138.7 (s), 129.0 (d), 125.1 (d), 124.9 (s), 123.0 (d), 114.4 (d), 112.8 (t), 56.3 (d), 41.7 (d), 30.5 (t), 30.1 (t), 29.4 (q), 24.8 (t), 24.1 (t); exact mass calcd for $C_{16}H_{19}NO$ m/e 241.1467, found 241.1462, major fragments (rel intensity) 174 (15), 173 (100).

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Supplementary Material Available: ^1H and ^{13}C NMR spectra of the quinolone dimers and quinolone–alkene adducts (15 pages). Ordering information is given on any current masthead page.

Pyridyl Dicyanoquinodimethane Acceptors for Electroactive Solids

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A new synthetic strategy for dicyanoquinodimethane electron acceptors is presented and used to synthesize six such compounds for the first time. The general sequence is substitution of α,α'-dicyanoxylene α anions with electrophiles followed by oxidative dehydrogenation. Unlike most previous examples, these quinodimethanes (QDs) are α substituted, rather than ring substituted; thus, the substituents increase the aspect ratio of the QDs and extend the π systems. All contain at least one pyridyl substituent at an α position, and the set includes polar, cationic, and phosphonic acid derivatives. The particular compounds were chosen for incorporation into specific types of potentially electroactive solids, although, in principle, the syntheses could accommodate a wide variety of other functional groups. The neutral QD compounds display two reversible reductions, while the cations show single, partially reversible electrochemical transitions. Syn–anti isomerism was noted for several of the QDs, and proton NMR assignments obtained by 2D COSY methods are reported.

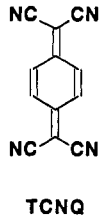
Introduction

Quinodimethanes (QDs), exemplified by tetracyanoquinodimethane (TCNQ), are among the most widely used acceptors in electron donor–acceptor complexes. These complexes may crystallize as electrically conductive[1] or magnetically interesting[2] solids. Nontrivially substituted QDs have recently been explored for the purpose of controlling the crystal packing forces in conductive[3] and ferromagnetic[2] complexes and as components in multilayer diodes prepared using Langmuir–Blodgett (LB) methods.[4] Unsubstituted[5] and amphiphilic[6] TCNQ's have been incorporated into conductive LB films by codeposition with surface-active electron donors.

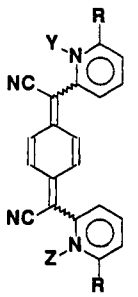
Much of the previously reported synthetic chemistry of electron-accepting QDs depends on multistep transformations of lightly substituted p-xylenes[7] or of cyclohexanediones that initially lack the α carbons.[8] The important substituents are typically placed on ring positions of the QD and are not conjugated with the QD π-electron system. The substituents would screen the QD cores from electron donors and from each other in the solid state, and the substituents considered (except for halogen or alkoxy) impart little electronic tunability to the molecules.

Here, we describe synthetic methods for functionalizing QDs at the α positions, such that the substituents may influence both the electronic behavior of the QDs and also the types of solids that might be formed from them. For the most part, the substituents are pyridine nuclei that are conjugated with the QD chromophore, so that the QD π

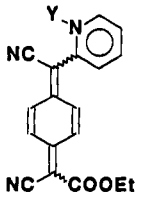
Chart I



TCNQ



1. R = H, Y = Z = lone pair (lp)
2. R = H, Y = Z = Me (+)
3. R = H, Y = Me (+), Z = lp
4. R = $PO(OEt)_2$, Y = Z = lp
5. R = $PO(OH)_2$, Y = Z = lp



6. Y = lp
7. Y = Me (+)

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system is extended, rather than blocked, by the added functional groups. This would improve the overlap with neighboring electron donors and increase the "dimensionality" of conduction in solid donor–acceptor complexes. Among the new α,α'-dicyano-QDs (1–7; Chart I), which were prepared for future investigations of novel solids based on QDs, are three distinct types: dipolar neutral, cationic, and phosphonate-substituted. The dipolar derivative 6 might be expected to form self-segregated stacks because of self-attracting dipole–dipole forces, especially when cocrystallized with an apolar donor. The neutral species derived from 3 and 7 by one-electron reduction could act as neutral dopants in materials consisting primarily of other neutral, isostructural, oxidized QDs.[6a] Such a material would be "self-doped"[9] in that the units carrying the single electrons would not be associated with separate counterions. The QD diphosphonic acid 5 could serve as the electron-demanding component in a metal phosphonate-based multilayer solid assembly.[10] These multilayers are easier to prepare and more robust than LB analogues, and have already been demonstrated with electron-rich organic moieties. The deposition of separate layers of electron-deficient and electron-excessive compounds in a polar assembly may lead to a system that could undergo directional photoelectron transfer and charge separation.

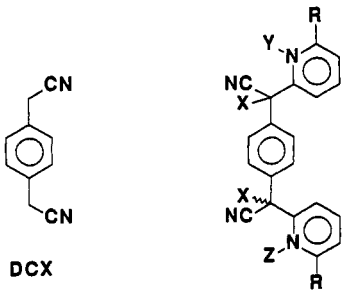
The most important reaction utilized in the preparation of these compounds is the nucleophilic aromatic substitution reaction of α,α'-dicyanoxylene (DCX) α-anions. This reaction is related to the previously reported alkoxycarbonylation of DCX[11] and to the recently described displacement of chloride from 2-chlorobenzonitrile by arylacetonitrile anions.[12] In carrying out the syntheses described here, other useful transformations were uncovered as well, including a regioselective phosphonylation of 2-chloropyridine *N*-oxide *O*-methyl triflate, the preparation and in situ reduction of an α,α'-dibromoxylene to a QD, the oxidation of a dihydro-QD to the QD state by (trimethylsilyl)sulfoxonium cation, and the selective monoalkylation of a bis(pyridyl)dihydro-QD.

