Angewandte
International Edition Chemie

DOI: 10.1002/anie.201002236

Push–Pull Chromophores

Homoconjugated Push–Pull and Spiro Systems: Intramolecular Charge-Transfer Interactions and Third-Order Optical Nonlinearities**

*Shin-ichiro Kato, Marten T. Roberts Beels, Philip La Porta, W. Bernd Schweizer, Corinne Boudon, Jean-Paul Gisselbrecht, Ivan Biaggio, and François Diederich**

Planar and non-planar push–pull chromophores (D-π-A), consisting of strong electron donors (D) and acceptors (A) connected by a π-conjugated spacer, feature intense intramolecular charge-transfer (CT) interactions[1,2] and have recently received considerable attention as functional components in molecular electronics and nonlinear optics (NLO).[3] Transannular CT interactions between nonconjugated donors and acceptors in rigid molecular frameworks have also been extensively investigated. Through-space CT interactions in cyclophane derivatives, in which the donor and acceptor moieties are parallel to one another, were established by Staab and Rebafka[4] and Misumi and Otsubo,[5] and further explored by others.[6] When donor and acceptor are separated by appropriately aligned, rigid σ-bond frameworks, long-range through-bond CT interactions were also observed in the UV/Vis spectra.[7] Only a few examples of transannular CT chromophores with a non-parallel arrangement, so-called homoconjugated push–pull systems, have been reported,[8–11] since Nakazawa and Murata published the first example of homoconjugated CT interactions in 9,10-dihydro-9,10-(1,2-tropylio)anthracene tetrafluoroborate in 1977.[8] In general, the reported homoconjugative CT interactions have been mostly restricted to bicyclic [2.2.2] π systems, and in particular triptycene derivatives.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is a popular strong oxidizing and dehydrogenating agent with many uses.[12,13] We envisaged that thermal [2+2] cycloaddition between donor-activated electron-rich alkynes and the electron-deficient C=C double bonds in DDQ could take place to give new push–pull systems.[2b] Very recently, during the completion of the present study, Trofimov et al. indeed described [2+2] cycloadditions of DDQ with pyrrole- or indole-activated alkynes to give a variety of cycloadducts.[14] Herein, we describe a new class of homoconjugated push–pull chromophores (±)-**1** to (±)-**9** by [2+2] cycloaddition of *N*,*N*-dialkylanilino (DAA) and ferrocene (Fc)-substituted alkynes to DDQ. They feature surprisingly strong intramolecular CT interactions and, to the best of our knowledge, are the first homoconjugated push–pull chromophores with promising third-order nonlinear optical (NLO) properties. We also report the synthesis and characterization of spiro compound (±)-**10** by an electrocyclic ring-opening reaction of (±)-**1** followed by a transannular rearrangement.

Good to excellent yields (63–94 %) of DAA-substituted chromophores (±)-**1** to (±)-**6** were obtained by [2+2] cycloaddition of DDQ with the acetylenic precursors **11** to **16** in 1,2-dichloroethane at 25 °C (Scheme 1). Analogously, the Fc-substituted chromophores (±)-**7** to (±)-**9** were formed in 62–90 % yield by reaction of DDQ with alkynes **17** to **19**, respectively. The chromophoric products are deeply colored solids that are stable at ambient temperature in air. Thermal gravimetric analysis (TGA) did not show any significant weight loss (< 5 %) below 160 °C. However, upon heating a 1,2-dichloroethane solution of (±)-**1** at 80 °C for 36 h, we discovered the formation of (±)-**10**, in which an unsaturated γ-lactone is spiro-annulated, in 16 % yield as a purple solid. It originates from electrocyclic ring-opening reaction of (±)-**1** to the intermediate cyclooctatrienedione **20**, followed by transannular reaction of the two carbonyl groups and migration of one cyanovinyl moiety to close the spiro system (Scheme 2).[15] Indeed, density functional theory (DFT) calculations for the three isomers (±)-**1**, (±)-**10**, and **20** at the PBE1PBE/6-311 + G(d)//PBE1PBE/6-31G(d) level predict that (±)-**10** is the most stable and (±)-**1** and **20** are less stable by 32.2 and 34.2 kcal mol^{-1}, respectively.[16]

