7,7-Dicyano-8,8-bis[4-(*N*,*N*-dimethylamino)phenyl]-*meta*-xylylenes: The First Stable Zwitterionic Metaxylylene Derivatives

Takeshi Kawase,* Tohru Iwata, and Masaji Oda*
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043

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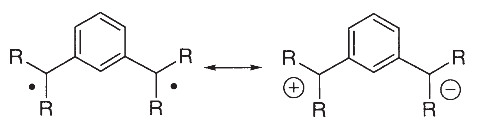
Treatment of 3-lithiophenyldicyanomethide ions with Michler's ketone afforded the title compounds as stable crystals upon weak-acidic work-up. The molecular structure and spectroscopic data reveal the zwitterionic nature of the compounds.

Metaxylylene **1** is potentially regarded as a resonance hybrid between a diradical form A and a zwitterionic form B. Although the diradical A has been received much attention mainly from the viewpoints of high-spin organic compounds,[1] few studies on the zwitter ion B have been performed so far.[2] Recently we have reported the highly polarized character of 7,7-dicyano-8,8-bis(4-dimethylaminophenyl)-*p*-quinodimethane (**2**).[3] The results suggest that appropriate substituents on each *exo*-methylene carbon would stabilize the zwitterionic structure to a great extent. Several nearly zwitterionic quinoid systems have been synthesized so far.[4] In these systems, steric crowding plays an important role in increasing the dipolarity. Here we report the synthesis, properties and molecular structure of the first zwitterionic metaxylylene derivative.



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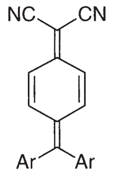

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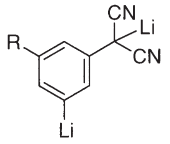
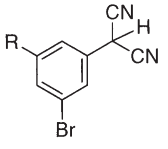
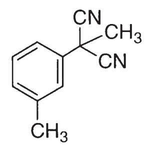


3a; R = H
3b; R = t-Bu



4a; R = H
4b; R = tBu



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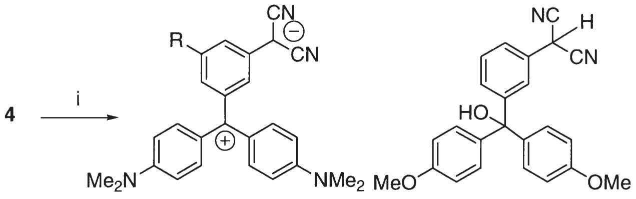
Treatment of 4-lithiophenyldicyanomethide lithium with diarylketones effectively afforded the highly polarized paraxylylenes.[3] The results suggest that 3-lithiophenyldicyanomethide lithiums **3** would be promising synthetic tools for **1B**. 3-Bromophenyl- and 3-bromo-5-*tert*-butylphenylmalononitrile (**4a**) and (**4b**)[5] were prepared from *m*-dibromobenzene or 1,3-dibromo-5-*tert*-butylbenzene and malononitrile by the Takahashi's method[6] in 67% and 80% yields, respectively. Treatment of **4a** with 2.4 equiv. of *n*-BuLi at −78 °C for 1 h cleanly generated the corresponding dianion **3a**. The generation was confirmed by quenching with methyliodide to give a dimethylated compound **5**[5] in 88% yield.

Quenching of **3a** and **3b** with Michler's ketone followed by addition of aqueous ammonium chloride gave zwitter ions **6a** and **6b** as green solutions. The compounds are extractable with ethyl acetate from the weak acidic solutions. Metallic green plates of **6a** precipitated from the extract upon standing for overnight. The crystal is poorly soluble in common organic solvents. On the other hand, the *tert*-butyl derivative **6b** is relatively soluble in organic solvents and readily purified by column chromatography on silica gel. The reaction of **3a** with 4,4′-dimethoxybenzophenone afforded a corresponding triarylmethanol **7**[5] in good yield upon similar work-up. Dehydrative treatments of **7** under several conditions have failed to give the corresponding zwitterionic species so far.



6a; R = H
6b; R = tBu

7

Scheme 1. (i) a) 2.2 eq. *n*-BuLi/THF, −78 °C, 1 h, b) Michler's ketone, rt, 1 h, c) sat. NH_4Cl aq, 64% for **6a**, 63% for **6b**.