In addition to the syntheses, the electrochemical reduction of the QDs is reported, and the distinction of isomers in syn–anti mixtures using 2-D NMR is also described. Although the generality of the synthetic routes was not extensively probed, it is likely that many variants could be envisioned in which a wide variety of functional groups not considered here could be incorporated into QDs.

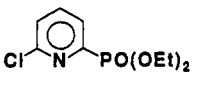
Results

Two symmetrically substituted dicyanoxylenes, 8 and 9, were prepared by treatment of DCX with 2 equiv of either 2-chloropyridine or diethyl (6-chloropyridyl)-2-phosphonate (15) and excess NaH (Chart II). The isolation of 8 was routine and was accomplished in high yield. Compound 9 was much more challenging. The required compound 15 was prepared using a modification of an existing method of phosphonite addition to pyridine *N*-oxide *O*-methyl salts,[13] in this case the reaction of lithium

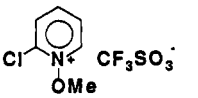
Chart II



8. R = X = H, Y = Z = Ip
9. R = $PO(OEt)_2$, X = H, Y = Z = Ip
10. R = $PO(OSiMe_3)_2$, X = H, Y = Z = Ip
11. R = X = H, Y = Z = Me (+)
12. R = X = H, Y = Me (+), Z = Ip
13. R = H, X = Br, Y = Z = Ip
14. R = $PO(OEt)_2$, X = Br, Y = Z = Ip



15.



16.

diethylphosphonite with 16. (*Attempted preparation of the recommended methyl sulfate salt*[14] *of 16 resulted in a violently unstable product*!) This surprisingly regioselective reaction of an ambident nucleophile with an electrophile containing five separate potential points of attack (Me, O, 2-C, 4-C, 6-C) proved more convenient than the conceptually more direct but lower yielding reaction of diethylphosphonite anion with 2,6-dihalopyridines. The reaction of 6-bromo-2-lithiopyridine with the phosphorus electrophiles bis(dimethylamino)phosphorochloridate and diethyl chlorophosphite was completely unsuccessful, resulting primarily in oxidative coupling of the pyridine.

The reaction of 15 with DCX was induced to yield a significant amount of 9 by careful control of the reaction time based on TLC analysis of the reaction mixture. Unfortunately, the phosphonate groups provide sites for side reactions with deprotonated DCX, the deprotonated monoadduct, and product anions. Purified 9 was resolvable into two TLC bands, presumably meso and *dl* isomers, that were indistinguishable by ^1H and ^{13}C NMR.

Unsymmetrically substituted dicyanoxylenes were obtained by the stepwise deprotonation and reaction of the α carbons of DCX. Initially, DCX was treated with 2 equiv of NaH and 1 equiv of 2-chloropyridine, diethyl carbonate, or 3,6-dichloropyridazine to give 17, 18, or 21 (Chart III), respectively, the third as a meso-*dl* mixture of the fully aromatized tautomer, rather than the bis(methylene)-tetrahydropyridazine that might have been expected based on a previously reported reaction of 3-chloropyridazine and malononitrile.[15] Compound 17 was further treated with excess NaH and diethyl carbonate to give 19. Intermediates 18 and 21 are envisioned as leading to more extended dihydro-QDs, but their chemistry has not yet been further developed.

Dihydro compounds 8 and 19 were methylated with methyl trifluoromethanesulfonate. The unsymmetrical compound 19 was cleanly monomethylated at its single nucleophilic site to give 20, but the symmetrical compound

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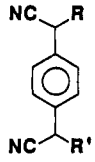
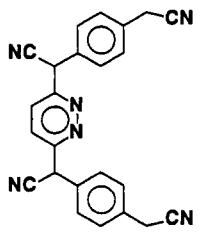
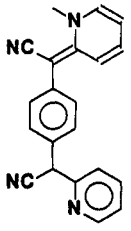
Chart III



17. R = 2-pyridyl, R' = H
18. R = COOEt, R' = H
19. R = 2-pyridyl, R' = COOEt
20. R = 1-Me-2-pyridinium, R' = COOEt



21.



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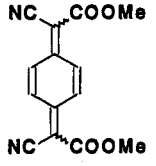

23.

8 possesses two equivalent nucleophilic nitrogens that could not be readily distinguished. Treatment of 8 with 2 equiv of methylating agent predictably gave mostly dimethylated product 11, while treatment with 1 equiv in homogeneous solution gave the expected statistical mixture of derivatives. The statistical distribution was altered in favor of monomethylation by conducting the reaction in toluene, from which 12 precipitates. Selective trituration and column chromatography increased the proportion of monomethylated material to 90% in the eluted sample, some of which was the neutral, α-deprotonated form of the monomethyl salt 22. Both 12 and 22 are potential precursors to 3.

The more electron-deficient dihydro-QDs, 11, 12, 19, and 20, were oxidized to the QD form with excess Br_2 in aqueous CH_3CN. No attempt was made to isolate the QD cations as salts of single anions, as they probably retained triflate as well as polybromide counterions. This was confirmed for 2 by elemental analysis. The NMR spectra of 2, 3, and 7 were clean, except for syn–anti isomerism (see below). The neutral ester 6 tenaciously retained a small amount of water after crystallization.

