Push-pull type of diphenoquinoid chromophores as novel near-infrared dyes

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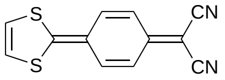
Novel push-pull diphenoquinoid chromophores, in which one of the terminal positions carries a strong donor group, benzo-1,3-dithiol-2-ylidene, and the other a strong acceptor group, dicyanomethylene, are synthesized and show a strong absorption in the near-infrared region.

The search for highly-coloured organic compounds has attracted current attention in terms of advanced optoelectronic materials, such as near-infrared dyes and nonlinear optics.[1,2] Push-pull types of conjugated π-electronic systems provide an entry to highly-coloured chromophores.[3] Such compounds containing a quinoid ring are especially interesting, because the push-pull stabilization can be promoted by the aromatization of the ring. Some time ago, Gompper *et al.* reported the quinoid compound **1** and benzo-fused derivative **2**, in which one of the terminal positions carries a strong donor group, 1,3-dithiol-2-ylidene, and the other a strong acceptor group, dicyanomethylene.[4] These compounds showed a strong intramolecular charge-transfer absorption band in the visible region (*vide infra*). The 1,4-naphthoquinoid analogue **3** and the 9,10-anthraquinoid one **4** were also prepared, but their absorption bands showed rather hypsochromic shifts.[4,5] The extensively conjugated diphenoquinoid systems **5** and **6**, so far unknown, are expected to show a bathochromic shift of the absorption band and serve as a receptor for near-infrared light. Here we report the synthesis and spectroscopic properties of the benzo derivatives **6a–c**.



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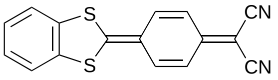

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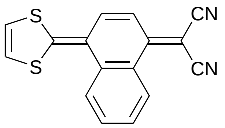

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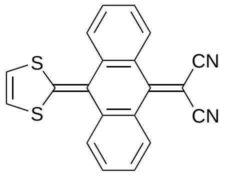

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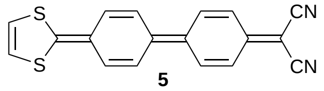

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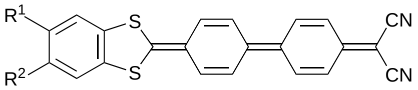
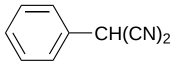


6a R^1, R^2 = H
b R^1 = Me, R^2 = H
c R^1, R^2 = C_8H_{17}



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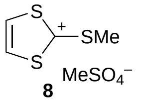

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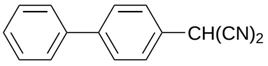

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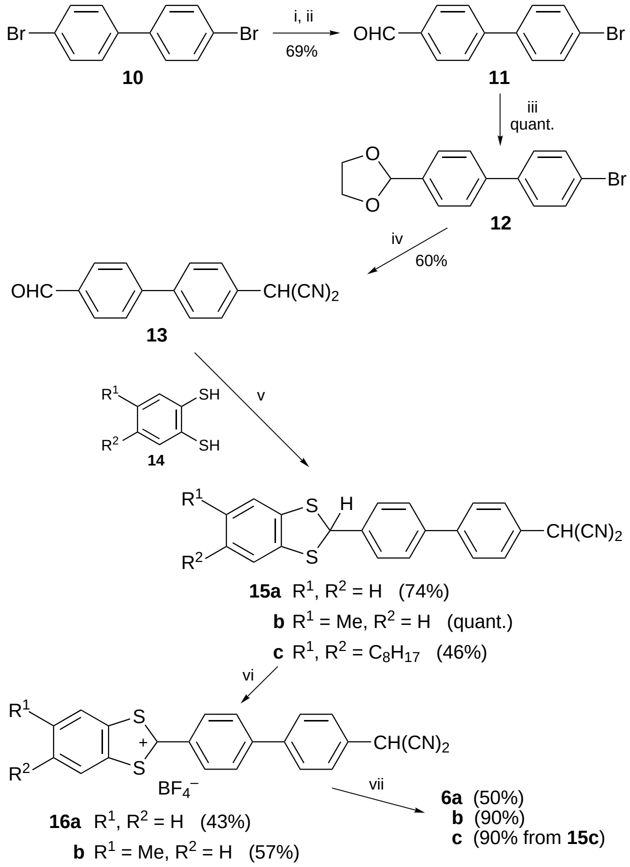
Although the Gompper method, involving reaction of dicyanomethylbenzene **7** with 2-methylthio-1,3-dithiolium methanesulfonate **8**, is very convenient and useful for the preparation of the benzoquinoid system,[4] attempted syntheses of the diphenoquinoid compounds **5** and **6** by the same method using 4-dicyanomethylbiphenyl **9** were unsuccessful. Alternatively, we synthesized **6a–c** by another route starting with 4,4′-dibromobiphenyl **10** as shown in Scheme 1: one of the functional groups of **10** was converted *via* lithiation to a formyl group, and then the other one to a dicyanomethyl group by the Takahashi reaction.[6] The intermediate **13** thus obtained was reacted with benzenedithiol **14** in the presence of a catalytic amount of toluene-*p*-sulfonic acid to give the dithioacetal **15**, which was then dehydrogenated *via* the carbonium salt **16** to the desired compound **6**.[7] All the reactions proceeded in reasonable to excellent yields.†

