Synthesis of Substituted 7,7,8,8-Tetracyanoquinodimethanes

R. C. Wheland* and E. L. Martin

Central Research and Development Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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Twenty-one 7,7,8,8-tetracyanoquinodimethanes substituted with Me, Et, *i*-Pr, F, Cl, Br, I, OMe, OEt, O-*i*-Pr, O-*i*-Bu, O-*i*-C₅H₁₁, $-0-CH_2OCH_2-$, SMe, and CN groups are reported along with several TCNQ dianion salts.

The charge transfer complex between tetrathiofulvalene and tetracyanoquinodimethane (TTF.TCNQ) 1 shows high



metallic electrical conductivity from room temperature down to ~60 K.¹⁻⁶ This chemistry has already been expanded by the preparation of selenium,⁷ tetrathiomethoxy,⁸ dimethyl,² tetramethyl,⁹ benzo,^{10,11} and tetramethylene¹¹ analogs of tetrathiofulvalene. Syntheses are reported here of a rather complete series of substituted TCNQ's, extended TCNQ's, and related anion salts that may aid in the systematic analysis of charge transfer salt conductivity.¹²

Substituted 7,7,8,8-tetracyanoquinodimethanes were synthesized according to procedures disclosed or claimed in Du Pont patents.¹³ These syntheses most frequently started with the corresponding *p*-xylylene dihalide 3. *p*-Xylylene dihalides **3b-g**, **3j-l**, and **3p-s** were prepared by direct bischloromethylation of the appropriately substituted benzene, as shown in Scheme I. *p*-Xylylene dihalides, **3a**, **3h**, **3i**, **3m**, and **3n** were prepared according to Scheme II, starting with p-xylenes 7 or terephthalic acids 8. The terephthalic acids were converted first to their acid chlorides, then reduced to glycols, and treated with hydrogen halide to give p-xylylene dihalides. 1,4-Bis(bromomethyl)-2,5-di-



COOMe NC CH₂X CH₂CN NC 1) NaOMe 1) KOH NaCN (MeO)₂CO 2) HCl 3) Br2 2) CICN HC 7 2 CN ĊH2X ĊH2CN NC NC 3 COOMe 6 Z W^f Y Z Y Х Y Ζ 6a, OMe, H TCNQ(OMe) 3a, Br, OMe, H b, OMe, OMe TCNQ(OMe)₂ 2b, OMe, OMe **b**, Cl, OMe, OMe c, OMe, OEt^b TCNQ(OMe)(OEt) c, OMe, OEt^b OEt^ø Cl, OMe, С, d, OMe, O-i-Pr d, OMe, O-i-Pr d, Cl, OMe, 0-i-Pr TCNQ(OMe)(O-i-Pr) e, OMe, O-i-Bu^d e, Cl, OMe, O-i-Bu^d e, OMe, O-i-Bu^a TCNQ(OMe)(O-i-Bu) f, OMe, O-i-C₅H₁₁ 0-*i*-C₅H₁₁ f, OMe, O-i-C₅H₁₁ $TCNQ(OMe)(O-i-C_5H_{11})$ **f**, Cl, OMe, g, Cl, g, OEt, SMe OEt, SMe g, OÉt, SMe TCNQ(OEt)(SMe) TCNQCI h, Cl, Cl, h, Cl, H н **TCNQBr** Cl, Br, i, Br, Η i, Η i, Cl, Cl, Cl, j, Cl, TCNQCIMe Me Me Me j, k, Br, Me k, CL, Me **TCNQBrMe** Br, k, Br, Me L CL I. ι. Me **TCNQIMe** Me LI. Me m, Cl, m, Cl, Cl, Cl Cl TCNQCl₂ Cl, Br, Br TCNQBr₂ n. n, Br, Br Br, I, I TCNQI₂ о, о, Ι. I p, OMe, OCH₂Ph Cl, OMe, -OCH₂OCH₂-OMe, -OCH, OCH, -TCNQ(OMe)(OCH,OCH.) p, p, Cl, Me, q, Me, Me q, Me Me, Me TCNQ(Me)₂ q, TCNQ(Et)₂ CL, Et. Et Et Et. Et r, Et, r, r, s, Cl, *i*-Pr, *i*-Pr TCNQ(i-Pr). s, *i*-Pr, *i*-Pr s. i-Pr. *i*-Pr

Scheme I

^a Me = CH₃. ^b Et = C₂H₅. ^c *i*-Pr = CH(CH₃)₂. ^d *i*-Bu = CH₂CH(CH₃)₂. ^e *i*-C₅H₁₁ = CH₂CH₂CH(CH₃)₂. ^f Substituent W is hydrogen unless otherwise specified.



iodobenzene (30) was prepared by oxidative iodination of p-xylene¹⁴ followed by halogenation with bromine.

Once the *p*-xylylene dihalides had been obtained, the syntheses of TCNQ's 6a-s ran closely parallel, as summarized in Scheme I and detailed below. Reaction of *p*-xylylene dihalide 3 with sodium cyanide gives *p*-xylylene dicyanide 4. Treatment of 4 with sodium methoxide in ben-



zene-dimethyl carbonate establishes an equilibrium with dianion 9 which may be driven to completion by distilling off a benzene-methanol azeotrope. Distilling cyanogen chloride into the same pot affords a good yield of tetracyanodiacetate 5. Treatment of 5 with KOH or NaOH hydrolyzes and decarboxylates the ester groups to dianion 10. This dianion may be precipitated as air-sensitive bis(tetran-butylammonium) salt 12 but most frequently is converted to dihydro TCNQ 11 with hydrochloric acid. Dihydro TCNQ 11 need not be purified extensively and can be oxidized directly to TCNQ 6 with bromine.

The first step in TCNQF₄ 15, TCNQ(CN)₂ 16, and TCNDQF₈ precursor 17 syntheses involved initial nucleophilic displacement of aromatic halogen by the *tert*-butyl malononitrile anion (Scheme III). Thermolysis of 13 and 14 with loss of isobutylene, followed by oxidation, gave TCNQ's 15 and 16. Bis(tetra-*n*-butylammonium) salt 17 may be used for incorporation of the octafluorotetracyanodiphenoquinodimethane moiety in complexes by metathesis. Octafluorotetracyanodiphenoquinodimethane was not isolated as a neutral compound.¹⁵

tert-Butylmalononitrile (19) was prepared by condensing acetone with malononitrile¹⁶ and then adding mathylmagnesium bromide.