The X-ray analyses of (±)-**1**, (±)-**2**, and (±)-**7** to (±)-**9** revealed that the cycloaddition was regioselective with respect to DDQ, and occurred at the dicyano-substituted C=C bond (Figure 1, and Figures S1–S5 in the Supporting Information). Interestingly, distinct bond length alternations were observed in the benzene rings in DAA-substituted cycloadducts (±)-**1** and (±)-**2**. The DAA rings in both (±)-**1** and (±)-**2** display quinoid character *δr* (for definition and bond lengths, see caption to Figure 1) of 0.031 Å, which is

---

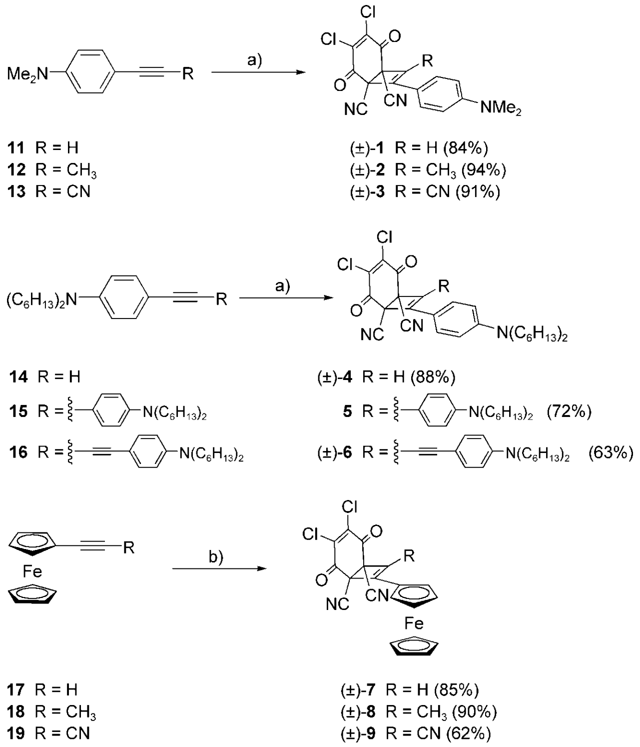
[*] Dr. S.-i. Kato, Dr. W. B. Schweizer, Prof. Dr. F. Diederich
Laboratorium für Organische Chemie, ETH Zürich
Hönggerberg, HCI, 8093 Zürich (Switzerland)
Fax: (+41) 446-321-109
E-mail: diederich@org.chem.ethz.ch

M. T. R. Beels, P. La Porta, Prof. Dr. I. Biaggio
Department of Physics and Center for Optical Technologies
Lehigh University
Bethlehem, PA 18015 (USA)

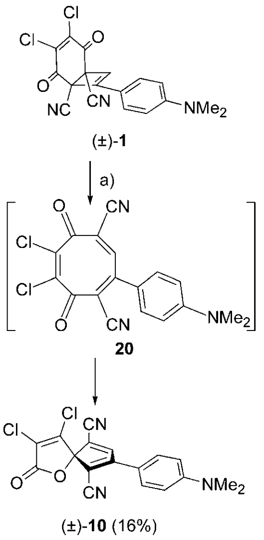
Prof. Dr. C. Boudon, Dr. J.-P. Gisselbrecht
Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide
Institut de Chimie-UMR 7177, C.N.R.S., Université de Strasbourg
4, rue Blaise Pascal, 67000 Strasbourg (France)

[**] This work was supported by a grant from the ETH research council and in part by the ERC Advanced Grant No. 246637 ("OPTELOMAC"). S.K. acknowledges the receipt of a JSPS Postdoctoral Fellowship for Research Abroad. We thank Dr. B. Bernet (ETHZ) for useful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201002236.



Scheme 1. Synthesis of homoconjugated push–pull chromophores (±)-**1** to (±)-**9**. Reagents and conditions: a) DDQ, 1,2-dichloroethane, 25 °C; b) DDQ, 1,2-dichloroethane, 25 °C ((±)-**7** and (±)-**8**) or 60 °C ((±)-**9**).



Scheme 2. Synthesis of donor-substituted spiro compound (±)-**10**. Reagents and conditions: a) 1,2-dichloroethane, 80 °C.

