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The effects of π-acceptor and π-donor substitution in cross-conjugated enynes

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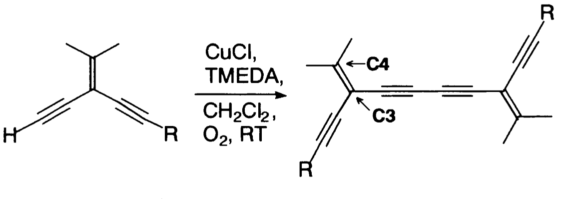
Abstract—Donor (p-$NMe_2C_6H_4$) and acceptor (p-$NO_2C_6H_4$) substitution has been appended onto two different cross-conjugated enyne scaffolds and the electronic effects as a function of substitution have been evaluated. Interestingly, the observed electronic effects are quite dependent on the constitution of the enyne framework. In the case of tetraynes **2a**–**c**, acceptor substituted **2b** shows an additional low energy absorption in the UV–vis spectrum as compared to **2a** and **2c**. In contrast, little difference in the electronic characteristics of **4a**–**b** is detected. The X-ray crystallographic analysis of **4a** is also described. © 2001 Elsevier Science Ltd. All rights reserved.

We,[1] and others,[2] have been intrigued by the electronic characteristics that are unique to cross-conjugated organic molecules.[3,4] In contrast to linearly conjugated chromophores, cross-conjugated molecules generally display reduced π-electron delocalization, the extent of which remains to be explored for most systems.[3] Recently, it has been suggested that the presence of electronic rich functionality can increase the degree of electronic communication in cross-conjugated systems.[5]

In an effort to probe the fundamental characteristics of cross-conjugated molecules, we have developed efficient synthetic techniques that allow for the rapid, often divergent, assembly of functionalized enyne derivatives.[1] We report herein the synthesis of several examples of extended, cross-conjugated enynes with bis(donor) and bis(acceptor) substituents and the interesting electronic absorption behavior that they exhibit.

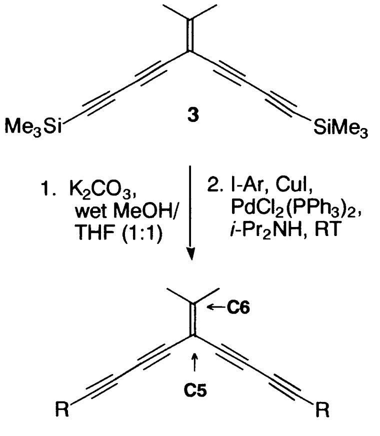


(1)

1a R = p-$Me_2NC_6H_4$
1b R = p-$O_2NC_6H_4$

2a R = p-$Me_2NC_6H_4$, 68%
2b R = p-$O_2NC_6H_4$, 87%
2c R = Sii-Pr_3

Oxidative homocoupling of terminal alkynes provided the first series of chromophores (Eq. (1)).[6] In the presence of CuCl, TMEDA, and oxygen,[7] donor and acceptor enynes **1a** and **1b** were cleanly coupled to give dimeric species **2a** and **2b**.[8] Both derivatives could be isolated as stable yellow solids via column chromatography. For the purpose of additional comparison, silyl substituted derivative **2c** was prepared as previously reported.[1c]



(2)

4a R = p-$Me_2NC_6H_4$, 80%
4b R = p-$O_2NC_6H_4$, 82%

The second series of bis(donor) and bis(acceptor) chromophores was based on an enetetrayne framework (Eq. (2)). Desilylation of precursor **3**[1c] with K_2CO_3 in MeOH/THF gave the terminal alkyne, which was then

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Keywords: enynes; donor/acceptor chromophores; tetrayne; cross conjugation.

