ORGANIC LETTERS

2012
Vol. 14, No. 1
54–57

N,*N′*-Dicyanoquinone Diimide-Derived Donor−Acceptor Chromophores: Conformational Analysis and Optoelectronic Properties[†]

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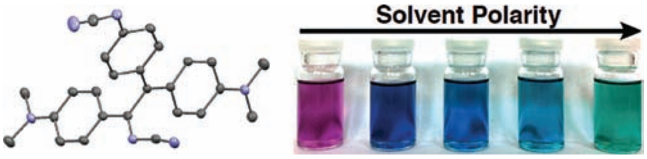
Received October 20, 2011

ABSTRACT



A formal [2 + 2] cycloaddition−cycloreversion (CA−CR) between *N*,*N′*-dicyanoquinone diimides (DCNQIs) and electron-rich alkynes was explored, providing a new class of π-conjugated donor−acceptor chromophores. These DCNQI adducts exist in the solid state as single diastereoisomers, but as two interconverting diastereoisomers in solution. Solid- and solution-state evidence for intramolecular charge transfer (CT) was obtained; additionally, the DCNQI adducts exhibit positive solvatochromism and significant solution-state third-order polarizabilities.

Formal [2 + 2] cycloaddition−cycloreversion (CA−CR) between electron-rich alkynes and electron-deficient alkenes, such as tetracyanoethene (TCNE) or 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), has been developed as a convenient and robust method for preparing nonplanar, π-conjugated, donor−acceptor chromophores that exhibit intense, low-energy, intramolecular charge-transfer (CT) bands.[1] These features render the 1,3-butadiene CA−CR products attractive for nonlinear optical (NLO) applications.[2] We therefore sought to expand the scope of acceptors for this reaction to include heteroatom analogues. Dicyanoquinone diimides (DCNQIs), first reported by Hünig and co-workers in 1984, emerged as prime CA−CR acceptor candidates,[3] as they are easily accessible in one step by condensation of commercially available 1,4-benzoquinones with bis(trimethylsilyl)carbodiimide.[4] Extensive studies have been performed on the conducting and magnetic properties of their intermolecular charge-transfer salts,[4−6]

[†] Dedicated to Prof. Dr. Dr. h. c. Siegfried Hünig on the occasion of his 90th birthday.

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(1) For a review on the CA−CR reaction, see: Kivala, M.; Diederich, F. *Acc. Chem. Res.* **2009**, *42*, 235–248.

(2) (a) Koos, C.; Vorreau, P.; Vallaitis, T.; Dumon, P.; Bogaerts, W.; Baets, R.; Esembeson, B.; Biaggio, I.; Michinobu, T.; Diederich, F.; Freude, W.; Leuthold, J. *Nat. Photonics* **2009**, *3*, 216–219. (b) Barlow, S.; Marder, S. R. *Functional Organic Materials*; Müller, T. J. J., Bunz, U. H. F., Eds.; Wiley-VCH: Weinheim, 2007; pp 393—437. (c) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372–1409. (d) Szablewski, M.; Thomas, P. R.; Thornton, A.; Bloor, D.; Cross, G. H.; Cole, J. M.; Howard, J. A. K.; Malagoli, M.; Meyers, F.; Brédas, J.-L.; Wenseleers, A.; Goovaerts, E. *J. Am. Chem. Soc.* **1997**, *119*, 3144–3154. (e) Tykwinski, R. R.; Gubler, U.; Martin, R. E.; Diederich, F.; Bosshard, C.; Günter, P. *J. Phys. Chem. B* **1998**, *102*, 4451–4465.

(3) Hünig, S; Herberth, E. *Chem. Rev.* **2004**, *104*, 5535–5563.

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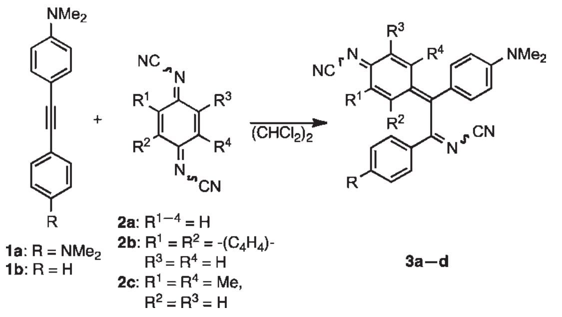
10.1021/ol202815q

but little has been reported on the reactivity of DCNQIs. Armed with the precedents that Lewis acids catalyze CA–CR reactions between *N*-tosylaldimines and alkynylated amines (ynamines),[7] sulfides,[8] and selenides,[9] however, we sought to investigate the reactivity of DCNQIs with electron-rich alkynes as well as to characterize the resulting products in the context of optoelectronic properties.