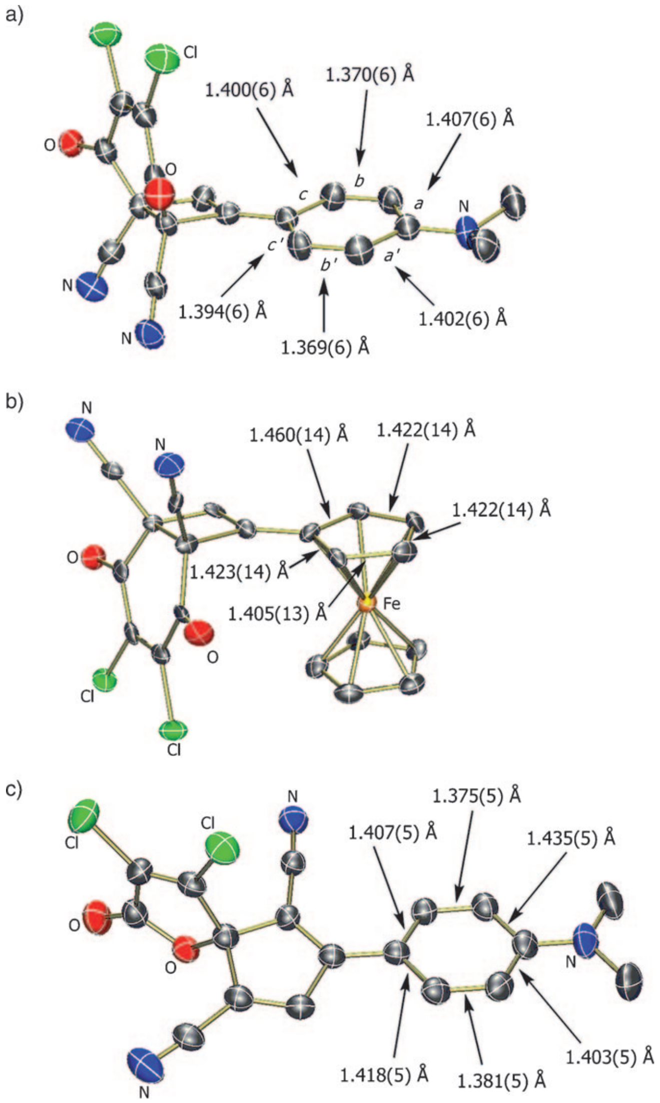


Figure 1. ORTEP plots of a) (±)-**1**, b) (±)-**7**, and c) (±)-**10** with vibrational ellipsoids at 173 K at the 50% probability level. Arbitrary numbering. Quinoid character: $\delta r = (((a+a')/2-(b+b')/2)+((c+c')/2-(b+b')/2))/2)$. In benzene, δr equals 0; in fully quinoid rings, $\delta r = 0.08$—00.1 Å. For details of the X-ray analyses, including CCDC numbers, see the Supporting Information.

indicative of a substantial contribution of the quinoidal structures as a result of efficient homoconjugative CT interactions. In Fc derivatives (±)-**7** to (±)-**9**, however, clear bond-length alternations in the substituted cyclopentadienyl (Cp) rings are not observed, which hints at additional mechanisms of donor–acceptor interactions.[17] Short intramolecular C–H···O and/or C–H···C contacts at van der Waals distances between the Fc donor moiety and the dichloroenedione acceptor moiety are seen in the crystal structures (Supporting Information, Figures S3–S5). These observations suggest that through-bond interactions are dominant for the intramolecular CT transition in DAA-substituted cycloadducts (±)-**1** to (±)-**6**, whereas through-space CT interactions probably make an additional important contribution in Fc-substituted cycloadducts (±)-**7** to (±)-**9**. Spiro compound (±)-**10**, in which donor and part of the acceptor are π-conjugated, was also characterized by X-ray analysis (Figure 1). As a result of the direct π conjugation, its DAA ring features a higher δr value of 0.038 Å relative to homoconjugated (±)-**1** and (±)-**2**.