Experimental Section

The synthetic procedures described in this report are of a highly repetitive nature. TCNQ's **6a-s**, for example, were all prepared by the sequence of steps shown in Scheme I. Within this sequence actual experimental conditions vary sufficiently that four detailed examples are necessary in the Experimental Section: TCNQIME **61**, TCNQ(i-Pr)₂ **6s**, TCNQ(OMe)₂ **6b**, and TCNQCl₂ **6m**. The syntheses of the remaining TCNQ's in the **6a-s** series can then be described in terms of one of these four model compounds. Necessary data are summarized in Table I, the numbering of formulas corresponding to intermediates shown in Scheme I. Table I indicates melting points, yields, and conditions (by reference to the appropriate model TCNQ, **61**, **63**, **6b**, or **6m**, in the Experimental Section). Generally the crude product from each step was run directly into the next step after withdrawal of a small sample for purification and analysis.

Full spectral data for all TCNQ's in this paper are included in Table II. Frequently NMR spectra could not be taken of the TCNQ's as a result of low solubility complicated by radical anion formation with solvent impurities.

Those preparations requiring hydrogen halide-formaldehyde mixtures may generate the carcinogens, chloromethyl methyl ether and bis(chloromethyl) ether.¹⁷

2-Iodo-5-methyl-7,7,8,8-tetracyanoquinodimethane (61). A. 2,5-Bis(chloromethyl)-4-iodotoluene (31). A 200-g (0.92 mol) sample of p-iodotoluene was melted in the bottom of a flask held at 50°C in an oil bath, and then 80 g of powdered zinc chloride was added with mechanical stirring followed by 80 g (2.7 mol) of paraformaldehyde. Hydrogen chloride gas was blown over the surface of the reaction mixture. It became necessary to replace the oil bath with occasional ice bath cooling in order to control the temperature. Once the exotherm moderated, the mixture was heated to ~70°C and 4 g of zinc chloride plus 4 g (0.13 mol) of paraformaldehyde added every hour for the next 6-7 hr. The cooled reaction mixture was beaten to near homogeneity with 1 l. of methylene chloride. One liter of water was added and then solid sodium sulfite with stirring until the iodine color disappeared. The organic layer was separated, washed with 2×1000 ml of water, dried over magnesium sulfate, treated with decolorizing carbon, and filtered. Stripping on a rotary evaporator with periodic addition of hexane gave a slurry. Vacuum filtration gave 76 g of pink solid, that was recrystallized from toluene as 48.66 g (16%) of pale yellow needles, mp 139-144°C. The material was suitable for the next step: ¹H



^a Procedure similar to that for TCNQCl₂. ^b Procedure similar to that for TCNQ(OMe)₂. ^c Procedure similar to that for TCNQ(OMe)₂ except acetic acid not included in reaction mixture. ^a Procedure similar to that for TCNQICH₃. ^e Reflux 2,5-diiodo-*p*-xylene 8-10 hr with Br₂ in BrCH₂CH₂Br, recrystallize from BrCH₂CH₂Br. ^f DMF, ^cCF₃COOH, NaCN, 0^oC. ^e Procedure similar to that for TCNQ(*i*-Pr)₂. ^h Yields most frequently of crude material for next step. ^f Melting points generally of analytical sample. ^f See introduction to Experimental Section.

Table II
Tetracyanoquinodimethanes ^b

TCNQ	Мр, ℃	Ir (KBr), ^µ	¹ h nmr, ^a s	Parent mass spectrum	Yield,%
TCNQ(OMe), 6a	214-215	4.48	· · · · · · · · · · · · · · · · · · ·	234.0517	87
		6.20		(calcd 234.0541)	
		6.42		impurity at mass	
		6.48		250	
		8.03			
		8.87			
		10.03			
		11.65			
TCNQ(OMe) ₂ , 6b	300305	4.52		264.0593	83-98
		6.39	4.03,6 H,s	(calcd 264.0647)	
		6.55	6.45,2H,s		
		8.07			
		9.93			
		12.64			
TCNQ(OMe)(OEt), 6c	243-244	4.48		278.0781	96-98
		6.36	1.59,3 H,t	(calcd 278.0803)	
		6.49	4.03,3 H,s	impurity at mass 280,	
		8.05	4.25, 2 H, q	probably TCNQH ₂ (OMe)(OEt)	
		11.64	6.42,1 H,s		
			6.44,1 H,s		
TCNQ(OMe)(O-i-Pr), 6d	193-195	4.48		292.0933	93
		6.37	1.5,6 H,d		
		6.51	4.2,3 H,s	(calcd 292.0959)	
		8.05	~5.1, 1 H, m		
		8.67	6.7, 2 H, s		
		11.65			
TCNQ(OMe)(O-i-Bu), 6e	219-220	4.47	1.13,6 H,d	306.1099	52-98
		6.37	2.32,1 H,m	(calcd 306.1116)	
		6.48	3.93,2 H,d		
$TCNQ(OMe)(O-i-C_5H_{11}), 6f$		8.04	4.03, 3 H, s		
		10.06	6.43,1 H,s		
		11.63	6.45,1 H,s		
	228-230	4.49	0.97, d	320.1276	92
	dec	6.38	1.84, m	(calcd 320.1272)	
		6.52	4.02, s		
		8.04	4.19,t		
		8.68	6.44, S		
	000 000	11.07	6 06 1 TT -	204 0547	09.05
TCNQ(OEt)(SMe), 6g	232-233	4.48	6.80, I H, S	294.0047 (color 004.0575)	93-95
	aec	0.22	0.01, 1 H, S	(carca 294.0575)	
		0.07	4.28, 2 H, q		
		11.73	2.04, 3 11, 5		
montool sh	910-919	4 4 9	1.00, 3 H, L	222 0025	02_06
TCNQCI, on	210-212	4.40	(.2-(.(,111	(a) ad 238 0046)	93-90
		0.54		(Calcu 230.0040)	
		10.04			
		11.02			
MONOR - 6	203-204	4 4 8	74 - 78 m	281 9541	95
ICN&BI, 01	203-204	6 4 8	1.1 1.0, 11	(ca)cd 281 9541)	00
		6.57		Possible contamination	
		9.83		with	
		10.96		NC / H	
		12.00			
TCNQC1Me, 6i	260-265	4.48	2.69.3 H.s	252.0181	84-93
	nah	6.48	7.32.1 H.s	(calcd 252.0202)	
	ucc	9.77	7.61.1 H.s	·,	
		10.98			
	265 dec	4.48	2.67,3 H.s	295.9691	75
I CNQBrme, ok		6.50	7.35, 1 H, s	(calcd 295.9698)	
		9.89	7.86,1 H,s	· · ·	
		10.97			