Table 1. Synthesis of DCNQI CA–CR Adducts[a]



alkyne	DCNQI (equiv)	temp/°C	time/h	product	yield/%
1a	**2a** (1.2)	25	1	**3a**	95
1a	**2b** (1.5)	45	4	**3b**	88
1a	**2c** (1.5)	80	4	**3c**	85
1b	**2a** (2.0)	80	8	**3d**	83

[a] Reaction concentration was 0.05 M with respect to alkyne.

Internal, *N*,*N*-dimethylanilino-susbstituted alkynes **1a**,**b** underwent CA–CR with DCNQIs **2a**–**c**[10] to yield dicyanoimine chromophores **3a**–**d** in good yields as dark blue-green solids (Table 1). Compounds **3a**–**d** are surprisingly robust and do not hydrolyze after heating for 12 h in 6 M HCl (353 K). They are also competent electron acceptors: reduction potentials of **3a**–**d** measured by cyclic voltammetry ($CH_2Cl_2 + 0.1$ M *n*-Bu_4NPF_6, against Fc^+/Fc) range from −0.81 to −0.95 V, compared to −0.25 to −0.45 V for the parent DCNQIs (for electrochemistry details, see the Supporting Information, section 2). Lewis acids did not catalyze the transformation, but those reactions using less electron-rich alkynes (e.g., **1b**) or less electron-deficient or sterically hindered DCNQIs (e.g., **2b**,**c**) required addition of excess DCNQI and heating to reach full conversion. In contrast, reactions using more activated substrates were completely inhibited by competing radical polymerization of the DCNQI starting materials.[11] Despite these constraints on substrate scope, several notable structural and optoelectronic features can be gleaned from the characterization of adducts **3a**–**d**.

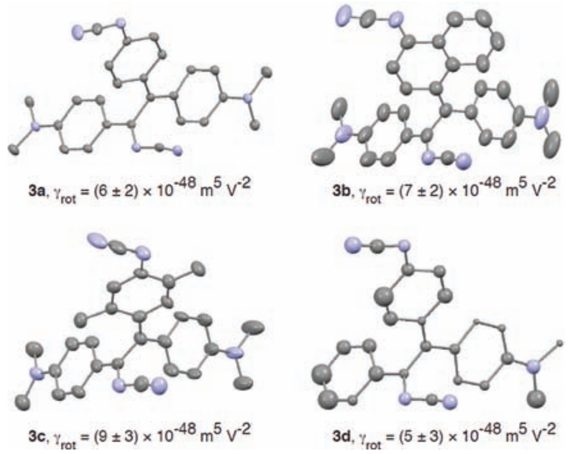


Figure 1. Third-order polarizabilities and ORTEP representations of the crystal structures of **3a**–**d** with thermal ellipsoids shown at the 50% probability level.

The identities and structures of DCNQI adducts **3a**–**d** were studied by NMR experiments and X-ray crystallography (Figure 1). Notably, the crystal structure of adduct **3d** confirms the absolute regioselectivity of the imine CA–CR reaction that is also observed by NMR spectroscopy: the iminoquinoid moiety is adjacent to the aniline moiety, analogous to regioselectivity observed in the CA–CR reaction using TCNQ as an acceptor.[12] For all four compounds, the same space group and cell dimensions were found when ≥10 crystals of each were diffracted, suggesting that only one diastereoisomer of each compound exists in the solid state.[13] NMR spectra of these compounds, on the other hand, indicated two fluxional species in solution, in a 1:1 ratio from 193 to 273 K. When crystals of the DCNQI adducts were redissolved, NMR spectra identical to those of the bulk solids were obtained. These results suggest that the two isoenergetic species are interconverting in solution but that crystallization of one is favored.[14]

Several dynamic processes occur simultaneously in **3a**–**d** (see the Supporting Information, section 5, for spectra and further details). Rotation about the C1–C2 single bond and inversion of the imine moiety[3] were not

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[7] Kuehne, M. E.; Sheehan, P. J. *J. Org. Chem.* **1968**, *33*, 4406–4413.

[8] Ishitani, H.; Nagayama, S.; Kobayashi, S. *J. Org. Chem.* **1996**, *61*, 1902–1903.