The efficiency of the intramolecular CT interactions in the new chromophores was further evaluated by UV/Vis spectroscopy, computational studies, and electrochemistry. Compounds (±)-**1** to (±)-**9** display very broad CT absorption bands of moderate intensity, with end absorptions reaching in some cases into the near-infrared region in CH_2Cl_2 (Figure 2). The CT character of these bands in (±)-**1** to (±)-**6** with DAA donors was confirmed by protonation experiments (Supporting Information, Figures S9–S15). When a CH_2Cl_2 solution of (±)-**1** was acidified with CF_3COOH, the color changed from purple to colorless and the broad absorption band at 529 nm completely disappeared. Neutralization with Et_3N regenerated the original spectra almost quantitatively. DAA-substituted cycloadducts (±)-**1** to (±)-**3** feature similar maxima of their lowest-energy intramolecular CT bands at $\lambda_{max} = 529$ nm (2.34 eV, (±)-**1**), 541 nm (2.29 eV, (±)-**2**), and 528 nm (2.35 eV, (±)-**3**). The CT bands of Fc-substituted cycloadducts (±)-**7** to (±)-**9** (620 nm ((±)-**7**), 635 nm ((±)-**8**), 635 nm ((±)-**9**)) are weaker in intensity but bathochromically shifted by about 100 nm relative to those in the spectra of (±)-**1** to (±)-**3** (Figure 2b). Incorporation of a second DAA donor results in a substantial bathochromic shift of the CT absorption bands in **5** and (±)-**6** relative to that of (±)-**4**, which contains only one DAA donor. Thus, the lowest-energy CT band of **5** is seen at 677 nm (1.83 eV) with an end-absorption near 980 nm (1.26 eV; Figure 2a; for solvatochromism, see the Supporting Information, Figure S17).

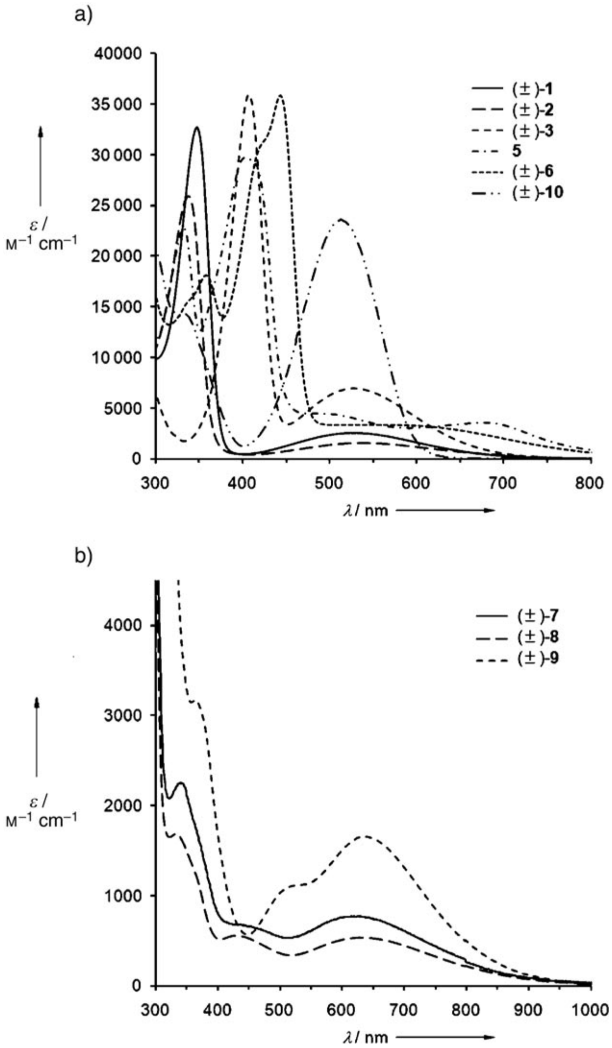


Figure 2. Electronic absorption spectra of a) DAA-substituted cycloadducts (±)-**1** to (±)-**3**, **5**, (±)-**6**, and (±)-**10** and b) Fc-substituted cycloadducts (±)-**7** to (±)-**9** (b) in CH_2Cl_2 at 298 K.

The electronic-transition analysis of (±)-**1** to (±)-**3** by time-dependent DFT (TD-DFT) at the TD-PBE1PBE/cc-pVDZ//PBE1PBE/6-31G(d) level compares well with experimental values (Supporting Information, Tables S5–S7). The longest-energy absorptions in all of the chromophores are derived from the transition between the DAA-centered HOMO and the enedione-centered LUMO. The HOMO and LUMO orbitals in all three chromophores partially overlap on the cyclobutene moieties (Supporting Information, Figure S20), suggesting a main pathway for the observed homoconjugative CT interactions through the cyclobutene rings.