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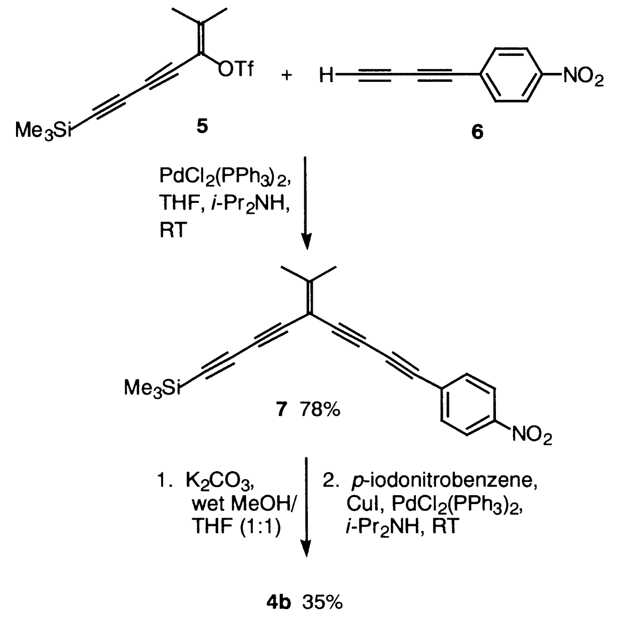
cross-coupled under Sonogashira conditions[9] with either *p*-iodo-*N*,*N*-dimethylaniline or *p*-iodo-nitrobenzene to give **4a** and **4b**, respectively. Whereas bis(donor) **4a** could be readily purified by column chromatography, the isolation of **4b** proved problematic. Despite the fact that it was formed in high yield, the isolation of **4b** was always hampered by contamination with side product(s) resulting from oxidative homocoupling reactions of the acetylenic precursor.

As a result, an alternative route was designed, as shown in Scheme 1. Coupling of vinyl triflate **5**[10] with 1,3-butadiyne **6**[11] using $PdCl_2(PPh_3)_2$/CuI gave tetrayne **7** in 78% yield. Removal of the trimethylsilyl group methanolic K_2CO_3 gave the terminal alkyne, which could be cross-coupled with *p*-iodonitrobenzene to give **4b** as a yellow solid that could be effectively purified by column chromatography.



Scheme 1.

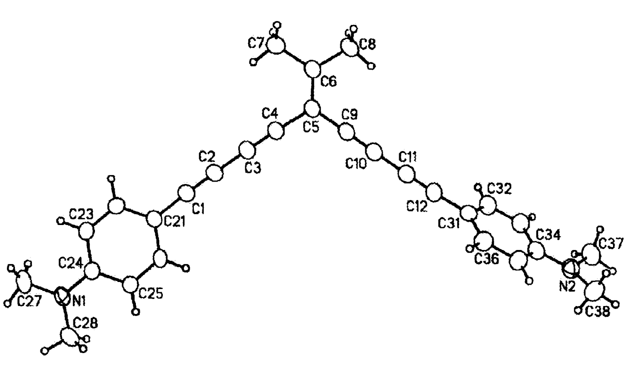


Figure 1. ORTEP drawing (20% probability level) of **4a** (molecule A). Selected bond lengths (Å) and angles (°): C(1)–C(21) 1.429(5), C(1)–C(2) 1.191(5), C(2)–C(3) 1.373(5), C(3)–C(4) 1.189(5), C(4)–C(5) 1.445(5), C(5)–C(6) 1.350(5), C(5)–C(9) 1.432(6), C(9)–C(10) 1.196(6), C(10)–C(11) 1.376(6), C(11)–C(12) 1.182(6), C(12)–C(31) 1.447(6); C(2)–C(1)–C(21) 177.1(4), C(1)–C(2)–C(3) 179.4(5), C(2)–C(3)–C(4) 178.8(5), C(3)–C(4)–C(5) 177.3(4), C(4)–C(5)–C(9) 115.0(4), C(5)–C(9)–C(10) 177.7(4), C(9)–C(10)–C(11) 177.6(5), C(10)–C(11)–C(12) 179.1(5), C(11)–C(12)–C(31) 177.1(5).

Complete spectroscopic characterization was accomplished for both types of donor/acceptor enynes, **2a**–**b** and **4a**–**b**. The ^{13}C NMR spectra provide an indication of the ability of pendant acceptor or donor groups to influence physical properties. For triisopropylsilyl end capped **2c**, which serves more or less as an electronically neutral model, the deshielded vinylidene carbon C(4) is observed at δ 158.8. As expected, based on resonance, this carbon, at δ 155.9, is more shielded for bis(donor) **2a**, whereas it is more deshielded for bis(acceptor) **2b** at 160.7 ppm. A similar trend is observed for enynes **3**–**4**. The vinylidene carbon C(6) for tetrayne **3**, at 163.9 ppm, is even more deshielded than for **2c**, as a result of the increased electron deficiency of the two butadiynyl groups. For bis(donor) **4a**, C(6) is shielded by nearly 4 ppm to δ 159.4, whereas for electron deficient **4b**, this vinylidene carbon at δ 165.0 is slightly more deshielded than for **3**. The other vinylidene carbons for **2**–**4**, C(3) and C(5), resonate between δ 99.7 and 100.9.