[9] Ma, Y.; Qian, C. *Tetrahedron Lett.* **2000**, *41*, 945–947.

[10] Parent DCNQI **2a** exists at room temperature as a mixture of *syn*/*anti* isomers. The barrier of inversion between these two isomers is ca. 15 kcal mol^{-1}. In contrast, naphthoquinone-derived **2b** and 2,5-dimethylbenzoquinone-derived **2c** exist exclusively in the *syn* and *anti* conformations, respectively, at room temperature. See ref 5 and Cossío, F. P.; de la Cruz, P.; de la Hoz, A.; Langa, F.; Martín, N.; Prieto, P.; Sánchez, L. *Eur. J. Org. Chem.* **2000**, 2407–2415 for further information.

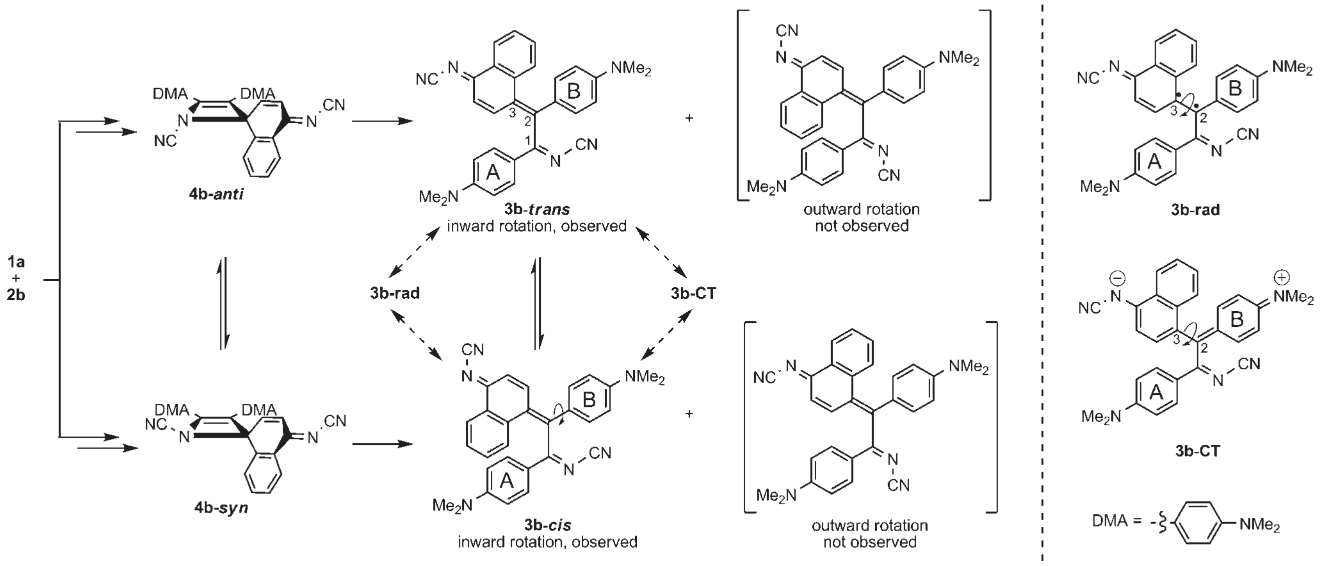
[11] When radical inhibitors (e.g., 2,6-di-*tert*-butyl-*p*-cresol) were added to these reaction mixtures, no consumption of the starting materials was observed. Addition of radical inhibitors to reaction mixtures that yielded the desired DCNQI adducts did not affect the rates or yields of those reactions.

[12] Kivala, M.; Boudon, C.; Gisselbrecht, J.-P.; Seiler, P.; Gross, M.; Diederich, F. *Chem. Commun.* **2007**, 4731–4733.

[13] Bulk DCNQI adducts **3a**–**d** are amorphous solids, so powder diffraction on the bulk solids was not possible.

[14] DFT calculations (B3LYP/6-31G(d)) show that $\Delta G_{f,298K}$ between **3b-*cis*** and **3b-*trans*** is ≤1 kcal mol^{-1}. See the Supporting Information, section 6, for details.