The UV/Vis absorption spectrum of spiro compound (±)-**10** is dominated by a CT band at $\lambda_{max} = 514$ nm (2.41 eV) with a large ε value of 23 500 $L\,mol^{-1}\,cm^{-1}$ (Figure 2a). DFT calculations reveal that the intramolecular CT in (±)-**10** predominantly arises from the π-conjugated D–A interaction between the DAA donor and the Cp acceptor moieties (Supporting Information, Figure S22). The electron-withdrawing, unsaturated γ-lactone moiety, however, should also contribute to the acceptor potency owing to the spiroconjugative effect.[18]

Cyclic voltammetry (CV; Table 1) and rotating-disk voltammetry (RDV; Supporting Information, Table S3) in CH_2Cl_2 (+0.1 mol L^{-1} $n$$Bu_4NPF_6$, internal standard Fc^+/Fc) revealed that all of the cycloadducts (±)-**1** to (±)-**9** display two 1 e^--reduction couples between −0.69 and −1.53 V that are centered on the quinone core. Each donor moiety (DAA or Fc) undergoes a 1 e^--oxidation step. The effect of homoconjugative CT interactions in the ground state is notably visible in the DAA-centered oxidation potentials of (±)-**4** and **5**. The H-substituted derivative (±)-**4** is oxidized at +0.65 V. In (±)-**4**, the DAA moiety retains nearly full planarity with the cyclobutene moiety (torsion angle C8-C7-C17-C18 = 10.4(8)° in (±)-**1**), thereby rendering the intramolecular CT interactions quite efficient. In contrast, substitution with a second DAA donor in **5** induces a twist around the C–C single bond connecting the DAA moiety to the cyclobutene moiety. This twisting causes a reduced transfer of electron density from the DAA donor to the dichloroenedione acceptor moiety, resulting in a significant cathodic shift of the first oxidation potential in **5** by 360 mV (+0.65 V in (±)-**4** and +0.29 V in **5**) and of the second oxidation potential by 130 mV (+0.52 V). A good linear correlation exists between the optical gap (ΔE_{opt}; energy of the longest-wavelength maxima) and the electrochemical gap (ΔE_{redox}) in (±)-**1** to (±)-**6** (Supporting Information, Figure S8).

High third-order optical nonlinearities have in the past been mostly reported for planar and non-planar π-conjugated chromophores. Consequently, this has limited the structural diversity that can be used to generate desirable nonlinear optical functionalities. We measured the rotational average of the third-order polarizability of (±)-**1** to (±)-**4**, (±)-**6**, and

Table 1: CV data[a] and a summary of electrochemical and optical energy gaps.

	Cyclic voltammetry $E°$ [V][b]	ΔE_p [mV][c]	E_p [V][d]	ΔE_{redox} [V][e]	ΔE_{opt} [eV][f]
(±)-**1**	+0.67	75		1.51	2.34
			−0.84[g]		
			−1.48[g]		
5	+0.52	90		1.13	1.83
	+0.29	60			
	−0.84	80			
	−1.53	100			
(±)-**6**	+0.52	80		1.17	1.98
	+0.36	60			
	−0.81	70			
			−1.51		
(±)-**7**	+0.32	65		1.08	1.99
	−0.76	75			
			−1.53[g]		
(±)-**10**	+0.76	75		1.76	2.41
			−1.00		

[a] Recorded in CH_2Cl_2 (+0.1 mol L^{-1} nBu$_4$NPF$_6$). All potentials are given versus the Fc$^+$/Fc couple used as internal standard. Working electrode: glassy carbon electrode, counter electrode: Pt, pseudo reference electrode: Pt. Scan rate: 0.1 V s^{-1}. The complete set of data for (±)-**1** to (±)-**10**, including those from rotating-disk voltammetry (RDV), are included in the Supporting Information. [b] $E° = (E_{pc} + E_{pa})/2$, where E_{pc} and E_{pa} correspond to the cathodic and anodic peak potentials, respectively. [c] $\Delta E_p = E_{ox} - E_{red}$, where the subscripts ox and red refer to the conjugated oxidation and reduction steps, respectively. [d] E_p = irreversible peak potential. [e] The electrochemical gap, ΔE_{redox}, is defined as the potential difference between the first oxidative and first reductive redox potentials. [f] The optical gap, ΔE_{opt}, is defined as the energy corresponding to the energy of the CT absorption ($\lambda_{\max}$). [g] Reversible electron transfer at scan rates higher than 1 V s^{-1}.