Single crystals of **4a** suitable for X-ray analysis were grown by diffusion of MeOH into a CH_2Cl_2 solution at 4°C.[†] The solid state structure for **4a** incorporates two geometrically similar, but crystallographically independent molecules into the unit cell. The cross-conjugated enyne core, including one of the dimethylaminophenyl groups, is quite nearly planar (Fig. 1). The second aryl moiety, however, is rotated out of this plane by 59.8° in the case of molecule A, and 72.3° for molecule B (not shown).

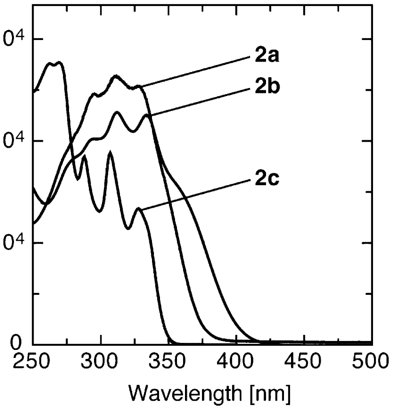


Figure 2. Electronic absorption spectra (ε [L M^{-1} cm^{-1}]) in $CHCl_3$ comparing the effects of substitution for **2a**–**c**.

[†] Crystal data for compound **4a**: $C_{28}H_{26}N_2$, $M=390.51$, monoclinic, space group $P2_1/c$ (no. 14), $a=15.9322(15)$ Å, $b=24.877(2)$, $c=11.8608(11)$ Å, $\beta=103.1956$ (19)°, $V=4576.8(7)$ Å^3, $Z=8$, $D_{\text{calcd}}=1.133$ g cm^{-3}. Final $R(F)=0.0739$, $wR_2(F^2)=0.2045$ for 553 variables and 9396 data with $Fo^2\geq-3\sigma(Fo^2)$ (2703 observed reflections $[Fo^2\geq2\sigma(Fo^2)]$). $S=0.939$ $[Fo^2\geq-3\sigma(Fo^2)]$. Crystallographic data (excluding structural factors) for compound **4a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 170231.

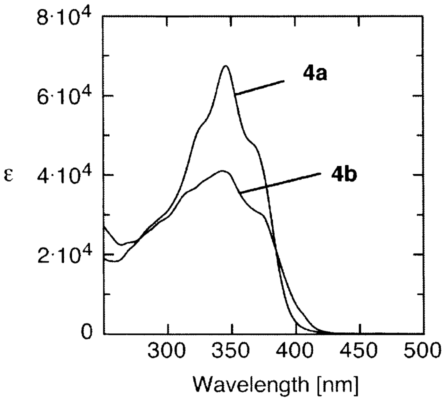


Figure 3. Electronic absorption spectra (ε [L M^{-1} cm^{-1}]) in $CHCl_3$ comparing the effects of substitution for **4a**–**b**.

The electronic absorption spectra for dimeric **2a**–**c** are shown in Fig. 2. Three low energy absorptions at ca. 290, 310 and 330 nm are observed for all three derivatives, and the energy of these absorptions changes little as a result of the different pendant groups of **2a**–**c**. The most surprising observation, however, is found in the spectrum of **2b**, where a significant shoulder absorption is found near 350 nm. Whereas previous studies have suggested enhanced communication in cross-conjugated molecules resulting from increasingly electron rich substitution,[5] in tetraynes such as **2**, it is clearly the electron poor functionality that has the more dramatic effect.

The UV–vis spectra for **4a**–**b** are shown in Fig. 3. In the spectrum of both **4a**–**b**, three low energy absorptions are visible, centered at approximately 327, 346, and 366 nm. Although electron rich **4a** shows a slightly higher molar absorptivity, the overall electronic absorption characteristics for **4a**–**4b** are quite analogous. Thus, the anomalous behavior resulting from π-electron acceptors appears limited to molecules such as **2**.