Appearance of NMR signals reveals little contribution of the diradical structure A in **6**.[5] The chemical shifts of the dicyanomethylene carbon ($C\beta$: δ 29.42) and the central quarternary carbon ($C\alpha$: δ 183.10) of **6b** in $CDCl_3$ are comparable to those of phenyldicyanomethyl anion **8** (δ 27.80 in CD_3OD) and Malachite Green **9** (δ 187.4 in DMSO-d_6),[7] respectively. The difference, $\Delta\delta$ ($C\alpha$-$C\beta$) = 153.7 ppm, is 38.3 ppm larger than that of **2** ($\Delta\delta$ = 115.4), and almost comparable to that of the ^{13}C shifts dependence on the π charge (167 ppm/π electron),[8] clearly suggesting the zwitterionic nature of **6b**. Although the signals of quarternary carbons of **6a** was not observed because of the low solubility, the similar IR frequencies of nitrile stretching as those of **6b** (ν/cm^{-1}: 2125, 2168 for **6a** and 2128, 2170 for **6b**) also indicate the zwitterionic nature of **6a**.

Careful crystallization of **6a** from an extract successfully afforded good single crystals.[9] The crystals contained both ethyl acetate and THF as inclusion (**6a** : ethyl acetate : THF = 1 : 0.75 : 0.25 by NMR). Recrystallization of **6a** in pure ethyl acetate or THF have failed to afford good single crystals so far. Figure 1 shows molecular structures of **6a**. Little pyramidization of both $C\alpha$ and $C\beta$ carbons and the low twisted angle between dicyanomethyl group and A ring (>2°) indicate that **6a** has a fully conjugated system on the metaxylylene structure. The molecule has a propeller structure similar to triphenylmethyl cation **10** as expected. The average of twisted angles between aryl groups (57.0°) is smaller than that of **10** (64.8°).[10] The zwitterion forms a dimeric structure in crystal: the dicyanomethylphenyl group A is faced to the dimethylaminophenyl group B of an adjacent molecule. The included solvent molecules are placed in

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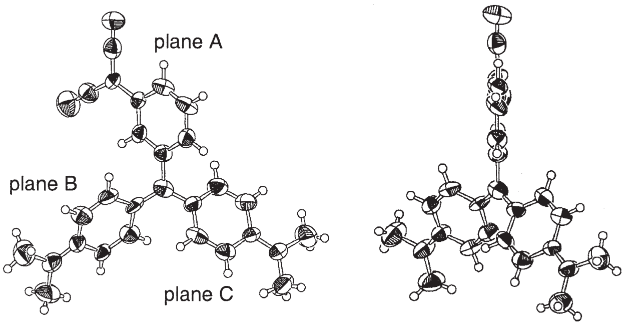


Figure 1. Left; ORTEP drawing of **6a**: right; side view. Included solvent molecules removed for clarity. Dihedral angle between planes (°). plane A–plane B = 58.75, plane A–plane C = 60.54, plane B–plane C = 51.75.

the interspace of **6a**. The disorder is responsible for the low accuracy of the analysis.

The absorption spectrum of **6a** similar to that of **9** shows small solvent effects (λ_{max} = 607 nm/CH$_3$OH; 608 nm/CH$_2$Cl$_2$). In contrary to the quinodimethane **2**, **6a** exhibits no charge-transfer band.[11] The absorption change of **6a** at various pH (Figure 2) indicates that pK_a of **11**, the conjugate acid of **6a**, is estimated to be 3.4 unit. Thus, **11** is the stronger acid than **8** (pK_a = 5.3) by 1.9 pK units. Whereas the color of **9** disappeared rapidly in strong basic media (EtOH-NaOH aq. pH = 13.22), the long wavelength absorption of **6a** slowly decreased under the conditions. After standing for a day, the solution of **6a** discolored completely. Regeneration of **6a** by neutralizing the solution ended in failure, which indicated that irreversible decomposition occurred in the basic media (Scheme 2). The accurate pK_{R^+} value was not determinable; however, the cationic character of **6a** is apparently higher than that of **9**. The presence of both charges in the molecule would play an important role in increasing the stability.

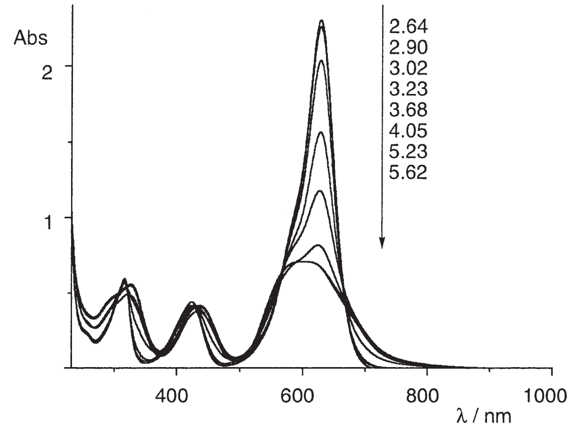
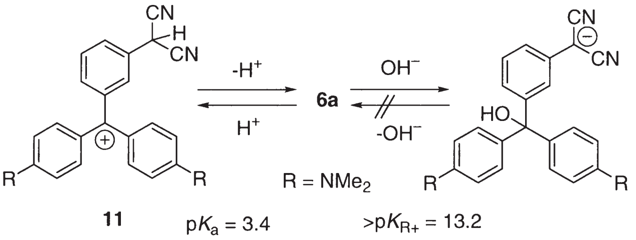


Figure 2. Change of electronic spectra of **6a** at various pH in EtOH–buffer solutions (CH$_3$COOH-CH$_3$COONa).