Synthesis of Substituted 7,7,8,8-Tetracyanoquinodimethanes

		(Cont	inued)		
TCNQ	Мр, ℃	Ir (KBr), ⁴	¹ h nmr, ^a 6	Parent mass spectrum	Yield,%
TCNQICH ₃ , 61	285-287	4.48	8.22,1 H,s	343.9571	49
		6.53	7.36,1 H,s	(calcd 343.9760)	
		6.58	2.66,3 H,s		
		10.01			
		10.98			
TCNQCl ₂ , 6m	305 dec	4.47		271.9668	93-96
		6.50		(calcd 271.9656)	
		6.55			
		9.37			
		9.90			
TCNOBr. 6n	316-318	4 51		350 9644	. 04
rengbr ₂ , on	310-310 dec	4.51		(an) and (an) (an)	54
	uec	6.0		(carca 353.8041)	
		9.52			
		10.02			
		10.98			
$TCNQI_2, 60$	>348	4.52		455.8405	51
		6.56		(calcd 455.8372)	
		6.67		Possible contamination	
		9.63		with TCNQBrI	
		10.17		and	
		11.01		I	
TCNQ(OMe)(OCH ₂ OCH ₂), 6p	>400	4.50	4.03.3 H.s	292.0576	89
		6.40	5.12, 2 H, s	(calcd 292.0596)	
		6.56	5.42, 2 H, s	•	
		7.94	6.41, 1 H, s		
		9.66			
		10.54			
TCNQ(Me) ₂ , 6q	277-279	4.48	2.67,6 H,s	232.0738	80
		6.40	7.30,2 H,s	(calcd 232.0748)	
TCNO(Ft) 6r		6.53			
		9.67			
		10.33			
	174-175	11.05	1224+	260 1059	00.00
	114 110	6 43	1.5,5 H,C 30 9 H e	(a) ad 260 (1061)	92-98
		6.55	731Hs	(carcu 200.1001)	
		6.85	1.0, 1 11, 5		
		9.53			
		10.95			
		12.37			
$TCNQ(i-Pr)_2, 6s$	193-195	4.50	7.50,2 H,s	288.1371	86
		6.40	3.77, 2 H, m	(calcd 288.1371)	
		6.58	1.33, 12H, d	· ·	
		9.18			
		11.23			
$TCNQF_4$, 15	295-300	4.47		276.0034	72-85
		6.23		(calcd 276,0059)	
		7.45			
TCNO(CN) 14		10.23			
TCNQ(CN) ₂ , 16	>360	4.50		254.0344	78
		t.54		(calcd 254.0341)	
		0.00 10.09			
		11 03			
		(mineral oil)			
		(

Table II

^a Most proton NMR spectra were taken at 220 MHz using Fourier transform methods to enhance signal strength: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; values given in δ parts per million; all spectra in CDCl₃ except 6d (CD₃COCD₃) and 6r (CD₃CN). ^b Satisfactory analytical values (±0.4% for C, H, N) for every compound in table were included in original manuscript. Ed.

NMR (CDCl₃, Me₄Si) 3 H singlet δ 2.4, 2 H singlet 4.53, 2 H singlet 4.62, 1 H singlet 7.3, and 1 H singlet 7.8.

Recrystallization of a small sample from 1,2-dichloroethane gave white needles, mp 142-144°C.

Anal. Calcd for $C_9H_9Cl_2I$: C, 34.32; H, 2.88; Cl, 22.51; I, 40.29. Found: C, 34.97; H, 3.14; Cl, 22.24; I, 39.28; C, 34.94; H, 3.06; Cl, 22.12; I, 39.21.

B. 2,5-Bis(cyanomethyl)-4-iodotoluene (41). A 1.4-g (4.5 mmol) sample of 2,5-bis(chloromethyl)-4-iodotoluene (mp 137-146°C) was added to a mixture of 1 g (20 mmol) of sodium cyanide, 1.2 ml of water, and 2.8 ml of dioxane with magnetic stirring. The mixture thickened nearly to a gel over several days. Vacuum filtration, washing with water, sucking dry, and crystallizing from ethanol-acetone gave 0.69 g (52%) of white solid, mp 181-185°C, acceptable for use in the next step.

Anal. Calcd for $C_{11}H_9IN_2$: C, 44.62; H, 3.06; N, 9.46. Found: C, 44.82; H, 3.22; N, 9.01; C, 44.80; H, 3.26.

¹H NMR (CDCl₃, Me₂SO- d_6 -Me₄Si) 3 H singlet δ 2.4, 4 H singlet 3.9, 1 H singlet 7.4, 1 H singlet 7.9.

С. Dimethyl α,α,α',α'-Tetracyano-2-iodo-5-methyl-1,4phenylenediacetate (51). A three-neck 500-ml round-bottom flask was equipped with a N2 inlet, strong mechanical stirrer, steam bath, and distillation head. The reaction vessel was charged with 100 ml (1 mol) of dimethyl carbonate, 18 g (0.33 mol) of sodium methoxide, and 38.6 g (0.13 mol) of 2,5-bis(cyanomethyl)-4iodotoluene. The thick solution turned pink and cleared considerably on warming with a steam bath. Within several minutes, however, a yellow precipitate formed that only the most vigorous stirring kept from gelling. An additional 100 ml of benzene was added and the slurry heated to reflux. The mixture became so thick that several hundred more milliliters of benzene were added. After ~ 2 hr of refluxing, 100-200 ml of solvent was allowed to distil off with replacement by benzene. The reaction mixture was cooled to 0 to -10° C with a wet ice-acetone bath as 25 ml (~0.5 mol) of liquid cyanogen chloride was blown in on a nitrogen stream. The solution loosened up markedly and was stirred at room temperature overnight. Vacuum filtering the thick slurry gave solid that was later combined with additional solid from reducing the filtrate on a rotary evaporator. This solid was ground in a mortar and added to water with stirring. Vacuum filtration, grinding up again, adding to water with stirring, and vacuum filtering a second time gave 30 g of light green solid. This solid was taken up in methylene chloride, treated with decolorizing carbon and magnesium sulfate, and filtered. Stripping to a heavy slurry on a rotary evaporator, adding methanol, and filtering gave 20.7 g (34%) of white solid, softening 190°C, mp 203-207°C

Anal. Calcd for C₁₇H₁₁IN₄O₄: C, 44.18; H, 2.40; N, 12.12. Found: C, 44.01; H, 2.28; N, 12.43.

¹H NMR (CDCl₃, Me₄Si) 3 H singlet δ 2.5, 6 H doublet 4.0, 1 H singlet 7.7, 1 H singlet 8.2.

D. 2-Iodo-5-methyl-7,7,8,8-tetracyanoquinodimethane (61). Ten grams (0.022 mol) of dimethyl $\alpha, \alpha, \alpha', \alpha'$ -tetracyano-2-iodo-5methyl-1,4-phenylenediacetate was added with stirring to 14 g of potassium hydroxide (0.22 mol) in 200-300 ml of water under nitrogen. The clear yellow solution obtained after 15 min was acidified by slow addition of 30 ml (0.37 mol) of concentrated hydrochloric acid in 30 ml of water (foaming). The precipitate was vacuum filtered and washed with water. The damp precipitate was stirred with 200 ml of water and treated with excess bromine water. The resulting orange solid was filtered, ground with mortar and pestle, and treated with excess bromine water as before. Vacuum filtration gave brick red solid that was taken into 2000 ml of methylene chloride, treated with magnesium sulfate and decolorizing carbon, and filtered. Stripping this filtrate to a slurry of red solid on a rotary evaporator, filtering, dissolving in methylene chloride, treating with decolorizing carbon, and stripping again gave 3.65 g (49%) of dark red crystals, mp 283-287°C.