Two of the other dihydro compounds, 8 and 9, were overoxidized by excess Br_2 to give dibromo addition compounds 13 and 14, as determined by NMR and elemental analysis. The NMR spectra revealed symmetry and sp^3 carbon counts that were consistent with the dibromide structures, and elemental analysis confirmed the presence of appropriate amounts of Br in 13. Tin powder or aqueous KI reduced 13 to 1 in CD_3CN, with the latter reagent causing pure 1 to precipitate as a red solid. Under similar conditions, 14 was decomposed. Elemental iodine did not cleanly oxidize either 8 or 9. Addition of exactly 1 equiv of Br_2 and a slight excess of pyridine to 9 in CD_3CN gave predominantly the desired 4, but 4 was not stable in the mixture and was reduced to 9 when treated with

Table I. Redox Potentials of QD Derivatives[a]

compd	solvent	$E_o(1)$[b]	$E_o(2)$
1	THF	−0.42 R	−0.82 R
2	10% MeOH 90% $(MeO)_2CO$	−0.16 partly R	
3	5% MeOH 95% $(MeO)_2CO$[c]	−0.06 partly R	−0.42 partly R
4[d]	THF	−0.32 R	−0.71 R
6	THF	−0.17 R	−0.67 R
7	THF	+0.16 R	
TCNQ	THF	+0.28 R	−0.41 R
23	CH_3CN	−0.1[e]	
methyl viologen	propylene carbonate	−0.7[f]	−1.1

[a] All in 0.05 M Bu_4NPF_6 unless otherwise noted, vs SCE. [b] R = reversible. [c] Electrolyte was 0.05 M $LiClO_4$. [d] Immediately after formation in CD_3CN, organic layer from CD_2Cl_2–D_2O partition. [e] Reference 11a. [f] Handbook of Electrochemistry. Up to 0.25 V less negative in other solvents.

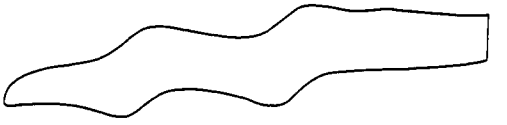

Figure 1. Cyclic voltammogram of 1, conditions as in Table I: Y-scale is 0.1 μA/in.; scan rate = 1 V/s.

Me_3SiBr to remove the ethyl groups from the phosphonates. Ultimately, 9 was treated with Me_3SiBr with the intention of oxidizing and hydrolyzing the resulting silyl ester 10 to make the QD diphosphonic acid 5. It was discovered that addition of DMSO-d_6 to a CD_3CN solution of 10 resulted in clean desilylation and oxidation, giving the target 5 as a red solid, separable from a supernatant smelling strongly of Me_2S. It was subsequently found that a mixture of DMSO and Me_3SiBr also oxidized 8 and 19 to QDs.

For the most part, all of the QD derivatives were obtained as mixtures of syn and anti isomers, as evidenced by pairs of spots on TLC plates and/or double sets of NMR peaks. The proton NMR patterns were sorted with the aid of selective decoupling and COSY methods, so that full complements of AB quartets were assigned to each isomer. The exception was 6, which appeared to precipitate as a single isomer. We presume this to be the syn isomer because the QD ring protons appeared in the NMR spectrum as an upfield AB quartet (2 protons shielded by the pyridine and carbonyl groups) and a downfield AB quartet (2 protons deshielded by the nitriles). This isomerically pure material partially polymerized and/or isomerized upon standing for several hours in $CDCl_3$.[16] The diphosphonic acid 5 was initially formed as a mixture of both isomers, but the anti isomer (one AB quartet with meta coupling for the QD ring protons) crystallized preferentially over the syn isomer (two doublets with meta coupling only, observed in the syn isomers of the symmetrically substituted 1 and 2).

Electrochemical data for all of the QDs except 5 are listed in Table I. All three neutral QDs showed two fully reversible waves (such as in Figure 1), while the cations displayed varying degrees of reversibility depending on concentration and solvent. The two dibromides 13 and 14, when subjected to cyclic voltammetry, were indistinguishable from their corresponding QDs, giving the same reversible waves except for a 0.1 V overvoltage for reduction on the first two sweeps, indicating facile in situ reduction of dibromides to quino compounds.

(16) Compound 23 polymerizes in the presence of a variety of initiators.[11]

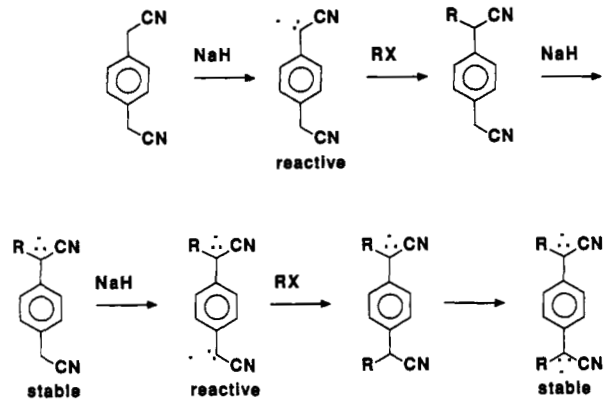

Figure 2. Mechanism of deprotonation/substitution reactions of DCX.

Discussion

The nucleophilic substitutions described here depend upon the greater reactivity of the secondary benzyl anions with alkylating or acylating agents compared to benzyl anions with two electron-withdrawing substituents. The general sequence of deprotonations and alkylations of DCX derivatives is illustrated in Figure 2. By judicious use of either stoichiometric amounts or excesses of base, and either 1 or 2 equiv of electrophile, it should be possible to introduce a wide variety of other substituents (carbonyls, other heterocycles, nitrophenyls, main-group elements) into symmetrical and unsymmetrical DCX derivatives, after which they could be further modified or oxidized to QD derivatives with a variety of redox potentials and crystalline forms. For example, the limited electronic effect of the phosphonate groups in **4** on the redox potentials vs those of **1** would be greater if the phosphonate groups were replaced by more electron-withdrawing moieties. Substituents could also be added to interact with known molecular receptor groups such as macrocyclic ethers and multiply hydrogen-bonding polyamides or to participate in transition-metal complexation.

