8N_2$ (168.20)	calc.	C 78.75	H 4.76	N 16.67
	found	78.52	4.83	16.59

Other solvents were tried in this procedure: the yields were 55.5 % using DMSO and 56.5 % with HMPA.

Indan-4,7-dicarboxylic Acid (21):
A mixture of 4,7-dicyanoindan (**20**, 202 mg, 1.2 mmol), 85 % KOH (319 mg, 4.8 mmol) and triethylene glycol (12 mL) was heated at 160 °C until the evolution of ammonia ceased (2 days). The resulting mixture was cooled and poured into 50 % aq H_2SO_4 (24 mL). A dark milky suspension was obtained. It was extracted with EtOAc (4 × 50 mL) and the organic layers were combined, washed with H_2O, and dried ($MgSO_4$). Evaporation of the solvent resulted in a dark residue out of which 156 mg (63 %) of **21** were isolated by column chromatography (THF/hexanes, 3:2): mp > 200 °C (dec) (H_2O).

^{1}H NMR (DMSO-d_6): $\delta = 9.68$ (s, 2 H, exchangeable), 7.78 (s, 2 H), 3.20 (t, 4 H), 2.01 (m, 2 H).

IR (KBr): $\nu = 3386$ (broad), 2947, 2891, 1681, 1488, 1409, 1294, 1044, 872, 758 cm^{-1}.

$C_{11}H_{10}O_4$ (206.20)	calc.	C 64.08	H 4.85
	found	64.19	5.12

8,8,9,9-Tetracyano-4,7-indanoquinodimethane (27):
Thionyl chloride (4 mL, 6.5 g, 55.1 mmol), was added to a dry flask containing **21** (103 mg, 0.5 mmol) and the mixture was warmed to 65 °C. 30 min later, the heterogeneous mixture was diluted with anhyd THF (4 mL). It became a homogenous solution and was refluxed for an additional 30 min. The excess $SOCl_2$ and THF were removed by vacuum distillation and a yellow oil of the diacid chloride was obtained. Anhyd $CHCl_3$ (10 mL), trimethylsilanecarbonitrile (0.6 mL, 0.45 g, 5.0 mmol), and *N*,*N*-dimethylaminopyridine (12 mg, 0.1 mmol) were added to the flask containing the diacid chloride. The resultant mixture was stirred at r.t. under N_2 for 5 h. Then, $POCl_3$ (0.4 mL, 0.66 g, 4.0 mmol) and anhyd pyridine (0.3 mL, 0.29 g, 4.0 mmol) were added. The dark mixture was refluxed for 24 h. After the reaction was cooled to r.t. H_2O (20 mL) was added and the result was extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were washed with H_2O, and dried ($MgSO_4$). After removal of the solvent, the remaining black oily residue was fractionated on a short silica gel column (EtOAc/hexanes, 4:1). Pressure was applied in order to speed the separation because the TCNQ, **27**, was unstable on the silica. 40 mg of the product were obtained (32 %): mp 194–195 °C (from EtOAc).

^{1}H NMR ($CDCl_3$): $\delta = 7.45$ (s, 2 H), 3.33 (t, 2 H), 2.26 (m, 2 H).

IR (KBr): $\nu = 3050, 2950, 2850, 2212, 1667, 1517, 1431, 1259, 1109, 809, 752$ cm^{-1}.

$C_{15}H_8N_4$ (244.25)	calc.	C 73.77	H 3.28	N 22.95
	found	73.81	3.32	22.84

5-Chloro-8,8,9,9-tetracyano-4,7-indanoquinodimethane (28):
Thionyl chloride (10 mL, 16.4 g, 140 mmol), was added to a dry flask containing 5-chloroindan-4,7-dicarboxylic acid **(26)** (700 mg, 2.8 mmol) (the latter was prepared in 6.3 % overall yield from tetrachloro-*o*-benzoquinone and cyclopentadiene following the procedure of Horner and Spietschka[11]) and the mixture was warmed to 65 °C. 30 min later, the heterogeneous mixture was diluted with anhyd THF (5 mL). It became a homogenous solution and was refluxed for additional 30 min. the excess $SOCl_2$ and THF were

X-ray Crystal Structure Analysis of 27:

Empirical formula	$C_{15}H_8N_4$		
Formula weight	244.25		
Temperature	293(2) K		
Wavelength	0.71073 A		
Crystal system	Monoclinic		
Space group	*C2/c*		
Unit cell dimensions	$a = 17.210(4)$ Å	$\alpha = 90°$	
	$b = 8.5490(10)$ Å	$\beta = 108.82(2)°$	
	$c = 17.827(3)$ Å	$\gamma = 90°$	
Volume	2482.6(8) Å^3		
Z	8		
Density (calculated)	1.307 Mg/m^3		
Absorption coefficient	0.082 mm^{-1}		
F(000)	1008		
Crystal size	0.34 × 0.58 × 0.76 mm		
Theta range for data collection	2.41 to 22.51°		
Index ranges	$0 \Leftarrow h \Leftarrow 11$	$0 \Leftarrow k \Leftarrow 9$	$-19 \Leftarrow l \Leftarrow 18$
Reflections collected	1156		
Independent reflections	1093 [R(int) = 0.0392]		
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	1093/0/173		
Goodness-of-fit on F^2	1.054		
Final R indices [l > 2s(l)]	$R^1 = 0.0551$	wR2 = 0.1570	
R indices (all data)	$R^1 = 0.0620$	wR2 = 0.1664	
Extinction coefficient	0.0033(12)		
Largest diff. peak and hole	0.212 and −0.184 e. Å^{-3}		