Anal. Calcd for $C_{13}H_5N_4I$: C, 45.38; H, 1.46; N, 16.28. Found: C, 45.36; H, 1.47; N, 16.02; C, 45.28; H, 1.52; N, 15.74.

Gradient sublimation of 2 g of this material at 170-190°C (0.01-0.05 mm) for several days gave a 1.79-g middle cut of spectacular purple lumps, mp 285-287°C. Anal. Found: C, 45.18; H, 1.45; N, 16.01; C, 45.18; H, 1.44; N, 16.00.

2,5-Diisopropyl-7,7,8,8-tetracyanoquinodimethane (6s). A. 1,4-Bis(chloromethyl)-2,5-diisopropylbenzene (3s). Into a 1-l., round-bottom flask fitted with mechanical stirrer, thermometer, condenser, and gas inlet tube were charged 243 g (1.5 mol) of p-diisopropylbenzene, 120 g (4.0 mol) of paraformaldehyde, and 150 g of pulverized anhydrous zinc chloride. A rapid stream of dry hydrogen chloride was passed into the vigorously stirred reaction mixture at $70 \pm 2^{\circ}$ C. The temperature was increased to $80 \pm 1^{\circ}$ C for 1 hr. It was necessary to add 50 ml of cyclohexane toward the end of the reaction in order to stir the reaction mixture. The reaction mixture was cooled, and the solid dichloride was collected and washed with cold water and finally with petroleum ether. The filter cake was taken up in methylene chloride, and the solution was washed twice with dilute hydrochloric acid and once with water. The resulting solution was treated with decolorizing charcoal and anhydrous magnesium sulfate, and the filtrate was concentrated until crystals began to separate. Anhydrous ether was added and the concentration continued until most of the methylene chloride had been displaced. After cooling, the crystals were collected and washed with cold methylene chloride followed by a washing with petroleum ether. After drying, there was obtained 300-318 g (80-82%) of dichloride, mp 129-131°C.

Anal. Calcd for C₁₄H₂₀Cl₂: C, 64.87; H, 7.78; Cl, 27.36. Found: C, 64.87; H, 7.81; Cl, 27.56.

B. 1,4-Bis(cyanomethyl)-2,5-diisopropylbenzene (4s). Into a mechanically stirred suspension of 11 g of finely powdered sodium cyanide in 55 ml of dimethyl sulfoxide was added in small portions 25.4 g (0.1 mol) of 1,4-bis(chloromethyl)-2,5-diisopropylbenzene. The temperature was maintained at $45-50^{\circ}$ C by controlling the rate of addition of the dichloride and by means of external cooling. The mixture was stirred for an additional 1-5 hr at 50° C and diluted to 500 ml with cold water, the dinitrile was collected and washed with water, and the washed filter cake was dissolved in about 200 ml of methylene chloride. After drying, the filtrate was concentrated until crystals separated, ether was added, and the concentration was continued with subsequent additions of ether until the solvent was essentially ether. The yield of granular crystals melting at 188-190°C was 74 g (100%).

Anal. Calcd for C₁₆H₂₀N₂: C, 79.95; H, 8.39; N, 11.66. Found: C, 79.67; H, 8.31; N, 11.79.

C. Dimethyl $\alpha, \alpha, \alpha', \alpha'$ -Tetracyano-2,5-diisopropyl-1,4-phenylenediacetate (5s). A mechanically stirred mixture of 24 g (0.1 mol) of 1,4-bis(cyanomethyl)-2,5-diisopropylbenzene, 100 ml (1.0 mol) of dimethyl carbonate, and 14 g (0.2 mol) of sodium methoxide was stirred until the exothermic reaction (to 50°C) had subsided and 50 ml of benzene was added. In order to stir the thick reaction mixture, it was necessary to add an additional 50 ml of dimethyl carbonate and 50 ml of benzene. The thick reaction mixture was stirred on total reflux for 3 hr, and then the benzenemethanol binary was distilled during the course of 1 hr and the distillation was continued for an additional 1 hr. After cooling to 5°C, 16 ml of cyanogen chloride was distilled into the reaction mixture at 5-10°C. The nearly colorless reaction mixture was warmed slowly to 50°C during the course of about 1 hr. After stirring overnight at room temperature, the reaction mixture was evaporated under reduced pressure to dryness by means of a Rinco evaporator. The crude solid mixture of dimethyl $\alpha, \alpha, \alpha', \alpha'$ -tetracyano-2,5-diisopropyl-1,4-phenylenediacetate and sodium chloride was stirred with cold water in a Waring Blendor. The tetracyanodiacetate was collected, washed with water, and, after air drying, dried over phosphorus pentoxide under reduced pressure. The yield of nearly colorless material was 39 g (96%). Crystallization from methylene chloride-ether gave colorless crystals, mp 228-229°C.

Anal. Calcd for $C_{22}H_{22}N_4O_4$: C, 65.00; H, 5.46; N, 13.78. Found: C, 64.76; H, 5.18; N, 13.86; C, 64.79; H, 5.27; N, 13.74.

D. 2,5-Diisopropyl-7,7,8,8-tetracyanoquinodimethane (6s). To an aqueous solution of 120 ml of 5% potassium hydroxide warmed to about 70°C was added 10.0 g of dimethyl $\alpha, \alpha, \alpha', \alpha'$ -tetracyano-2,5-diisopropyl-1,4-phenylenediacetate, and the solution was stirred for about 1 min, whereupon a homogeneous solution was obtained. The solution was acidified carefully by the addition of 6 N hydrochloric acid, and the solid was treated with a slight excess of bromine water (positive test with starch-potassium iodide paper).

The bright yellow precipitate was collected, washed with cold water, and dissolved in methylene chloride, and the solution was concentrated to a small volume. Anhydrous ether was added slowly whereupon the $TCNQ(i-Pr)_2$ separated as bright yellow crystals during continued concentration. After cooling, the crystals were collected, washed with ether, and dried. The yield was 6.1 g (86%) of bright yellow crystals, mp 193–195°C.

Anal. Calcd for $C_{18}H_{16}N_4$: C, 74.97; H, 5.59; N, 19.43. Found: C, 75.03; H, 5.66; N, 19.71.