Scheme 1. Torquoselective Formation of Observed Isomers **3b-*trans*** and **3b-*cis*** and Their Rotational and Interconversion Dynamics



observed, as they are too rapid and slow, respectively, on the NMR time scale. The most pertinent of the observed processes, illustrated for **3b** in Scheme 1, is slow interconversion between two isomers, which were identified as *cis/trans* isomers about the exocyclic, quinoidal C2−C3 bond (**3b-*cis*** and **3b-*trans***, Scheme 1); isomer **3b-*trans*** was the isomer identified by X-ray crystallography. Preferential formation of **3b-*cis*** and **3b-*trans*** can be attributed to torquoselectivity.[15,16] There are two presumed isomeric azetine intermediates in the CA−CR reaction,[16,17] **4-*syn*** and **4-*anti***, arising from inversion of the pyramidal azetine nitrogen (Scheme 1), in which the cyano groups occupy the same or opposite sides of the azacyclobutene ring, respectively. Because the cyano substituents on those nitrogens are electron-withdrawing, inward rotations of the cyano groups are favored in the thermally allowed, conrotatory ring-openings of **4-*syn*** and **4-*anti*** to yield the observed isomers, **3b-*cis*** and **3b-*trans*** (Scheme 1).[16,17] Based on comparisons between ROESY cross-peak volumes and line-shape analysis of variable temperature ^{1}H NMR spectra, the rate of interconversion between **3b-*cis*** and **3b-*trans*** is estimated to be $< 1\ \text{s}^{-1}$ at 223 K. This estimate is consistent with the fact that the naphthoquinoid proton signals of both isomers show no line broadening beyond 3 Hz even at 373 K.

Interconversion between the two *cis/trans* isomers in adducts **3b**−**c** results from apparent bond rotation about the C2−C3 bond (Scheme 1). For all four adducts, this C2−C3 bond length ranges from 1.38−1.41 Å, which is slightly longer than a typical C=C double bond (1.34 Å for ethylene[18]). Rotation about the C2−C3 bond at relatively low temperatures might therefore be possible because of this single-bond character, which is apparent in the diradical[19] and zwitterionic, charge-separated resonance forms of **3b**, **3b-rad** and **3b-CT**, respectively. In adducts **3a** and **3d**, which are derived from symmetric parent DCNQI **1a**, quinoidal imine inversion would also yield the observed *cis/trans* isomers.

Having established the structural dynamics of **3a**−**d**, we sought to examine their optoelectronic properties. Structural parameters derived from X-ray crystallographic data suggest a rough correlation between steric bulk and the degree of intramolecular CT in **3a**−**d**. In adducts **3a** and **3d**, the dihedral angle, θ, defined by C3−C2−C4−C5 is relatively large at ca. 170° (Table 2). In adducts **3b** and **3c**, which are derived from bulkier DCNQIs, the analogous dihedral angle is smaller (ca. 150°). Increasing steric bulk about the quinoid moiety therefore induces the quinoid and adjacent DMA moieties to deviate from coplanarity, thereby decreasing the conjugation between them. Conjugation between these moieties is, in turn, responsible for the intramolecular CT in the chromophores, which is manifested in the solid state as bond-length alternation in the aniline rings (δr, see Table 2 footnote for definition).[20] In sterically encumbered **3b** and **3c**, δr for ring B is small (0.03 Å) compared to

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(15) For a review on torquoselectivity, see: Dolbier, W. R.; Koroniak, H.; Houk, K. N.; Sheu, C. *Acc. Chem. Res.* **1996**, *29*, 471–477.

(16) For the torquoselectivity of azetine ring-openings, see: (a) Kallel, A. Ph.D. Thesis, University of California, Los Angeles, 1991. (b) Mangelinckx, S.; Van Speybroeck, V.; Vansteenkiste, P.; Waroquier, M.; De Kimpe, N. *J. Org. Chem.* **2008**, *73*, 5481–5488.

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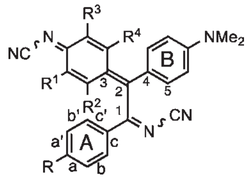
δr = 0.06–0.07 Å in unhindered adducts **3a** and **3d**. Thus, incorporation of DCNQIs with less sterically demanding quinoid moieties enables more effective conjugation and CT in the resulting CA–CR adducts.

Table 2. Selected Structural Parameters of **3a**–**d**



compd	θ^{a}/deg	$\delta r_{\mathrm{ringA}}{}^{b}$/Å	$\delta r_{\mathrm{ringB}}{}^{b}$/Å
3a	165.3(3)	0.04	0.06
3b	147.1(4)	0.03	0.03
3c	152.0(7)	0.04	0.03
3d	169(2)	0.03	0.07

[a] θ is the dihedral angle defined by C3–C2–C4–C5. [b] $\delta r = \{[(a + a')/2 - (b + b')/2] + [(c + c')/2 - (b + b')/2]\}/2$; for benzene, δr = 0.00 Å, and for fully quinoid rings, δr = 0.08–0.12 Å.