The benzoquinoid compounds **1** and **2** are blue in CH_2Cl_2 solution, and their electronic absorption spectra show a strong



Scheme 1 *Reagents and conditions*: i, Bu^nLi, Et_2O, −15 °C, 0.5 h; ii, DMF, −78 °C to room temp., 1 h; iii, $HOCH_2CH_2OH$, TsOH, benzene, reflux, 1 h; iv, $NaCH(CN)_2$, $Pd(PPh_3)_4$, THF, reflux, 4 h; v, TsOH, benzene, reflux, 1 h; vi, Ph_3CBF_4, CH_2Cl_2–MeCN, 60 °C, 3 h; vii, Et_3N, MeCN, room temp., 2 h

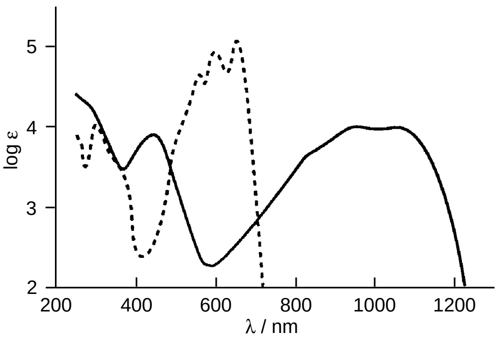
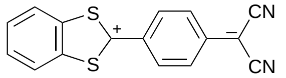


Fig. 1 Electronic spectra of **2** (- - -) and **6a** (——) in CH_2Cl_2

colour-determining band with fine structure in the region of 550–650 nm. The band shows very little solvent shift. On the other hand, the diphenoquinoids **6a**–**c** look green–black in the solid state but are faint yellow in solution, and their electronic spectra have a characteristic broad band in the near-infrared region as well as a second band at around 450 nm. Fig. 1 demonstrates the specific spectral features of **2** and **6a**, and Table 1 summarizes the electronic absorption maxima and nitrile vibrational absorptions of **1**, **2** and **6a**–**c**. Interestingly, the absorption bands of **6**, unlike those of **1** and **2**, show large negative solvatochromism with increasing solvent polarity: for example, λ_{max} of **6a** is 957 and 1045 nm in CH_2Cl_2, 934 nm in PhCN, and 790 nm in Me_2SO.

It is reasonable to assume that the push-pull quinoid systems **2** and **6** exist as a resonance hybrid with the zwitterionic forms **17** and **18**, respectively. Infrared spectra provide definite information on these resonance structures: the nitrile vibrational absorption of **2** appears at a much lower frequency (2195 cm^{-1}) than that of TCNQ (2226 cm^{-1}). This indicates a considerable contribution by the ionic form **17**. The absorptions of **6a**–**c** are further shifted (2174–2180 cm^{-1}) and comparable to those of lithium phenyldicyanomethanide (2178 cm^{-1}) and sodium phenyldicyanomethanide (2188 cm^{-1}). This indicates that the diphenoquinoid system **6** predominantly exists as the ionic form **18**, consistent compatible with the large negative solvatochromism. The predominance of the ionic form **18** must presumably be promoted by the benefit of gaining double aromaticity.



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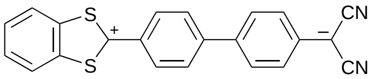

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Table 1 λ_{max} and ν_{CN} of quinoid compounds **1**, **2** and **6**

Compound	λ_{max}/nm[a]	ν_{CN}/cm^{-1} [b]
1	551(4.46), 592(4.78), 644(4.89)	2191
2	548(4.68), 589(4.93), 641(4.97)	2195
6a	957(3.71), 1045(3.91)	2174
6b	962(4.41), 1042(4.42)	2180
6c	963(4.46), 1031(sh, 4.25)	2180

[a] Measured in CH_2Cl_2. [b] Measured on a KBr disk.

The present results clearly demonstrate that the diphenoquinoid compounds **6a**–**c** are an interesting push-pull system with highly polar character and a new type of dyes strongly absorbing near-infrared light.

Footnotes

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† All the new compounds were characterized by spectroscopic measurements and elemental analyses.

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