In conclusion, we report the first synthesis of zwitterionic metaxylylene derivatives **6** as stable crystalline materials. With keeping their planarity, **6** retain the individual electronic properties of each component probably owing to the novel metaxylylene conjugation.



Scheme 2.

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References and Notes

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5 **4a**: colorless needles (Bz/*n*-Hex); mp 99–101 °C; ^{1}H NMR (CDCl$_3$, 270 MHz) δ ppm = 5.04 (s, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.47 (d, J = 7.9 Hz, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.67 (s, 1H); ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ ppm = 27.46, 111.29, 123.76, 125.81, 128.03, 130.20, 131.38, 133.57; IR (KBr) ν/cm^{-1} 2260 m (C≡N). **4b**: colorless needles (Bz/*n*-Hex); mp 72–74 °C; ^{1}H NMR (CDCl$_3$, 270 MHz) δ ppm = 1.33 (s, 9H), 5.02 (s, 1H), 7.41 (t, J = 1.7 Hz, 1H), 7.48 (t, J = 1.7 Hz, 1H), 7.63 (d, J = 1.7 Hz, 1H); ^{13}C NMR (CDCl$_3$, 67.8 MHz) δ ppm = 27.75, 31.00, 35.30, 111.38, 123.06, 123.79, 127.37, 127.64, 131.00, 155.80; IR (KBr) ν/cm^{-1} 2251 m (C≡N). **5**: colorless oil; ^{1}H NMR (CDCl$_3$, 270 MHz) δ ppm = 2.10 (s, 3H), 2.42 (s, 3H), 7.25–7.28 (m, 1H), 7.36–7.38 (m, 3H), IR (KBr) ν/cm^{-1} 2250 m (C≡N). **6a**: green plates; mp >220 °C; Mass (FAB): m/z = 392 (M)$^+$; ^{1}H NMR (CD$_3$OD, 270 MHz) δ ppm = 3.27 (s, 12H), 6.59 (d, J = 6.6 Hz, 1H), 6.82 (s, 1H), 7.00 (d, J = 9.2 Hz, 4H), 7.17–7.28 (m, 2H), 7.44 (d, J = 9.2 Hz, 4H). **6b**: green plates; m.p. 204–206 °C; Mass (FAB): m/z = 449 (M+H)$^+$; ^{1}H NMR (CDCl$_3$, 600 MHz) δ ppm = 1.25 (s, 9H), 3.28 (s, 6H), 6.47 (t, J = 1.8 Hz, 1H), 6.78 (d, J = 9.3 Hz, 4H), 6.79 (t, J = 1.8 Hz, 1H), 7.39 (d, J = 9.3 Hz, 4H), 7.45 (t, J = 1.8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 150 MHz) δ ppm = 29.42, 31.27, 34.74, 40.71, 112.76, 122.72, 123.67, 123.93, 126.92, 127.59, 139.26, 141.13, 142.74, 150.77, 156.70, 183.10. **7**: colorless needles (Bz/*n*-Hex); mp 96–98 °C; ^{1}H NMR (CDCl$_3$, 400 MHz) δ ppm = 3.77 (s, 6H), 4.99 (s, 1H), 6.82 (AA'BB', J = 2.6, 8.9 Hz, 4H), 7.12 (AA'BB', J = 2.6, 8.9 Hz, 4H), 7.33–7.37 (m, 1H), 7.39–7.41 (m, 2H), 7.53 (s, 1H); IR (KBr) ν/cm^{-1} 2255 w (C≡N), 3489 br (OH).
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9 Crystal data for **6a**· (CH$_3$COOC$_2$H$_5$)$_{0.75}$(THF)$_{0.25}$ (The composition was determined by NMR.): monoclinic; space group $P2_1/c$ (*#14*), a = 10.147(1) Å, b = 22.508(3) Å, c = 10.837(1) Å, β = 99.723(4)°, V = 2439.6(5)3, Z = 4, D_{calcd} = 1.069 g·cm^3, $R1$ = 9.0%. The data were deposited in Cambridge Crystallographic Data Center (CCDC 202240).
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