2,5-Dimethoxy-7,7,8,8-tetracyanoquinodimethane (6b). A. 1,4-Bis(chloromethyl)-2,5-dimethoxybenzene (3b). A slow

stream of dry hydrogen chloride was passed into a mechanically stirred mixture of 82 g (0.6 mol) of p-dimethoxybenzene, 45 g (1.5 mol) of paraformaldehyde, 100 ml of glacial acetic acid, and 200 ml of concentrated hydrochloric acid at 50-55°C for a period of 2 hr. It was necessary to cool the reaction mixture externally until the exothermic reaction ceased. Crystals of the dichloride started to separate within about 15 min after the start of the reaction, and at the end of 2 hr, a crystalline, thick reaction mass was obtained. The reaction product was collected by suction filtration and washed with about 21. of cold water. The moist filter cake was dissolved in about 21. of methylene chloride and the organic layer was treated with decolorizing charcoal and anhydrous magnesium sulfate. The resulting colorless filtrate was concentrated to a thick paste of colorless crystals, the mixture was cooled to 0°C, and the dichloride was collected, washed with cold methylene chloride, and, after air drying, dried under reduced pressure over phosphorus pentoxide-potassium hydroxide. The yield of colorless crystals, mp 167-169°C, was 90-92 g (64-65%).

Anal. Calcd for C₁₄H₁₂O₂Cl₂: C, 51.08; H, 5.15; Cl, 30.16. Found, C, 50.88; H, 5.32; Cl, 30.27; C, 50.83; H, 5.24.

B. 1,4-Bis(cyanomethyl)-2,5-dimethoxybenzene (4b). To a mechanically stirred suspension of 35 g (0.7 mol) of sodium cyanide in 200 ml of dimethyl sulfoxide was added in small portions 71 g (0.3 mol) of 2,5-dimethoxy-1,4-xylylene dichloride. The temperature was maintained at 50°C by controlling the rate of addition of the dichloride and by means of external cooling. The reaction mixture was maintained at 50°C for an additional 1 hr after the addition of the dichloride was completed and then the temperature was increased to 85°C for 5 min. After cooling to about 40°C. the reaction mixture was diluted to a volume of about 1 l., and the precipitated dinitrile was collected and washed with water until essentially neutral. The moist filter cake was dissolved in about 21. of methylene chloride, and the organic layer was dried and concentrated until a thick paste of crystals was obtained. After cooling to room temperature, the dinitrile was collected and washed in turn with methylene chloride and ether. After drying under reduced pressure over phosphorus pentoxide at 50°C, there was obtained 51 g (81%) of 2,5-dimethoxy-1,4-xylylene dicyanide: mp 198-200°C; ¹H NMR (CDCl₃, Me₄Si) 4 H singlet δ 3.7, 6 H singlet 3.9, 2 H singlet 7.0.

Anal. Calcd for $C_{12}H_{12}O_2N_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.53; H, 5.35; N, 13.00.

C. Dimethyl $\alpha, \alpha, \alpha', \alpha'$ -Tetracyano-2,5-dimethoxy-1,4-phenylenediacetate (5b). A mechanically stirred mixture of 43 g (0.2 mol) of 2,5-dimethoxy-1,4-xylylene dicyanide, 250 ml (2.5 mol) of dimethyl carbonate, and 27 g (0.5 mol) of sodium methoxide was warmed to 70°C whereupon a spontaneous reaction occurred, the temperature increased to 80°C, the sodium methoxide partially dissolved, and after a few minutes a solid began to precipitate. About 50 ml of benzene was added and the reaction mixture was refluxed for 3 hr. The benzene-methanol binary was removed by distillation during the course of 1 hr, additional benzene being added as required. The suspension of the disodium derivative of dimethyl α, α -dicyano-2,5-dimethoxy-1,4-phenylenediacetate was cooled to 5°C and 35 ml of cyanogen chloride was distilled into the reaction mixture at 5-10°C. After a slight exothermic reaction, the temperature was increased to 65°C during the course of about 2 hr. After stirring overnight at room temperature, the temperature of the reaction mixture was increased to 50°C, and the reaction mixture was evaporated to dryness in a Rinco evaporator under reduced pressure in a bath at 50-60°C. The solid residue of dimethyl $\alpha, \alpha, \alpha', \alpha'$ -tetracyano-2,5-dimethoxy-1,4-phenylenediacetate and sodium chloride was stirred in a Waring Blendor with cold water. The crude ester was collected and washed with cold water, and the moist filter cake was dissolved in methylene chloride. The organic layer was treated with decolorizing carbon and anhydrous magnesium sulfate, and the filtrate was concentrated until crystals began to separate. Addition of ether precipitated the tetracyanodiacetate. After cooling to -5° , the colorless crystals were collected, washed with cold ether, and dried. The yield of compound melting at 200-201°C was 72 g (95%).

Anal. Calcd for $C_{18}H_{14}O_6N_4$: C, 56.54; H, 3.69; N, 14.66. Found: C, 56.62; H, 3.85; N, 14.60.

¹H NMR (CDCl₃, Me₄Si) 2 H singlet δ 7.3 and 12 H singlet 4.0.

D. 7,7,8,8-Tetracyano-2,5-dimethoxyquinodimethane (6b). To 3.8 g (0.1 mol) of dimethyl $\alpha, \alpha, \alpha', \alpha'$ -tetracyano-3,5-dimethoxy-1,4-phenylenediacetate was added 40 ml of 10% aquous potassium hydroxide solution and the mixture was stirred until a homogeneous solution was obtained. The solution was acidified by the addition of 6 N hydrochloric acid, and a slight excess of bromine water was added to the suspension of the dihydro compound. The resulting red product was collected, washed with cold water, and dissolved in about 600 ml of methylene chloride. The organic layer was dried, treated with decolorizing charcoal, and concentrated to a small volume, whereupon deep red crystals of TCNQ(OMe)₂ separated. The crystals were collected, washed with methylene chloride, and dried. The yield was 2.2–2.6 g (83–98%), mp 300–305°C dec.

Anal. Calcd for $C_{14}H_8O_2N_4$: C, 63.63; H, 3.05; N, 21.20. Found: C, 63.32; H, 2.85; N, 21.22.

2,5-Dichloro-7,7,8,8-tetracyanoquinodimethane (6m). A. 1,4-Bis(hydroxymethyl)-2,5-dichlorobenzene. Into a 3-l., fournecked flask fitted with reflux condenser, mechanical stirrer, thermometer, and dropping funnel was added 17 g (0.45 mol) of LiAlH₄ followed by the addition of 300 ml of anhydrous ether. All reactions were carried out under an atmosphere of nitrogen. The stirrer was started and the mixture was refluxed for 0.5 hr. The steam was turned off and a solution of 68 g (0.25 mol) of 2,5-dichloroterephthaloyl chloride (prepared from 2,5-dichloroterephthalic acid and thionyl chloride in the presence of a few drops of dimethylformamide) in 600 ml of anhydrous ether was added dropwise over the course of 1 hr. The reaction mixture refluxed gently at this rate for an additional period of 1 hr. Ethyl acetate (30 ml) was added dropwise followed by the careful addition of 35 ml of water. Hydrogen evolution usually ceased before the addition of the water was complete. A solution of 30 ml of concentrated hydrochloric acid and 400 ml of water was added and the ether was evaporated in a stream of nitrogen while stirring vigorously at 20-25°C. To the resulting gray suspension of the glycol was added about 100 ml of concentrated hydrochloric acid and the mixture was warmed to 50°C. The reaction mixture was filtered, and the filter cake was washed first with dilute hydrochloric acid, then with water until the washings were neutral. The yield of colorless crystals melting at 198-200°C was 52 g (99%). Crystallization from methanol-ether did not change the melting point.

