Dicyanodiaryl-*p*-quinodimethanes : An Efficient Synthesis Using a New Dilithium Reagent and Their Solvent-Dependent Properties

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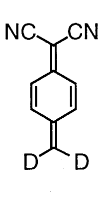
A series of 7,7-dicyano-8,8-diaryl-*p*-quinodimethane are readily prepared by the reaction of 4-lithiophenyldicyanomethyllithium with diaryl ketones; the 8-(4-dimethylaminophenyl) compounds thus obtained show solvent-dependent absorption spectra and bond rotation of the exocyclic double bonds and form a head-to-tail dimeric structure in the crystal.

Highly dipolar π-electron systems have attracted considerable attention in relation to developement of new materials.[1] Dicyanoquinodimethanes **1** having electron-donor(s) on the other side of methylene carbon are a class of molecules with highly dipolar property and a number of such molecules have been reported.[2-4] Gompper and co-workers reported the synthesis of a number of dicyanoquinodimethanes including 7,7-dicyano-8,8-diphenyl-*p*-quinodimethane (**2a**).[2] Introduction of substitutent(s) in the phenyl group(s) of **2a** would allow tuning of polarity and provide valuable information for design of novel quinodimethanes of physicochemical interest. Gompper's synthetic method for **2a** seems, however, not effectively applicable to the synthesis of its derivatives. Here we report a new and efficient synthesis of dicyanodiarylquinodimethanes **2a**-**2e**, X-ray structure of **2d**, and thier properties involving substituent effects.



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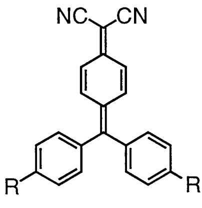
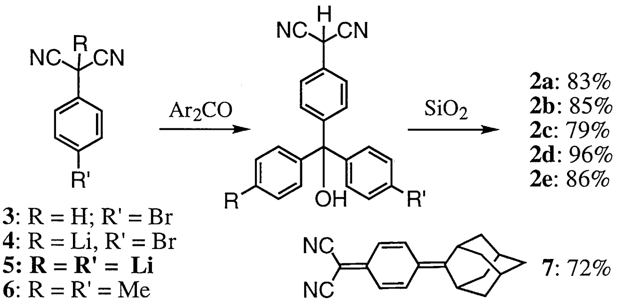


2a: R = R' = H
2b: R =R' = Me
2c: R = R' = OMe
2d: R = NMe_2; R' = H
2e: R = R' = NMe_2

It was found that 4-lithiophenyldicyanomethyllithium **5** is a new versatile synthon for dicyanoquinodimethanes.

When (4-bromophenyl)malononitrile (**3**)[5] was treated with 2.2 equiv. of n-BuLi in THF at -78 °C, the bromine-lithium exchange forming dilithio compound **5** was considerably slow probably due to electronic effect of the negative charge in monoanion **4** formed initially; however, 6 hours' reaction (1.0 mmol scale; 15 ml of THF) was found enough for the dilithiation as judged by dimethylation to **6** (85% yield; MeI quenching). Shorter time or higher temperature for the lithiation resulted in poorer yield of **6**. The cyano groups remain intact under the lithiation condition, although intramolecular electronic repulsion should increase nucleophilic reactivity of the aryllithium part of **5**.

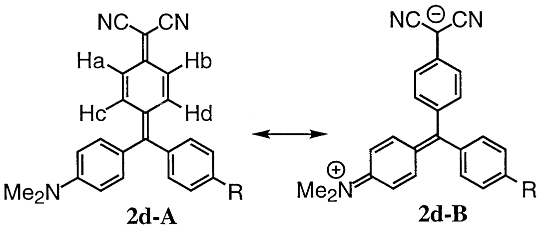
Reactions of **5** with benzophenone and its derivatives followed by chromatography on silica gel, where dehydration mostly takes place, afforded **2a-e** in good yields (Scheme 1).[6,7] Adamantanone, an unenolizable dialkyl ketone, also yielded dicyanoquinodimethane **7**.[7] However, enolizable ketones such as cyclohexanone and camphor were not successful enough, because their reactions produced mixtures mainly owing to aromatizing tendency of the corresponding quinodimethanes.



Scheme 1.