(±)-**10** by degenerate four-wave mixing (DFWM) at a wavelength of 1.5 micrometers in CH_2Cl_2 solutions (see the Supporting Information). Homoconjugated chromophores (±)-**1** to (±)-**4** and (±)-**6** displayed moderate to large third-order polarizabilities (γ_{rot} values), which must be ascribed to efficient intramolecular CT interactions (Supporting Information, Table S4). Whereas (±)-**4** showed a γ_{rot} value of $(2.0 \pm 1.0) \times 10^{-48}$ m^5 V^{-2}, the more extended (±)-**6**, which incorporates two DAA donors, gave $\gamma_{\text{rot}} = (5.0 \pm 0.5) \times 10^{-48}$ m^5 V^{-2}. Remarkably, this value is comparable to those obtained for the most efficient planar and nonplanar D-π-A chromophores of similar size (Supporting Information, Table S4).[19,20] Substituents (H, Me, and CN) on the cyclobutene ring only slightly affected the γ_{rot} value in (±)-**1** to (±)-**3**: $< 1.0 \times 10^{-48}$ m^5 V^{-2} in (±)-**1**, $(0.8 \pm 0.8) \times 10^{-48}$ m^5 V^{-2} in (±)-**2**, and $(1.6 \pm 1.0) \times 10^{-48}$ m^5 V^{-2} in (±)-**3**). The spiro system is also NLO-active; (±)-**10** showed a γ_{rot} value of $(2.5 \pm 0.5) \times 10^{-48}$ m^5 V^{-2}.

In summary, we prepared a new family of homoconjugated push–pull chromophores by [2+2] cycloadditions of DDQ to donor-substituted alkynes, and exploited their unique reactivity to access the first member of a new class of D–A-functionalized spiro compounds. These cycloadducts feature intense intramolecular CT interactions as a result of effective homoconjugation that arises from the rigid bicyclic framework. Transannular CT interactions presumably also contribute in the Fc-derived push–pull systems. Remarkable third-order polarizabilities suggest new design opportunities for the development of NLO chromophores, which we are now fully exploiting.

Received: April 15, 2010

Keywords: charge transfer · conjugation · cycloadditions · nonlinear optoelectronic properties · spiro compounds