Anal. Calcd for C₈H₈O₂Cl₂: C, 46.40; H, 3.90. Found: C, 46.69; H, 3.77.

B. 1,4-Bis(chloromethyl)-2,5-dichlorobenzene (3m). Replacement of the hydroxyl groups in 1,4-bis(hydroxymethyl)-2,5-dichlorobenzene requires extremely vigorous conditions, but by heating the glycol with hydrogen chloride and hydrochloric acid, an essentially quantitative yield of dichloride was obtained.

A mixture of 100 g (0.49 mol) of 1,4-bis(hydroxymethyl)-2,5-dichlorobenzene, 400 ml of concentrated hydrochloric acid, and 100 g of hydrogen chloride was heated in a bomb with agitation at 120° C for 8 hr. After cooling, the tube was vented and the solid dichloride was collected, washed with water, and dissolved in methylene chloride. After the methylene chloride layer was dried, the solution was concentrated until crystals began to separate. Ether was added slowly to displace the methylene chloride. After cooling thoroughly, the crystals were collected, washed with cold ether, and dried. An analytical sample crystallized in this manner melts at 98– 100°C.

Anal. Calcd for C₈H₆Cl₄: C, 39.38; H, 2.48; Cl, 58.14. Found: C, 39.41, H, 2.41; Cl, 57.95.

¹H NMR (CDCl₃, Me₄Si) 2 H singlet δ 7.6, 4 H singlet 4.6.

C. 1,4-Bis(cyanomethyl)-2,5-dichlorobenzene (4m). Sixteen unsuccessful attempts were made to prepare the dinitrile from the dichloride by the usual procedures. If hydrogen cyanide is not present, intractable products are obtained. The following procedure gave the desired compound in excellent yield.

Into a 500-ml three-necked flask fitted with mechanical stirrer, thermometer, and stopper was charged 210 ml of dimethyl sulfoxide and 29 g (0.6 mol) of finely powdered sodium cyanide was added to the stirred reaction mixture. After cooling to 20°C, 35 ml of liquid hydrogen cyanide was added slowly, the resulting mixture was cooled to 12°C, and 49 g (0.2 mol) of 1,4-bis(chloromethyl)-2,5-dichlorobenzene was added in one portion. The reaction mixture was stirred at 14-16°C for 0.5 hr, then the temperature was allowed to increase slowly to 20-22°C during about 1 hr. The reaction mixture was diluted to about 1500 ml with cold water, and the precipitate was collected and washed with cold water until the washings were neutral. The moist filter cake was dissolved in about 1500 ml of methylene chloride at the reflux temperature, and the organic layer was separated, treated with decolorizing charcoal, and dried with anhydrous magnesium sulfate. The nearly colorless filtrate was concentrated to a thick paste of colorless crystals. After cooling in ice, the crystals were collected and washed in turn

with cold methylene chloride, ether, and pentane. After drying at 60° C (10–15 mm) over phosphorus pentoxide, the yield was 40.5–43.6 g (90–96%). The compound melts at 184–186°C.

Anal. Calcd for $C_{10}H_6N_2Cl_2$: C, 53.36; H, 2.69; N, 12.45; Cl, 31.50. Found: C, 53.49; H, 2.47; N, 12.16; Cl, 31.40.

¹H NMR (CDCl₃-CF₃COOH, Me₄Si) 2 H singlet δ 7.7, 4 H singlet 4.0.

D. Dimethyl $\alpha, \alpha, \alpha', \alpha'$ -Tetracyano-2,5-dichloro-*p*-phenylenediacetate (5m). Into a jacketed Waring blender were charged 45 g (0.02 mol) of 1,4-bis(cyanomethyl)-2,5-dichlorobenzene, 28 g of sodium methoxide, and a mixture of 225 ml of dimethyl carbonate and 75 ml of dried benzene. The stirrer was started and as soon as the exothermic reaction had ceased, the reaction mixture was heated to gentle reflux. All operations were carried out under an atmosphere of nitrogen. It was necessary to add additional benzene (about 150-200 ml) in order to obtain a mixture that could be stirred. The reaction mixture was stirred at gentle reflux for a period of about 3 hr, then the binary of methanol and benzene was allowed to distil during the course of about 1 hr. The reaction mixture was cooled to 20°C and 30-32 ml of cvanogen chloride was distilled into the stirred mixture, the temperature being maintained at 20°C during the addition of the cyanogen chloride and for an additional 0.5 hr. The temperature was gradually increased to 35-40°C during the course of about 1.5 hr and the orange-colored suspension was transferred to a 2-l. round-bottom flask and evaporated to drvness on a Rinco evaporator in a bath at 70-80°C. The resulting solid was scraped from the walls of the flask, transferred to a funnel, and washed with cold water until the washings were essentially colorless. The moist filter cake was dissolved in ca. 450-500 ml of methylene chloride, the aqueous layer was separated, and the organic layer was dried with anhydrous magnesium sulfate and treated with decolorizing charcoal. The resulting reddish-orange filtrate was stirred with a few grams of aluminum oxide (Woelm neutral). The resulting light yellow filtrate was concentrated until crystals began to separate, then ether was added so as to maintain a constant volume. The tetracyano-p-phenylenediacetate separated as colorless crystals. After cooling in ice the crystals were collected and washed with -40 to -30° C ether until the washings were colorless, then with pentane. The yield of dried product melting at 186-187°C was 53.3-63.3 g (68-80%). Crystallization from methylene chloride-ether gave colorless crystals melting at 187-189°C. A total of 20 runs (9 at low yield, 11 at the above indicated range) were made.

Anal. Calcd for $C_{16}H_8O_4N_4Cl_2$: C, 49.13; H, 2.06; N, 14.32; Cl, 18.13. Found: C, 48.94; H, 2.09; N, 13.97; Cl, 18.63.

¹H NMR (CDCl₃, Me₄Si) 2 H singlet δ 8.1, 6 H singlet 4.1.