Table 1 lists the selected physical data of **2a-2e** and **7**. ^{13}C NMR spectra clearly show the large dipolar property of **2a-2e** as well as the strong substituent effects: the chemical shift difference between C7 and C8 [$\Delta\delta$ (C8-C7)] increases sharply from 64.8 ppm of **2a** to 115.4 ppm of **2e**. Charge separation of **7** ($\Delta\delta$ = 61.0 ppm) is smaller than **2a**. It has been reported that there is a lenear correlation between the nitrile stretching frequency and degree of charge transfer in TCNQ CT-complexes.[8] As far as **2a-2e** are concerned, there seems also present a lenear correlation between the nitrile stretching frequencies and the C7 chemical shifts of **2a-2e** (Figure 1).[9] This correlation indicates clear and strong substituent effects on the resonance contribution of the dipolar structures such as **2d-B**.[10]

Quinodimethanes **2a-2e**, in particular **2d** and **2e**, show large solvent effects on absorption spectra; for example, **2d** exhibits a visible absorption at 611 nm in benzene, whereas much stronger absorptions at 696 nm in methanol. The solvent effects, which are attributable mainly to twisted intramolecular charge transfer (TICT[11]), are more prominent than those observed for the corresponding *p*-quinone methides.[12]



2d-A
2e-A

2d-B
2e-B

Temperature-dependent ^{1}H-NMR spectra of unsymmetrical **2d** agree with the solvent-dependent TICT. In bromobenzene-d_5, **2d** shows broadening of the four non-equivalent protons in the quinodimethane moiety (Ha-Hd, see **2d-A**) only above 110 °C ($\Delta G^{\ddagger}$ > 18 kcal·mol^{-1} for the rotation of C4-C8 bond). However, in dimethylformamide (DMF)-d_7, Hc and Hd are observed to be

Table 1. Selected spectral and electrochemical data of **2a-e**

Compound	CN stretching [a] (cm^{-1})	δ C7 [b] (ppm)	δ C8 [b] (ppm)	Δδ (C8-C7) (ppm)	Longest absorption maxima λ_{max} nm(log ε)/CH_2Cl_2	Redox potentials (V) [c] E^1_{ox} [d]	E^1_{red}	E^2_{red} [d]
2a	2209	80.22	145.03	64.8	495 (4.59)	1.38	-0.44	-1.46
2b	2204	78.18	152.62	74.4	514 (4.56)	1.29	-0.47	-1.46
2c	2199	66.09	155.61	89.5	558 (4.65)	1.15	-0.51	-1.47
2d	2196	63.00	166.65	103.7	648 (4.61), 690sh (4.55) 611 (4.51)/C_6H_6 696 (4.72)/MeOH	0.83	-0.56	-1.45
2e	2186	55.13	170.48	115.4	640sh (4.50), 698 (4.82) 646 (4.69), 690sh(4.60)/C_6H_6	0.76	-0.72	-1.60
7	2211	96.14	157.14	43.6	436 (4.63), 457 (4.59)	0.33	-1.73 [d]	—

[a] KBr disk. [b] In $CDCl_3$. [c] V vs Ag/AgCl, in 0.1 M nBu_4NClO_4/DMF, sweep rate 100 mVsec^{-1} at 25 °C, Fc^+/Fc = 0.52 V. [d] Peak potential.

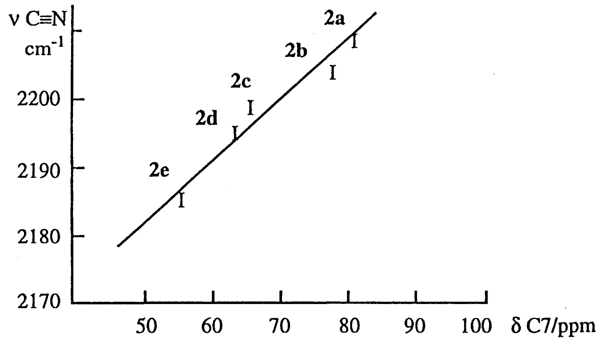


Figure 1. Correlation of nitrile stretching frequencies and dicyanomethylene carbon chemical shifts of **2a-e**.