A wide variety of oxidizing agents have been employed for the conversion of dihydro-QDs to QDs. Aqueous Br_2 has commonly been used for compounds resembling those in this study.[7a,11] The isolation of dibromo addition products from these reactions has not been reported; nor has the chemical or electrochemical reduction of such compounds to QDs. On the basis of the insolubility of **1** compared to the solubility of **13**, QD–Br_2 addition products may be viewed as soluble QD equivalents in the presence of reducing agents or in electrochemical cells at sufficiently negative potentials. The in situ reduction of the dibromides at electrodes is a possible new way to grow crystals of the corresponding QDs.

The use of trimethylsilyl-DMSO cation as an oxidizing agent has limited and poorly understood precedent,[17] but is related to the general class of activated DMSO oxidations that includes the Swern oxidation.[18] None of these effect the dehydrogenation of carbon skeletons. A plausible mechanism for the reaction is illustrated in Figure 3; an analogous one could be written invoking attack of the benzylic carbon on S instead of O. The cleanliness of the conversion of **10** to **5**, much as the other oxidations employed here, was due in large measure to the precipitation of the product at a rate faster than its medium-induced decomposition.

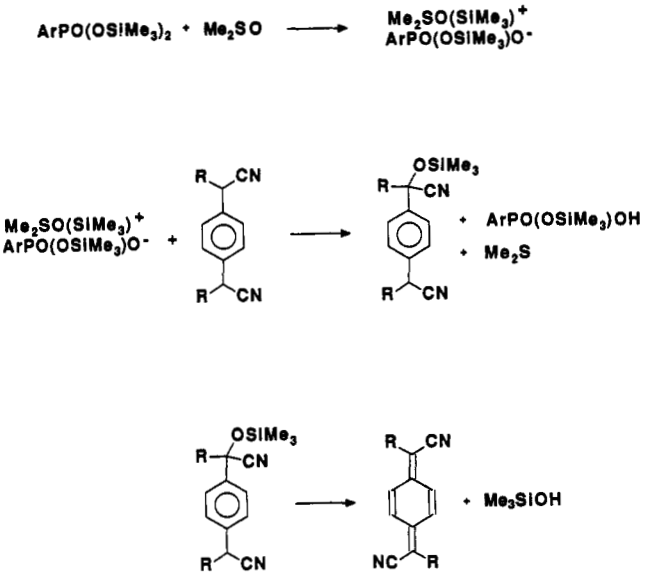

Figure 3. Proposed mechanism of dehydrogenation of dihydro-QDs by DMSO in the presence of electrophilic trimethylsilyl groups.

The observation of stereoisomerism by NMR in most of the QDs discussed here, and in some of the dihydro-QDs, is in contrast to the earlier conclusions of Iwatsuki et al.[11b] in which no such distinction between geometrical isomers could be made, but in agreement with spectra reported by Hall et al.[11a] for bis(alkoxycarbonyl)dicyano-QDs. We observed slight differences in TLC and/or NMR behavior for the meso-*dl* pairs and striking differences between syn and anti QDs. Although no special effort has yet been made to separate these isomers, separation occurred spontaneously in the cases of **5** and **6**. The electrochemical properties of pairs of isomers appear identical, but they would be expected to form solids with different packing arrangements and intermolecular interactions.

From the redox potentials in Table I, it may be concluded that the 2-pyridyl group is less effective than the alkoxycarbonyl group at stabilizing the radical anion forms of the QDs, probably because of the partial noncoplanarity of the pyridine and QD rings, as well as innate differences in their electron-withdrawing ability. The methylpyridinium group is approximately as effective as alkoxycarbonyl, except for distortions in potentials due to the irreversibility of the cation reductions and allowing for the fact that the data were not all obtained in the same solvent due to solubility differences. The peak splitting in **2** is 0.15 V, while the reoxidation peaks in **3** are greatly broadened. Inductive effects may play a role in easing the reduction of the cationic QD derivatives. On the other hand, the greater tendency of neutral radicals to recombine compared to charged radicals and deviations from planarity caused by the sterically significant methyl group may be factors in causing the QD cation reductions to tend toward irreversibility. Our results confirm the previous assertion that nitriles are more effective than esters in this type of radical-anion stabilization and also show that the QD linkage increases the electron-accepting ability of a viologen-like compound **2** vs methyl viologen itself. Dication **2** may act as an effective charge-relay site in settings where methyl viologen is now employed.

Conclusion

A series of new, pyridine-substituted QDs have been synthesized, many of which display reversible electrochemical reductions. The QDs are distinguished from

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Table II. Proton Chemical Shifts of Dihydro Quinodimethanes

compd	solvent	methine	phenyl	pyridyl	other
8	$CDCl_3$	5.28 (s)	7.41 (s)	7.26 (t), 7.34 (d), 7.67 (t), 8.55 (d)	
9	$CDCl_3$	5.38 (s)	7.45 (s)	7.45, 7.8, 7.9	1.3 (t), 4.2 (m) (Et)
11	CD_3CN	6.10 (s)	7.56 (s)	8.01 (t), 8.11 (d), 8.55 (t), 8.70 (d)	4.18 (s) (Me)
12[a]	CD_3CN	5.54 (s) 6.01 (s)	7.5 and 7.6 (ab q)	7.3, 7.7, 8.0, 8.15, 8.52, 8.64	4.15 (s) (Me)
13[b]	CD_2Cl_2		7.72 (s)	7.35 (t), 7.8, 8.65 (d)	
19	$CDCl_3$	4.71 (s) 5.36 (s)	7.5 (collapsed q)	7.5, 7.75 (t), 8.70 (d)	1.25 (t), 4.24 (q) (Et)
20	CD_3CN	5.09, 5.11, 6.00, 6.10 (4s)	7.51, 7.58	8.0, 8.15 8.55, 8.7	1.2, 4.2 (Et) 4.17 (s) (Me)

[a] Compound 22: 5.42 (s), 6.15, 6.95, 7.05, 7.3, 3.54 (br s, me). [b] HBr salt.