---

[1] R. Gompper, H.-U. Wagner, *Angew. Chem.* **1988**, *100*, 1492–1511; *Angew. Chem. Int. Ed. Engl. Ed.* **1988**, *27*, 1437–1455.
[2] a) M. Kivala, F. Diederich, *Acc. Chem. Res.* **2009**, *42*, 235–248; b) S.-i. Kato, F. Diederich, *Chem. Commun.* **2010**, *46*, 1994–2006.
[3] a) S. Barlow, S. R. Marder in *Functional Organic Materials* (Eds.: T. J. J. Müller, U. H. F. Bunz), Wiley-VCH, Weinheim, **2007**, pp. 393–437; b) Special issue on Organic Electronics and Optoelectronics, *Chem. Rev.* **2007**, *107*, 923–1386, edited by S. R. Forrest and M. E. Thompson.
[4] a) W. Rebafka, H. A. Staab, *Angew. Chem.* **1973**, *85*, 831–832; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 776–777; b) H. A. Staab in *New Aspects of Organic Chemistry I* (Eds.: Z. Yoshida, T. Shiba, Y. Oshiro), VCH, Weinheim, **1989**, pp. 227–236.
[5] S. Misumi, T. Otsubo, *Acc. Chem. Res.* **1978**, *11*, 251–256.
[6] a) *Cyclophanes* (Ed.: F. Vögtle), Springer, Heidelberg, **1983**; b) F. Diederich, *Cyclophanes*, Royal Society of Chemistry, Cambridge, **1991**; c) *Modern Cyclophane Chemistry* (Eds.: R. Gleiter, H. Hopf), Wiley-VCH, Weinheim, **2004**.
[7] H. Oevering, J. W. Verhoeven, M. N. Paddon-Row, J. M. Warman, *Tetrahedron* **1989**, *45*, 4751–4766.
[8] a) T. Nakazawa, I. Murata, *J. Am. Chem. Soc.* **1977**, *99*, 1996–1997; b) T. Nakazawa, N. Abe, K. Kubo, I. Murata, *Tetrahedron Lett.* **1979**, *20*, 4995–4998; c) K. Yamamura, T. Nakazawa, I. Murata, *Angew. Chem.* **1980**, *92*, 565–566; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 543–545; d) T. Nakazawa, Y. Niimoto, K. Kubo, I. Murata, *Angew. Chem.* **1980**, *92*, 566–567; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 545–546; e) T. Nakazawa, K. Kubo, I. Murata, *Angew. Chem.* **1981**, *93*, 195–196; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 189–190; f) K. Yamamura, K. Nakasuji, I. Murata, S. Inagaki, *J. Chem. Soc. Chem. Commun.* **1982**, 396–397; g) K. Yamamura, K. Nakasuji, H. Yamochi, I. Murata, S. Inagaki, *Chem. Lett.* **1983**, 627–630; h) K. Nakasuji, H. Yamochi, I. Murata, N. Yasuoka, M. Kusunoki, *Chem. Lett.* **1986**, 969–972.
[9] H. Iwamura, K. Makino, *J. Chem. Soc. Chem. Commun.* **1978**, 720–721.
[10] R. Gleiter, T. Doerner, H. Irngartinger, *Liebigs Ann.* **1996**, 381–391.
[11] Y. Kim, Z. Zhu, T. M. Swager, *J. Am. Chem. Soc.* **2004**, *126*, 452–453.
[12] D. Walker, J. D. Hiebert, *Chem. Rev.* **1967**, *67*, 153–195.
[13] a) J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney, A. M. Marguerettaz, *J. Org. Chem.* **1987**, *52*, 827–836; b) F. Diederich, H. A. Staab, *Angew. Chem.* **1978**, *90*, 383–385; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 372–374.
[14] B. A. Trofimov, L. N. Sobenina, Z. V. Stepanova, I. A. Ushakov, L. M. Sinegovskaya, T. I. Vakul'skaya, A. I. Mikhaleva, *Synthesis* **2010**, 470–476.
[15] E. Ghera, Y. Gaoni, S. Shoua, *J. Am. Chem. Soc.* **1976**, *98*, 3627–3632. An alternative mechanistic proposal was kindly made by one of the referees, involving a homolytic cleavage of a C(=O)–C(CN) bond in **20**, followed by a radical cyclization cascade.

[16] All calculations were conducted with Gaussian 09 (Revision A.02): M. J. Frisch et al. (see the Supporting Information).

[17] Bond-length alternations in the substituted Cp rings indicate a contribution of fulvene-type resonance structures in the ground state. For some recent work, see: a) T. Mochida, S. Yamazaki, *J. Chem. Soc. Dalton Trans.* **2002**, 3559 – 3564; b) S.-i. Kato, M. Kivala, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, F. Diederich, *Chem. Eur. J.* **2009**, *15*, 8687 – 8691; c) T. L. Kinnibrugh, S. Salman, Y. A. Getmanenko, V. Coropceanu, W. W. Porter III, T. V. Timofeeva, A. J. Matzger, J.-L. Brédas, S. R. Marder, S. Barlow, *Organometallics* **2009**, *28*, 1350 – 1357.

[18] For a review on spiroconjugation, see: a) H. Dürr, R. Gleiter, *Angew. Chem.* **1978**, *90*, 591 – 601; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 559 – 569; See also: b) P. Maslak, M. P. Augustine, J. D. Burkey, *J. Am. Chem. Soc.* **1990**, *112*, 5359 – 5360; c) P. Maslak, A. Chopra, *J. Am. Chem. Soc.* **1993**, *115*, 9331 – 9332; d) Y.-Y. Chien, K.-T. Wong, P.-T. Chou, Y.- M. Cheng, *Chem. Commun.* **2002**, 2874 – 2875; e) P. Sandín, A. Marínez-Grau, L. Sánchez, C. Seoane, R. Pou-Amérigo, E. Ortí, N. Martín, *Org. Lett.* **2005**, *7*, 295 – 298.

[19] a) J. C. May, J. H. Lim, I. Biaggio, N. N. P. Moonen, T. Michinobu, F. Diederich, *Opt. Lett.* **2005**, *30*, 3057 – 3059; b) J. C. May, I. Biaggio, F. Bureš, F. Diederich, *Appl. Phys. Lett.* **2007**, *90*, 251106.

[20] T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio, F. Diederich, *Chem. Commun.* **2005**, 737 – 739.