equivalent at 100 ℃, appreciably broadened at 30 ℃, almost disappearing at 10 ℃, and two doublets (δ 7.23 and 7.61) below -50 ℃ [$\Delta G^{\ddagger}$ = 11.5 ± 0.5 kcal·mol^{-1} (Tc = -10 ± 5 ℃)]. The energy barrier for the rotation is intermediate in less polar acetone-d_6 ($\Delta G^{\ddagger}$ = 13.0 ± 0.5 kcal·mol^{-1}).[13]

The cyclic voltammograms of **2a**-**2e** are composed of one irreversible oxidation wave and the first reversible and second irreversible reduction waves. Adamantylidene compound **7** behaves differently showing only one irreversible reduction wave at higher potential to suggest instability of its anion radical. Although much weaker than TCNQ (E^1_{red} = 0.06 V, E^2_{red} = -0.33 V), the electron affinity of **2a** is comparable to that of *p*-benzoquinone (E^1_{red} = -0.45 V, E^2_{red} = -1.33 V).

X-ray structure analysis of **2d**[14] (Figure 2) revealed two interesting features, although the accuracy is lowered due to high disorder of the included solvent molecules. First, while diaminophenyl group is twisted by only 16° from the plane of quinodimethane, the phenyl group largely by 50° to indicate effective conjugation between the qinodimethane and diaminophenyl groups. Second, the molecules are faced each other in a head-to-tail manner in crystal probably owing to large intermolecular dipole interaction.

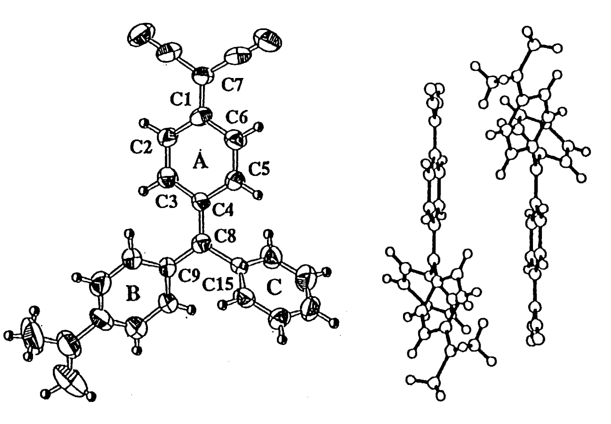


Figure 2. Left: ORTEP drawing of **2d** (50% probability). Right: Head-to-tail arrangement of **2d** in the crystal.

Further studies on dicyanoquinodimethanes and synthetic application of **5** are in progress.

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6 Treatment of the intermediate crude alcohols with phosphoryl chloride or methanesulfonyl chloride in pyridine also effect the dehydration.

7 All new products gave satisfactory analytical and spectral data other than those given in Table 1. **2a:** dark red needles; mp 162.5-163.5 ℃ (lit.2 : 162 ℃). **2b:** dark red needles; mp 218-219 ℃. **2c:** dark purple needles; mp >300 ℃. **2d**: mettalic green needles; mp 106-107 ℃. **2e:** metallic green needles; mp >290 ℃ dec. **6**: colorless oil; IR (oil) ν= 2252 cm^{-1} (CN); ^{1}H-NMR (270 MHz, $CDCl_3$) δ = 2.09 (s, 3H), 2.39 (s, 3H), 7.29 (2H, AA'BB', J = 1.6, 8.6 Hz) , 7.45 (2H, AA'BB', *J* = 1.6, 8.6 Hz). **7:** orange crystals; mp 283℃ dec.

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9 Simple extrapolation of the correlation to the nitrile frequency of TCNQ (2227 cm^{-1}) gives an estimated value of ca. δ 100 for the yet unknown chemical shift of C7(8) of TCNQ.

10 The nitrile stretching frequency of **2e** (2186 cm^{-1}) corresponds to that of TCNQ complexes with about 0.9 unit charge transfer.[9]

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14 Crystal data for **2d**·C_6H_6·0.12(CH_2Cl_2) (the composition was determined by elemental analysis): crystalized from benzene-dichloromethane; monoclinic, space group *C2/c(#15), a* = 9.434(4), *b* = 24.609(8), *c* = 20.880(5) Å, b = 90.09(2)°, *V* = 2153(1) Å^3, *Z* = 8, r_{calc} = 1.215 gcm^{-3}, m = 2.80 cm^{-1}, 1713 independent observed reflections with [F>3s(F), 3°≤2q ≤54.9°], refined to R(Rw) = 0.090(0.092).