Table III. Proton Chemical Shifts of Quinodimethanes

compd	solvent	syn quino[a]	anti quino[b]	others
1	DMSO-d_6	7.62 (narrow m) 8.12 (narrow m)	7.51 and 8.23 (ab q)	7.51, 7.83, 8.00, 8.77 (pyr-H)
2	CD_3CN	6.9 (br d), 7.8 (s)	7.12 and 7.45 (ab q)	4.27 (s) (Me), 8.25, 8.75, 9.28 (pyr-H)
3[c]	CD_3CN	6.82 and 7.23 (ab q) 7.73 (collapsed q)	6.97 and 7.54 (ab q) 7.43 and 7.52 (ab q)	4.28 (Me) 8.1, 8.6, 8.85 (pyr-H)
3[d]	CD_3CN	6.85 and 7.51 (ab q) 7.46 and 8.49 (ab q)	6.77 and 8.30 (ab q) 7.59 and 7.77 (ab q)	4.28 (Me) 7.42, 7.7–8.0, 8.1, 8.55–8.85 (pyr-H)
5	DMSO-d_6	7.60 (s), 8.12 (s)[e]	7.48 and 8.59 (ab q)	7.83 (t), 7.91 (d), 8.06 (m) (pyr-H)
6	$CDCl_3$	7.44 and 7.69 (ab q) 8.42 and 8.46 (ab q)		1.35 (t), 4.33 (q) (Et) 7.35, 7.87, 8.77
7	CD_3CN	6.91 and 7.40 (ab q) 7.60 and 8.52 (ab q)	6.82 and 8.26 (ab q) 7.6 (collapsed q)	1.36 9t), 4.32 (q) (Et) 4.30 (s) (Me), 8.06 (d), 8.14 (t), 8.60 (t), 8.86 (d) (pyr-H)

[a] Cyclohexadiene ring H for isomer with both CN's on same side, as drawn in structure diagrams. [b] Isomer with CN's on opposite sides, opposite of that drawn in diagrams. [c] Protonated. [d] Deprotonated. [e] From reaction mixture.

those previously reported because the substituents diverge along the major axis of the molecule, extending the π system and allowing for end-to-end packing morphology in layered or polymeric solids. The new QDs may be effective photoacceptors in arrays with organic donors or inorganic semiconductors or in mixed solids with neutral radicals derived from monoreduced cationic QDs. The variety of substituents that could in principle be introduced into these compounds affords tunability in redox potential and new possibilities for solid-state design in QD-containing materials.

Experimental Section

General. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl before use. DCX was obtained from Pfaltz and Bauer or synthesized from α,α'-dichloro-*p*-xylene using the procedure of Liotta.[19] All other reagents were used as received. Electrochemical experiments were performed under a stream of N_2 with a Princeton Applied Research Model 174A polarographic analyzer, with a Model 175 universal programmer using a 1-mm diameter Pt disk working electrode, a Pt wire counter electrode, and a Fisher saturated calomel electrode (SCE). The 2D COSY experiments were run on a Bruker AM-360 NMR spectrometer using the Bruker COSY.AUR program for homonuclear shift-correlated 2D-NMR. A recycle time of 1 s was employed and eight transients collected for each t_1 value. A total of 256 spectra were recorded and the matrix zero-filled to 512 by 1024 points. The data were symmetrized after Fourier transformation.

Bis[cyano(2-pyridyl)methyl]benzene (8). A mixture of 3.05 g (20 mmol) of DCX, 4.42 g (39 mmol) of 2-chloropyridine, and 3.7 g (92 mmol) of 60% NaH in oil was stirred in 250 mL of THF at reflux under Ar. In 0.5 h, the mixture was deep red-violet, and in 2 h, the color was brown. After 24 h, the mixture was cooled and AcOH was cautiously added until the solids dissolved and the pH of the mixture on wet pH paper was 4. Ether and H_2O were added to separate the layers, and the organic layer was concentrated to a brownish solid. Trituration with petroleum ether, MeOH, and Et_2O gave 5.1 g (84%) of 8 as a beige solid: NMR (see Table II). Anal. Calcd for $C_{20}H_{14}N_4$: C, 77.41; H, 4.55; N, 18.05. Found: C, 77.07, H, 4.50, N, 17.65.

2,5-Cyclohexadiene-1,4-diylidenebis(pyridine-2-acetonitrile) (1). A 1-g portion of 8 was dissolved in 35 mL of warm CH_3CN, and the solution was allowed to recool. To the ambient-temperature solution was added 10 mL of H_2O and 1.6 g of Br_2 dissolved in 5 mL of CH_3CN. A red precipitate formed quickly. After 18 h, most of the solids were redissolved by swirling, and solvent was removed at reduced pressure until yellow crystals formed. Elemental analysis indicated that this solid was predominantly the monohydrobromide salt of 13. The supernatant was decanted, and the solid was redissolved in CH_3CN and treated with 1.05 g of KI in minimal aqueous CH_3CN. After standing 24 h, a red solid separated and was collected and dried, yielding 0.46 g (47%) of 1: NMR (see Table III). Anal. Calcd for $C_{20}H_{12}N_4$: C, 77.91; H, 3.92; N, 18.16. Found: C, 77.59; H, 3.99; N, 18.04.