E, 2,5-Dichloro-7,7,8,8-tetracyanoquinodimethane (6m). To a solution of 39.1 g (0.1 mol) of dimethyl $\alpha, \alpha, \alpha', \alpha'$ -tetracyano-2,5dichloro-p-phenylenediacetate in 125 ml of dioxane at 70-75°C was added, slowly and with swirling, 400 ml of a 10% aqueous potassium hydroxide solution at 70-75°C. (The reaction is very exothermic at the start and the alkali solution must be added slowly and with care to prevent boil over.) The addition of the alkali required about 1.5 min and the temperature of the solution was about 75°C. After stirring for an additional period of 2 min, the solution was cooled rapidly in a mixture of ice-salt to 20-25°C and about 75 ml of 6 N hydrochloric acid was added slowly with stirring. The mixture was cooled to 10-12°C and transferred to a 3-l. beaker and a few pieces of ice were added. The solution was acidified by the dropwise addition of 3 N hydrochloric acid and an excess of bromine water was added. The resulting bright yellow suspension of the tetracyanoquinodimethane was warmed rapidly to 40°C on a steam bath and stirred for 0.5 hr at this temperature. The amount of bromine water added should be sufficient to produce a red coloration to the aqueous solution. Otherwise only part of the dihydrotetracyanoquinodimethane is oxidized. The bright yellow precipitate was collected by filtration and washed with cold water until the washings were colorless and free of bromine and bromide ion. The moist filter cake was divided into four portions and one portion was dissolved in about 3.5-4.0 l. of refluxing methylene chloride. The methylene chloride solution was transferred to another 5-l. flask, the solution was dried with anhydrous magnesium sulfate, and the filtrate was concentrated using two 3-l. flasks. The methylene chloride was recovered for use in purifying the other portions of the filter cake. Crystals of the compound separated during the concentration and the process was continued to a small volume. The yellow-orange crystalline product was collected and washed twice with methylene chloride and several times with ether. The yield of TCNQCl₂ was 25.4-26.2 g (93-96%)

Anal. Calcd for C₁₂H₂N₄Cl₂: C, 52.78; H, 0.74; N, 20.52; Cl, 25.97.

Found: C, 52.75; H, 0.63; N, 20.65; Cl, 25.93; C, 52.51; H, 0.60; N, 20.68.

tert-Butylmalononitrile (19). A solution of 159 g (1.5 mol) of isopropylidenemalononitrile¹⁶ in 200 ml of anhydrous benzene was added to 550 ml (1.6 mol) of 3 M methylmagnesium bromide in diethyl ether at 30–35°C under an atmosphere of nitrogen. The mixture was stirred at 45–47°C for 1 hr and poured onto excess ice. The mixture was made faintly acidic with 20% sulfuric acid. The aqueous layer was extracted once with 1:1 ether-benzene. The combined organic layers were washed twice with water, made faintly acidic with dilute hydrochloric acid, and washed twice with saturated sodium chloride solution. After drying with anhydrous magnesium sulfate and concentration under reduced pressure, the residue was distilled, giving 136 g (75%) of tert-butylmalononitrile, bp 80–85°C (7 mm), as a waxy solid that melted at about 80°C: ¹H NMR (CDCl₃, Me₄Si) 9 H singlet δ 1.3, 1 H singlet 3.6.

Anal. Calcd for C₇H₁₀N₂: Č, 68.81; H, 8.25; N, 22.94. Found: C, 68.66; H, 8.40; N, 22.73.

2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (15). A. 2,3,5,6-Tetrafluoro-1,4-bis(tert-butyldicyanomethyl)benzene (13). To a magnetically stirred suspension of 2.88 g (0.12 mol) of sodium hydride in 30 ml of glyme was added a solution of 15 g (0.12 mol) of tert-butylmalononitrile in 15 ml of glyme. The addition was carried out at 10-15°C under an atmosphere of nitrogen. To the resulting homogeneous solution was added 9.3 g (0.05 mol) of hexafluorobenzene (20) and the reaction mixture was heated to reflux. After about 2 hr, a white solid began to precipitate and appeared complete after about 12-16 hr. Most of the glyme was removed by distillation under reduced pressure, the reaction mixture was diluted with water, and the precipitate was collected, washed until neutral with water, then washed with methanol until the washings were colorless, and finally washed with ether. The yield of nearly colorless to light yellow 2,3,5,6-tetrafluoro-1,4-bis(tertbutyldicyanomethyl)benzene (13) was 15.7 g (81%). Colorless crystals, mp 295-300°C dec, were obtained after crystallization from a large volume of acetone.

Anal. Calcd for $C_{20}H_{18}N_4F_4$: C, 61.53; H, 4.65; N, 14.35; F, 19.47. Found : C, 61.58; H, 4.61; N, 14.47; F, 19.44.

2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane R. (15). Diphenyl ether (350 ml) was heated to reflux with stirring under an atmosphere of nitrogen and 7.8 g (0.02 mol) of 2,3,5,6tetrafluoro-1,4-bis(tert-butyldicyanomethyl)benzene (13)was added rapidly in one portion. The resulting solution was heated to reflux for 3.0-3.5 min, cooled with air to 195°C, then cooled to 40°C with cold water. An equal volume of ether was added followed by the addition of 100 ml of 4% sodium bicarbonate solution. The resulting mixture was shaken vigorously, and the organic layer was extracted with three 30-ml portions of 1% sodium bicarbonate solution. The combined aqueous layers were filtered and extracted once with ether. To the resulting aqueous solution was added 7.5 g of potassium acetate and 5 ml of acetic acid. Bromine water was added until a positive test for free bromine was obtained, the precipitated TCNQF4 was filtered and washed with water, and the moist filter cake was dissolved in about 2.5 l. of methylene chloride at 25°C. The aqueous layer was separated, the organic layer was treated with anhydrous magnesium sulfate and decolorizing charcoal, and the clear, bright yellow filtrate was concentrated until a thick paste of yellow crystals of TCNQF4 was obtained. The crystals were collected and washed with cold methylene chloride followed by a wash with ether. The yield of yellow crystals was 4.0-4.7 g (72-85%), mp 295-300°C dec.

Anal. Calcd for C₁₂N₄F₄: C, 52.20; H, 0.00; N, 20.29; F, 27.52. Found: C, 52.02; H, 0.00; N, 20.17; F, 27.43.

2,5-Dicyano-7,7,8,8-tetracyanoquinodimethane (16). A. 2,5-Dicyano-1,4-bis(tert-butyldicyanomethyl)benzene (14). To a suspension of 1.68 g (0.07 mcl) of sodium hydride in 10 ml of glyme was added a solution of 5.91 g (0.07 mcl) of tert-butylmalononitrile in 15 ml of glyme at 10°C. To the resulting solution was added 5.91 g (0.3 mcl) of 2,5-dichloroterephthalonitrile (21) and the reaction mixture was refluxed with stirring under an atmosphere of nitrogen for 20 hr. Most of the glyme was removed by evaporation under reduced pressure, the residue was diluted with water, and the solid material was collected, washed neutral with water, then with methanol until the washings were colorless, and finally with ether. The yield of nearly colorless crystals of 14, mp 265°C dec, was 8.6 g (78%). Crystallization of a small portion from methylene chloride gave colorless crystals.