See Table 2 for bond lengths and angles.

removed by vacuum distillation and a yellow oil was obtained. Its IR spectrum showed a very strong adsorption at 1793 cm^{-1} for the diacid chloride carbonyl groups: the broad peak at 3000 cm^{-1} and strong peak at 1684 cm^{-1} of the starting material, **26**, had disappeared. Anhyd $CHCl_3$ (15 mL), trimethylsilanecarbonitrile (2.5 mL, 1.8 g, 18.7 mmol) and DMAP (45 mg, 0.4 mmol) were added to the flask containing the yellow oil (diacid chloride). The resultant mixture was stirred at r.t. under N_2 for 1 h. Then $POCl_3$ (1.5 mL, 2.5 g, 16.0 mmol) and anhyd pyridine (0.8 mL, 0.78 g, 10 mmol) were added. The dark mixture was refluxed for 24 h. After the reaction was cooled to r.t., H_2O (20 mL) was added and the result was extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were washed with H_2O, and dried ($MgSO_4$). After removal of the solvent, the remaining black oily residue was first fractionated on a short silica gel column (EtOAc/hexanes, 3:2) and the brown fraction was put on a second short column (EtOAc/hexanes, 4:1). Pressure was applied in order to speed the separation because the TCNQ, **28**, was unstable on the silica. 200 mg of product were obtained (30 %); mp: 135–136 °C (from EtOAc/hexanes).

^1H NMR ($CDCl_3$): $\delta = 7.51$ (s, 1 H), 3.40 (t, 2 H), 3.27 (t, 2 H), 2.26 (m, 2 H).

IR (KBr): $\nu = 3037, 2925, 2850, 2203, 1672, 1513, 1406, 1255, 1141, 1088, 1027, 883, 739$ cm^{-1}.

$C_{15}H_7ClN_4$ (278.70)		C	H	Cl	N
	calc.	C 64.63	H 2.61	Cl 12.40	N 20.11
	found	64.68	2.51	12.61	20.00

The work was supported by the National Science Foundation-Mississippi EPSCoR Project (Grants OSR 91-08767 and EPS 94-52857).

(1) Geddes, N. J.; Sambles, J. R.; Jarvis, D. J.; Parker, W. G.; Sandman, D. J. *Appl. Phys. Lett.* **1990**, *56*, 1916.

(2) Mallouk, T. E.; Lee, H. *J. Chem. Ed.* **1990**, *67*, 829.

(3) Metzger, R. M.; Panetta, C. A.; Heimer, N. E.; Bhatti, A. M.; Torres, E.; Blackburn, G. G.; Tripathy, S.; Samuelson, L. A. *J. Mol. Electronics* **1986**, *2*, 119.

(4) Torres, E.; Panetta, C. A.; Metzger, R. M. *J. Org. Chem.* **1987**, *52*, 2944.

(5) Miura, Y.; Torres, E.; Panetta, C. A.; Metzger, R. M. *J. Org. Chem.* **1988**, *53*, 439.

(6) Fang, Z. The Synthesis of New TCNQ Acceptors, Ph. D. Dissertation, The University of Mississippi, 1995.

(7) Torres, E.; Panetta, C. A.; Heimer, N. E.; Clark, B. J.; Hussey, C. L. *J. Org. Chem.* **1991**, *56*, 3737.

(8) Panetta, C. A.; Heimer, N. E.; Hussey, C. L.; Metzger, R. M. *Synlett* **1991**, 301.

(9) Coutts, R. T.; Malicky, J. L. *Can. J. Chem.* **1974**, *52*, 381.

(10) Yamaguchi, S.; Hanafusa, T. *Chem. Lett.* **1985**, 689.

(11) Horner, L.; Spietschka, W. *Justus Liebigs Ann. Chem.* **1953**, *579*, 159.

(12) Bondinell, W. E.; Chapin, F. W.; Girard, G. R.; Kaiser, C.; Krog, A. J.; Pavloff, A. M.; Schwartz, M. S.; Silvestri, J. S.; Vaidya, P. D.; Lam, B. L.; Wellman, G. R.; Pendleton, R. G. *J. Med. Chem.* **1980**, *23*, 506.

(13) Ishikawa, F.; Yamaguchi, H.; Saegusa, J.; Inamura, K.; Mimura, T.; Nishi, T.; Sakuma, K.; Ashida, S.-I. *Chem. Pharm. Bull.* **1985**, *33*, 3336.

(14) Metzger, R. M.; Laidlaw, R. K.; Torres, E.; Panetta, C. A. *J. Cryst. Spect. Res.* **1989**, *19*, 475.

(15) Iwasaki, F. *Acta Crystallogr.* **1971**, *B27*, 1360.

(16) This mp was 20 °C below that reported by Dallacker and Van Wersch for **12** (Dallacker, F.; Van Wersch, J. *Chem. Ber.* **1972**, *105*, 2565). However, since its spectral data was consistent with the structure, this product was used as the starting material for the preparation of indano-4,7-quinone (**13**). The latter was obtained in good yield and with a mp that was identical to that reported in reference 17.

(17) Baker, W.; McOmie, J. F. W.; Ulbricht, T. L. V. *J. Chem. Soc.* **1952**, 1825.