2,2'-[2,5-Cyclohexadiene-1,4-diylidenebis(cyanomethyl)]-bis(1-methylpyridinium) Dication (2). A solution of 8 (0.30 g, 0.95 mmol) and methyl trifluoromethanesulfonate (0.22 mL, 1.9 mmol) in 15 mL of CH_2Cl_2 was stirred for 18 h. Concentration of the mixture left a pink solid that was 80 mol % 11: NMR (see Table II). A portion of this solid (150 mg) dissolved in 3 mL of CH_3CN and 1 mL of H_2O was treated with 5 drops of Br_2. A precipitate formed within minutes. After 18 h, the solids were collected and dried to yield 98 mg (60%) of 2 as a mixed bromide/tribromide/triflate salt: NMR (see Table III). Anal. Calcd for C/N: 4.71 (assuming no triflate). Found: 4.84. The analysis

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was consistent with 5 equiv of Br (1.7 equiv of Br_3^-) and 0.33 equiv of triflate per equiv of 2. Anal. Calcd: C, 34.06; H, 2.30; N, 7.11; Br, 50.73; F, 2.41. Found: C, 33.93; H, 2.53; N, 7.01; Br, 49.61; F, 2.36.

2-[Cyano[4-[cyano(2-pyridyl)methylidene]-2,5-cyclohexadienylidene]methyl]-1-methylpyridinium Cation (3). A solution of 8 (1.20 g, 3.8 mmol) in 80 mL of toluene was prepared by heating and then cooling to room temperature. Methyl trifluoromethanesulfonate (0.44 mL, 3.8 mmol) was added with stirring. After 18 h, the supernatant liquid was decanted away from 1.6 g of a solid precipitate, consisting of 12 contaminated with 17 mol % each of 8 and 11: NMR (see Table II). This was washed with 22 mL of hot toluene. NMR showed 12 and 11 in a 2:1 mole ratio. The remaining solids were dissolved in 4 mL of hot CH_3CN and eluted through 4 g of silica gel with EtOAc. An orange oil (270 mg) was obtained. This was treated with 15 drops of Br_2 in 10 mL of CD_3CN and 5 mL of H_2O overnight. The solution was concentrated to a semisolid that was separated from an aqueous supernatant. The organic component of the semisolid consisted entirely of protonated 3: NMR (see Table III). Deprotonation in CH_2Cl_2–dilute $NaHCO_3$ (pH 5) gave 3 as the monocation: NMR (see Table III).

Diethyl (6-Chloro-2-pyridyl)phosphonic Acid (15). The HCl salt of 2-chloropyridine *N*-oxide (25 g) was freed by dissolving in 80 mL of H_2O containing 6.3 g of NaOH. The solution was extracted with 2 × 350 mL of CH_2Cl_2, and the organic layers were concentrated to 18.1 g of white solid. This solid (16 g, 0.124 mol) was dissolved in 110 mL of dry CH_2Cl_2, and the solution was cooled in an ice bath. The contents of two 10-g ampules of methyl trifluoromethanesulfonate (1 equiv) were added to the solution, and the ice bath was removed. After 1.5 h at room temperature, 110 mL of Et_2O was added in portions with stirring. White crystals formed and were collected, yielding 34.1 g (94%) of 16, mp 114–116 °C.

A flask containing 18 mL (0.107 mol) of 2,2,6,6-tetramethylpiperidine was cooled to −70 °C. Butyllithium (0.117 mol) was slowly added with stirring under Ar; the mixture was allowed to warm to 0 °C, and then was recooled to −70 °C. Diethyl phosphite (15 mL, 0.116 mol) was added, and the warming/recooling cycle was repeated. This solution was added to a frozen slurry of 16 (34 g, 0.116 mol) and 25 mL of dioxane under Ar. The combined reagents were swirled without cooling while the internal temperature was monitored. When the temperature reached 15 °C, an exothermic reaction began and a dry ice bath was *immediately* applied to moderate the temperature. When the temperature had fallen to 0 °C, the process of warming to 15 °C and recooling was repeated. The mixture was then left to stir uncooled overnight.

Concentrated aqueous $NaHCO_3$ (200 mL) and 50 mL of Et_2O were added. The organic layer was discarded, and the aqueous layer was extracted with 2 × 150 mL of CH_2Cl_2. The CH_2Cl_2 extracts were dried with $MgSO_4$, filtered, and concentrated to 36 g. This was eluted on 95 g of silica gel with CH_2Cl_2, collecting the first 400 mL of pyridyl solution, which was concentrated and determined by NMR to contain 11.4 g (39%) of 15 as the predominant heteroaromatic component, contaminated mostly with more volatile impurities, solvents, and tetramethylpiperidine. Fractional Kugelrohr distillation gave 7.0 g (24%) of material suitable for further reaction, bp 170–190 °C (0.2 Torr): NMR ($CDCl_3$) δ 1.3 (t, 6), 4.2 (m, 4), 7.4 (d, 1), 7.7 (m, 1), 7.8 (t, 1); GC–MS (93% pure), 249 (M^+), 220, 205, 176, 113 (bp).

6,6′-[2,5-Cyclohexadiene-1,4-diylidenebis(cyanomethyl)]-bis(2-pyridine)diphosphonic Acid (5). A mixture of 15 (4.6 g, 18 mmol), DCX (1.22 g, 8 mmol), and NaH (64 mmol) was stirred in 120 mL of THF under Ar, and heated to reflux. The color darkened and became dark orange-red as reflux was reached. The intensity of the TLC spot with R_f 0.05 (EtOAc–silica gel) was optimized, typically in 1–3 h. The mixture was cooled with an ice bath, and AcOH was added until H_2 evolution subsided and the pH was 3–4. The solution was diluted with H_2O and Et_2O. The aqueous layer was extracted with additional Et_2O to remove any remaining product, as deemed necessary by TLC. The combined Et_2O layers were concentrated and chromatographed on 45 g of silica gel, eluting with 400 mL of EtOAc, 225 mL of 5% MeOH in EtOAc, and 300 mL of 10% MeOH in EtOAc. Product 9 was obtained after the first 250 mL of elution, 1.53 g (34%) of clear viscuous oil: NMR (see Table II).