UV/vis spectroscopy provided further evidence for intramolecular CT in **3a**–**d**. A main absorption band with $\lambda_{\max}$ = 600–640 nm in CH_2Cl_2 (Figure 2) is observed; in **3a**–**c**, a second absorption band occurs with $\lambda_{\max}$ = 390–430 nm. The lower energy transition is attributed to CT between DMA ring B and the quinoid moiety, and the higher energy transition is derived from CT between DMA ring A and the adjacent cyanoimine moiety. Since **3d** lacks DMA ring A, the higher energy band is absent. Adducts **3a**–**d** also exhibit positive solvatochromism. Less polar solutions of **3a**–**d** (e.g., toluene) are green, and more polar solutions (e.g., MeOH) are purple (Figure 2); corresponding bathochromic shifts of ca. 50–120 nm for both absorption maxima in **3a**–**c**, and of ca. 50 nm for the single CT band in **3d** were observed. The excited-state dipole moments of DCNQI adducts **3a**–**d** are therefore greater than those of their ground states.

Having established that adducts **3a**–**d** exhibit intramolecular CT, we turned to investigating their third-order NLO properties. The rotational average of the third-order molecular polarizability (γ_{rot}) for each cyanoimine adduct was measured near the zero-frequency limit in degenerate four-wave mixing experiments. A narrow range of γ_{rot} values was observed ((5–9) × 10^{-48} m^5 V^{-2}, Figure 1) for DCNQI adducts **3a**–**d**, which are significant given the small molecular weights of these compounds and the energies of their absorption maxima.[2e] Their high γ_{rot} values and their nonplanar structures make adducts **3a**–**d** promising for nonlinear optical applications, as has been shown for a similar TCNE-derived CA–CR chromophore that was used in an integrated NLO device for all-optical switching.[2a,21]

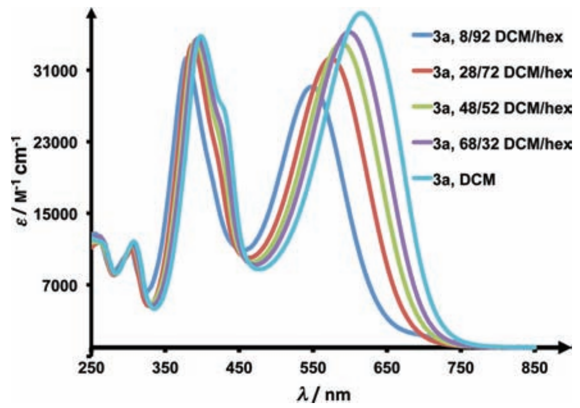


Figure 2. Representative UV/vis spectra of **3a** in varying ratios of DCM/*n*-hexane (T = 298 K). DCM = CH_2Cl_2, hex = *n*-hexane.

In summary, the CA–CR reactivity of DCNQIs with electron-rich alkynes has been developed, yielding a new class of cyanoimine-based, donor–acceptor chromophores. The CA–CR reaction proceeds torquoselectively to give two isomers that are *cis*- and *trans*-oriented about the exocyclic, quinoidal C=C bond. These two isomers interconvert in solution, but crystallization of one is favored. The cyanoimine CA–CR adducts exhibit intramolecular CT and positive solvatochromism. They also function as competent third-order nonlinear optical chromophores. This work therefore expands the scope of the CA–CR reaction, extends the known reactivity of DCNQIs, and demonstrates the potential utility of cyanoimine chromophores in optoelectronic applications.

Acknowledgment. We thank Dr. Dee-Hua Huang (Scripps Research Institute) for help with acquisition of NMR data. Igor Pochorovski and Yi-Lin Wu (ETH Zürich) are acknowledged for reviewing the manuscript. This work was supported by ERC Advanced Grant No. 246637 and an ETH Research Fellowship (M.C.).

Supporting Information Available. Synthesis, NMR spectra, X-ray crystallography details, CIF files, electrochemical data, UV/vis spectra, DFT calculations, and degenerate four-wave mixing experimental details. This material is available free of charge via the Internet at http://pubs.acs.org

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(21) See the Supporting Information, section 8, for details.