Acknowledgements

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References

1. (a) Ciulei, S. C.; Tykwinski, R. R. *Org. Lett.* **2000**, *2*, 3607–3610; (b) Eisler, S.; McDonald; Loppnow, G. R.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2000**, *122*, 6917–6928; (c) Zhao, Y.; Campbell, K.; Tykwinski, R. R. *J. Org. Chem.* **2001**, submitted; (d) Zhao, Y. M.; McDonald, R.; Tykwinski, R. R. *Chem. Commun.* **2000**, 77–78; (e) Campbell, K.; McDonald, R.; Branda, N. R.; Tykwinski, R. R. *Org. Lett.* **2001**, *3*, 1045–1048.
2. (a) Diederich, F. *Chem. Commun.* **2001**, 219–227; (b) Faust, R.; Göbelt, B.; Weber, C.; Krieger, C.; Gross, M.; Gisselbrecht, J.-P.; Boudon, C. *Eur. J. Org. Chem.* **1999**, 205–214; (c) Bryce, M. R.; Coffin, M. A.; Skabara, P. J.; Moore, A. J.; Batsanov, A. S.; Howard, J. A. K. *Chem. Eur. J.* **2000**, *6*, 1955–1962; (d) Wang, W. L.; Helgeson, R.; Ma, B.; Wudl, F. *J. Org. Chem.* **2000**, *65*, 5862–5867; (e) Song, Y.; Spencer, L.; Euler, W. B.; Rosen, W. *Org. Lett.* **1999**, *1*, 561–564.
3. (a) Hopf, H. *Angew. Chem., Int. Ed.* **1984**, *23*, 948–960; (b) Hopf, H. *Classics in Hydrocarbon Synthesis*; Wiley-VCH: Weinheim, 2000; Chapter 11.
4. Phelan, N. F.; Orchin, M. *J. Chem. Ed.* **1968**, *45*, 633–637.
5. (a) Schreiber, M.; Tykwinski, R. R.; Diederich, F.; Spreiter, R.; Gubler, U.; Bosshard, C.; Poberaj, I.; Günter, P.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Jonas, U.; Ringsdorf, H. *Adv. Mater.* **1997**, *9*, 339–343; (b) Nielsen, M. B.; Schreiber, M.; Baek, Y. G.; Seiler, P.; Lecomte, S.; Boudon, C.; Tykwinski, R. R.; Gisselbrecht, J.-P.; Gramlich, V.; Skinner, P. J.; Bosshard, C.; Günter, P.; Gross, M.; Diederich, F. *Chem. Eur. J.* **2001**, *7*, 3263–3280.
6. Siemsen, P.; Livingston, R. C.; Diederich, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2633–2657.
7. Hay, A. S. *J. Org. Chem.* **1962**, *27*, 3320–3321.
8. Compound **2a**: Mp 185°C (decomp). IR (μscope) 2904, 2202, 2133, 1609, 1585, 1521, 1363. ^1H NMR (300 MHz, $CDCl_3$) 7.32 (d, $J=9.0$ Hz, 4H), 6.61 (d, $J=9.0$ Hz, 4H), 2.95 (s, 12H), 2.086 (s, 6H), 2.084 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) 155.9, 150.1, 132.6, 111.9, 110.2, 101.4, 93.1, 83.4, 79.4, 75.7, 40.3, 23.0(2×). HRMS calcd for $C_{32}H_{32}N_2$ (M^+) 444.2566, found 444.2559.
   Compound **2b**: Mp=176–178°C. IR (μscope) 3103, 2910, 2209, 1515, 1342. ^1H NMR (400 MHz, $CDCl_3$) 8.16 (d, $J=8.4$ Hz, 4H), 7.57 (d, $J=8.4$ Hz, 4H), 2.14 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, APT) 160.7, 147.0, 132.0, 130.0, 123.6, 100.4, 90.4, 90.2, 78.5, 76.1, 23.3(2×). HRMS calcd for $C_{28}H_{20}O_4N_2$ (M^+) 448.1423, found 448.1419.
   Compound **4a**: Mp=148°C (decomp). IR (μscope) 2903, 2198, 2134, 1522 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, $J=9.0$ Hz, 4H), 6.59 (d, $J=9.0$ Hz, 4H), 2.97 (s, 12H), 2.09 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, APT) δ 159.4, 150.4, 133.6, 111.6, 108.0, 100.8, 84.0, 77.1, 77.0, 72.2, 40.1, 23.3. EI HRMS calcd for $C_{28}H_{26}N_2$ (M^+) 390.2096, found 390.2099.
   Compound **4b**: Mp=117°C (decomp). IR (μscope) 3103, 2931, 2201, 1343 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, $J=8.6$ Hz, 4H), 7.62 (d, $J=8.6$ Hz, 4H), 2.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, APT) δ 165.0, 147.5, 133.2, 128.6, 123.7, 99.8, 80.2, 79.6, 78.6, 76.2, 23.5. EI HRMS calcd for $C_{24}H_{14}N_2O_4$ (M^+) 394.0954, found 394.0954.
9. Sonogashira, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F.; Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1997.
10. Stang, P. J.; Ladika, M. *Synthesis* **1981**, 29–30.
11. Graham, E. M.; Miskowski, V. M.; Perry, J. W.; Coulter, D. R.; Stiegman, A. E.; Schaefer, W. P.; Marsh, R. E. *J. Am. Chem. Soc.* **1989**, *111*, 8771–8779.