To 400 mg of 9 in 10 mL of dry CH_2Cl_2 was added 1.2 mL of Me_3SiBr. After 3.5 days, the solution was concentrated to a deliquescent beige solid whose NMR spectrum showed no ethyl signals and whose mass spectrum included the parent and parent − 15 for 10 (758, 743, respectively). The solid was taken up in 0.3 mL of DMSO-d_6 and 4 mL of CD_3CN. Within minutes, a red solid was deposited and an odor of Me_2S was detected. The red solid was collected, yielding 224 mg (69%) of 5. The analytical sample (all anti) was recrystallized from DMSO–CH_3CN and washed with EtOH and Et_2O: mp 115 (contraction), 220 (decolorization); NMR (see Table III). Anal. Calcd for 5 + 1.5H_2O, $C_{20}H_{17}N_4P_2O_7$: C, 48.51; H, 3.43; N, 11.31; P, 12.51. Found: C, 48.50; H, 3.69; N, 10.38; P, 12.18.

2-[Cyano[4-(cyanomethyl)phenyl]methyl]pyridine (17). To 150 mL of THF were added DCX (10.9 g, 69 mmol), 2-chloropyridine (7.9 g, 69 mmol), and NaH (3.0 g, 0.125 mol, oil-free). The mixture was stirred at reflux under Ar for 2 h, cooled, and diluted with H_2O and sufficient AcOH to bring the pH to 4. The acidified solution was extracted with Et_2O, and the organic layer was washed with H_2O and concentrated to 15.4 g (94%) of crude 17. Recrystallization from CH_2Cl_2–toluene–petroleum ether followed by washing with MeOH gave 4.6 g of pure solid product. Chromatography of the mother liquors and washings with CH_2Cl_2 on 30 g of silica gel gave an additional 2.2 g of pure product and 1.7 g contaminated with a polar impurity: NMR ($CDCl_3$) δ 3.7 (s, 2), 5.3 (s, 1), 7.3–7.4 (m, 6), 7.6 (m, 1), 8.6 (m, 1). Anal. Calcd for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01. Found: C, 76.83; H, 4.75; N, 17.58.

Ethyl 2-Cyano-2-[4-[cyano(2-pyridyl)methylidene]-2,5-cyclohexadienylidene]acetate (6). Recrystallized 17 (2.0 g, 8.6 mmol), 1.01 g of diethyl carbonate (8.6 mmol), and NaH (26 mmol) were stirred in 50 mL of THF at reflux under N_2 overnight. Acetic acid, Et_2O, and H_2O were added to make two phases at pH 5. The organic phase was concentrated to a mixture that was 70 mol % 19. Elution through 20 g of silica gel with petroleum ether–EtOAc removed colored impurities, leaving 0.9 g of oil: NMR (see Table II); MS 305 (M^+, bp), 232, 205. A solution of 0.5 g of this oil in 10 mL of CH_3CN, 10 mL of H_2O, and 0.25 g of Br_2 was left to stir overnight. An orange powder, 0.37 g (74%), was collected from this mixture: NMR (see Table III); MS 303 (M^+), 274 (bp), 230. An analytical sample was prepared by precipitation from CH_2Cl_2–MeOH. Anal. Calcd for $C_{18}H_{13}N_3O_2$ + 0.25H_2O: C, 70.24; H, 4.72; N, 13.66. Found: C, 69.96; H, 4.36; N, 13.67.

2-[Cyano[4-[cyano(ethoxycarbonyl)methylidene]-2,5-cyclohexadienylidene]methyl]-1-methylpyridinium Cation (7). Compound 19 was converted quantitatively to 20 by treatment of 0.9 g with 0.35 mL of methyl trifluoromethanesulfonate in 25 mL of CH_2Cl_2 over 40 h followed by concentration to a foam: NMR (see Table II). The foam was dissolved in 25 mL of CH_3CN. Addition of 50 mL of H_2O resulted in a cloudy mixture, to which 0.4 g of Br_2 was added with stirring. The color became yellow, then orange, and an orange solid separated. After 24 h, an orange supernatant was filtered from a brown solid, and the supernatant was extracted portionwise with 400 mL of CH_2Cl_2. The extracts were concentrated to 0.8 g. Trituration of the residue with CH_2Cl_2–Et_2O left 0.6 g of a hard foam whose organic component consisted entirely of 7: NMR (see Table III).

Ethyl 2-Cyano-2-[4-(cyanomethyl)phenyl]acetate (18). A solution of 3.1 g of DCX (20 mmol), 2.95 g of diethyl carbonate (25 mmol), and 50 mL of THF was heated with 45 mmol of NaH for 2.5 days at reflux under N_2. After the solution was cooled, 3 mL of AcOH was cautiously added, followed by H_2O and Et_2O. The undissolved solids were taken up in additional portions of the three additives. The organic layers were concentrated, and the residue was chromatographed on 30 g silica gel, eluting with CH_2Cl_2. A fraction containing 2.3 g of 18 (51%) as a yellow oil was obtained: NMR ($CDCl_3$) δ 1.30 (t, 3), 3.78 (s, 2), 4.22 (q, 2), 4.74 (s, 1), 7.39 and 7.49 (ab q, 4); MS 228 (M^+), 184, 156, 129 (bp). The major impurities removed by the column were carbonyl-linked diadducts of DCX and 18.