Anal. Calcd for C₂₂H₂₀N₆: C, 71.72; H, 5.47; N, 22.81. Found: C, 71.39; H, 5.31; N, 22.58.

B. 2,5-Dicyano-7,7,8,8-tetracyanoquinodimethane (16). To

150 ml of diphenvl ether at 230°C was added rapidly in one portion 1.3 g of 2,5-dicyano-1,4-bis(tert-butyldicyanomethyl)benzene (14). The mixture was stirred at this temperature for 3 min, cooled rapidly to 40°C, and diluted with an equal volume of ether and 100 ml of 1% sodium bicarbonate was added. The organic layer was extracted with 100 ml of a 1% sodium bicarbonate solution and with two 15-ml portions of 1% sodium bicarbonate and the combined aqueous solutions were filtered. The deep red solution was neutralized with hydrochloric acid and bromine water was added to the resulting solution until the anion radical disappeared and a brownish-yellow precipitate was obtained. The crude TCNQ(CN)2 was isolated by filtration (very slow), washed with water, and dried. The crude TCNQ(CN)₂ was dissolved in a large volume of hot acetonitrile and the filtered solution was concentrated to a small volume under reduced pressure. The deep yellow crystals were collected, washed with ether, and dried.

Anal. Calcd for C14H2N6: C, 66.14; H, 0.79; N, 33.06. Found: C, 65.94; H, 0.79; N, 33.19.

Bis(tetra-n-butylammonium)-2,2',3,3',5,5',6,6'-octafluoro-7,7,7',7'-tetracyanodiphenoquinodimethanide (17). A solution of 1 g of 18 and 2 g of sodium bicarbonate in 700 ml of water was pressure filtered under N2 into 3 g of tetra-n-butylammonium bromide in 100 ml of water. The precipitate was pressure filtered under N₂ the next day and blown dry, 1.97 g (94%) of light tan powder, mp, 197-200°C.

Anal. Calcd for C₅₀H₇₂N₆F₈: C, 66.06; H, 7.98; N, 9.24. Found: C, 66.21; H, 7.99; N, 9.30; C, 66.07; H, 7.94; N, 9.24.

 $^{19}\mathrm{F}$ NMR (CH₂Cl₂, CFCl₃) multiplets 144.4 and 147.9 ppm downfield from CFCl₃.

Bis(tetra-n-butylammonium)-7,7,8,8-tetracyanoquinodimethanide (12). A solution of 3 g of sodium hydroxide in 100 ml of water was stirred under nitrogen with 3 g of dimethyl $\alpha, \alpha, \alpha', \alpha'$ -tetracyano-1,4-phenylenediacetate (5, Y = W = Z = H). The clear orange solution that resulted after about 1 hr was treated with decolorizing carbon and pressure filtered under nitrogen into 10 g of tetra-n-butylammonium bromide in 300 ml of water. Washing with water and blowing dry under nitrogen for about 1 week affords 6.22 g (95%) of light tan solid, that turns deep orange on prolonged exposure to air, mp ~100°C dec. Store under nitrogen.

Anal. Calcd for C44H76N6-1/2H2O: C, 75.70; H, 11.12; N, 12.04. Found: C, 76.12; H, 10.77; N, 12.14; C, 76.09; H, 10.69; N, 11.96.

¹H NMR (CDCl₃, Me₄Si) δ 0.5-2.0, m, 28 H; 2.9-3.4, m, 8 H; 7.3, s, intensity decreases on storage relative to n-Bu₄N absorptions.

Registry No.-2b, 150-78-7; 2c, 5076-72-2; 2d, 20744-02-9; 2e, 54929-09-8; 2f, 20744-00-7; 2g, 33733-78-7; 2j, 106-43-4; 2k, 106-38-7; 21, 624-31-7; 2p, 6630-18-8; 2q, 106-42-3; 2r, 105-05-5; 2s, 100-18-5; 3a, 46045-95-8; 3b, 3752-97-4; 3c, 56403-19-1; 3d, 56403-20-4; 3e, 56403-21-5; 3f, 56403-22-6; 3g, 56403-23-7; 3h, 10221-08-6; 3i, 56403-24-8; 3j, 56403-25-9; 3k, 56403-26-0; 3l, 56403-27-1; 3m, 50987-90-1; 3n, 56403-28-2; 3o, 56403-29-3; 3p, 56403-30-6; 3q, 6298-72-2; 3r, 56403-31-7; 3s, 28782-17-4; 4a, 56403-32-8; 4b, 38439-93-9; 4c, 56403-33-9; 4d, 56403-34-0; 4e, 56403-35-1; 4f, 56403-36-2; 4g, 56403-37-3; 4h, 56403-38-4; 4i, 56403-39-5; 4j, 56403-40-8; 4k. 56403-41-9; 4l. 56403-42-0; 4m. 56403-43-1; 4n. 56403-44-2; 40, 56403-45-3; 4p, 56403-46-4; 4q, 1134-68-5; 4r, 56403-47-5; 4s, 56403-48-6; 5a, 56403-49-7; 5b, 21172-01-0; 5c, 56403-50-0; 5d, 56403-51-1; 5e, 56403-52-2; 5f, 56403-53-3; 5g, 56403-54-4; 5h, 56421-59-1; 5i, 56403-55-5; 5j, 56403-56-6; 5k, 56403-57-7; 51, 56403-58-8; 5m, 21004-02-4; 5n, 56403-59-9; 5o, 56403-60-2; 5p, 56403-61-3; 5q, 21004-07-9; 5r, 56403-62-4; 5s, 21004-00-2; 6a, 56403-63-5; 6b, 21003-99-6; 6c, 28998-01-8; 6d, 29075-37-4; 6e, 28998-09-6; 6f, 28998-03-0; 6g, 56403-64-6; 6h, 56403-65-7; 6i, 56403-66-8; 6j, 56403-67-9; 6k, 56403-68-0; 6l, 56403-69-1; 6m, 21004-03-5; 6n, 56403-70-4; 6o, 56403-71-5; 6p, 56403-72-6; 6q, 1487-82-7; 6r, 56403-73-7; 6s, 21004-01-3; 12, 56403-74-8; 13, 29097-86-7; 14, 29097-88-9; 15, 29261-33-4; 16, 29097-90-3; 17, 56403-76-0; 18, 56403-77-1; 19, 4210-60-0; 20, 392-56-3; 21, 1897-43-4; zinc chloride, 7646-85-7; paraformaldehyde, 30525-89-4; sodium cyanide, 143-33-9; dimethyl carbonate, 616-38-6; sodium methoxide, 124-41-4; cyanogen chloride, 506-77-4; potassium hydroxide, 1310-58-3; isopropylidenemalononitrile, 13166-10-4; tetra-n-butylammonium bromide, 1643-19-2.

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