4,4′-[(3,6-Pyridazinediyl)bis(cyanomethyl)]bis(benzeneacetonitrile) (21). A solution of 4.7 g of DCX (30 mmol), 1.5 g of 3,6-dichloropyridazine (10 mmol), and 60 mmol of NaH was stirred and heated in 50 mL of THF at reflux under Ar. After the solution was cooled, the excess NaH was cautiously quenched with H_2O, and Et_2O and HCl were added to separate layers and

protonate the products. The organic layer was concentrated to 5 g of a light brown solid. This was chromatographed on 75 g of silica gel eluting with 1600 mL of 0–20% EtOAc in CH_2Cl_2. The most polar of three major bands was isolated from the 15% eluate and concentrated to 0.80 g (20%) of **20** as an off-white solid: NMR ($CDCl_3$) δ 3.72 (2 s, 4, CH_2CN), 5.66 (2 s, 2, CHCN), 7.35 and 7.50 (ab q, 8, Ph), 7.60 (s, 2, pyridazine-H); MS 388 (M^+, bp), 360. Anal. Calcd for $C_{24}H_{16}N_6$: C, 74.21; H, 4.15; N, 21.64. Found: C, 74.51: H, 4.05; N, 21.23.

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Registry No. 1, 134881-87-1; 2, 134881-88-2; 3, 134881-89-3; 5, 134881-90-6; 6, 134881-91-7; 7, 134881-92-8; 8, 134881-93-9; 9, 134881-94-0; 10, 134881-95-1; 11 triflate, 134881-97-3; 12 triflate, 134881-99-5; 13·HBr, 134882-00-1; 15, 134882-01-2; 16, 134882-02-3; 17, 134882-03-4; 18, 134882-04-5; 19, 134882-05-6; 20, 134882-06-7; 21, 134882-07-8; DCX, 622-75-3; 2-chloropyridine, 109-09-1; 2-chloropyridine oxide hydrochloride, 20295-64-1; 2-chloropyridine *N*-oxide, 2402-95-1; 3,6-dichloropyridazine, 141-30-0.

Kinetics and Mechanism of the Aminolysis of *O*-Ethyl *S*-Aryl Dithiocarbonates

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The reactions of *O*-ethyl *S*-phenyl dithiocarbonate (**1**) and *O*-ethyl *S*-(*p*-nitrophenyl) dithiocarbonate (**2**) with a series of secondary alicyclic amines, namely, piperidine, piperazine, 1-(β-hydroxyethyl)piperazine, morpholine, 1-formylpiperazine, and (with **2** only) piperazinium ion, are subject to a kinetic study at several pH values. The reaction leads to the corresponding thiocarbamates and thiophenols (measured as thiophenoxide ion by UV–vis spectrophotometry). Pseudo-first-order rate coefficients (k_{obsd}) are found throughout (amine excess). The kinetics are first order in amine for the reactions of **2**. The plots of k_{obsd} vs [amine] for the reactions of **1**, except with 1-formylpiperazine, are linear, but near the origin they are curved, showing a more complex rate equation. The reaction of **1** with 1-formylpiperazine shows a second-order dependence on the amine. No dependence on pH of the second-order rate constant values is observed. The findings are well-accommodated by a mechanistic model involving reversible nucleophilic attack on the thiocarbonyl group, two tetrahedral intermediates, **3** and **4**, and a deprotonation step. The Bronsted-type plots obtained are linear ($\beta_1 = 0.22$) for the reaction of **1** and curved for **2** ($\beta_1 = 0.2$ and $\beta_2 = 0.8$). The Bronsted-type plot obtained with the rate constants for amine expulsion from **3** is linear with $\beta_{-1} = -0.67$ and -0.54 for the reactions of **1** and **2**, respectively.

Introduction

The chemistry of *O*-alkyl and *O*-aryl dithiocarbonates has been subject to much study because these compounds are widely used in the laboratory and industry. One of the reactions most investigated of these compounds is the thione to thiol Lewis acid catalyzed rearrangement, giving *S,S*-dithiocarbonates; these reactions have been studied from both synthetic[1-4] and mechanistic[5] points of view. A large increase of the reaction rate in going from apolar to polar solvents has been found, suggesting that the rearrangement reaction occurs through highly polar transition states. Another well-investigated reaction is olefin formation from dithiocarbonate pyrolysis (Chugaev reaction).[6] Recently, the kinetics and Arrhenius parameters of the thermal decomposition of *S*-alkyl *O*-phenyl and *O*-alkyl *S*-phenyl dithiocarbonates have been described,[7] leading to a mechanistic proposal for the former reaction, suggesting a more E*i*-like rather than E1-like transition state; but for the latter the rearrangement reaction appears as a competing side reaction, which precludes a meaningful analysis of the rate data. On the other hand, the *O,S*-dithiocarbonates have been much studied as precursors or intermediates in the syntheses of thiols,[8] alkyl halides,[9] S-linked functions,[10] olefins,[11] and 1,3-dithiol-2-ones and 2-thiones,[12] in the deoxygenation of secondary alcohols,[13] in the stereoselective synthesis of allylic sulfides,[14] and recently in obtaining the *S,S*-dithiocarbonates as bidentate ligands in organometallic complexes.[15]

Although a great number of studies on the kinetics and mechanism of nucleophilic reactions on carbonyl compounds have been carried out showing important features affecting the product formation pathway,[16] the same reactions of thiocarbonyl compounds have received little attention. As far as we know no kinetic studies have been carried out on the hydrolysis and aminolysis of *O*-alkyl and *O*-aryl dithiocarbonates.

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