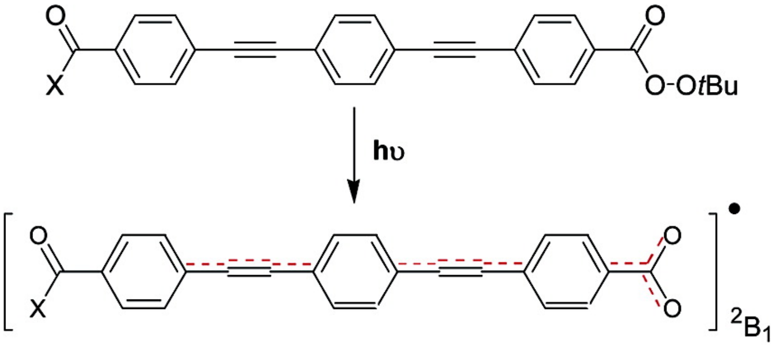
JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Delocalization of Free Electron Density through Phenylene–Ethynylene: Structural Changes Studied by Time-Resolved Infrared Spectroscopy

Dmitry E. Polyansky, Evgeny O. Danilov, Sergey V. Voskresensky, Michael A. J. Rodgers, and Douglas C. Neckers

J. Am. Chem. Soc., **2005**, 127 (39), 13452-13453• DOI: 10.1021/ja053120l • Publication Date (Web): 08 September 2005



X = -O-O-tBu; -O-Ph

J|A|C|S
COMMUNICATIONS

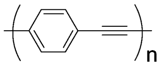
Delocalization of Free Electron Density through Phenylene−Ethynylene: Structural Changes Studied by Time-Resolved Infrared Spectroscopy[1]

Dmitry E. Polyansky, Evgeny O. Danilov, Sergey V. Voskresensky, Michael A. J. Rodgers, and Douglas C. Neckers*

Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

Received May 12, 2005; E-mail: neckers@photo.bgsu.edu

Organic compounds with the phenylene−ethynylene motif appear suited for engineering molecular electronic devices, in that electronic conduction through oligo phenylene−ethynylene molecular wires was demonstrated,[2] prominent electrical rectifying current−voltage dependencies and negative differential resistances were observed,[3,4] and approaches to conductance switching and current control have been proposed.[5,6] Such conductive properties have been directly attributed to extended π-conjugation along the linear backbone and the relative orientation of the phenylene rings.



One electron reduction triggers conformational change, transforming the phenylene−ethynylene backbone into a conductive medium and at the same time providing a charge carrier for current flow through the system,[5] implying that in the singly reduced state the wave function is delocalized over the conjugated core of the planar molecule, whereas it has a localized character in alternating conformations.[7] Bridge-mediated charge transfer was proposed to explain the distance dependence of electronic coupling along the molecule,[2,8,9] although evidence suggested that stochastic switching of the molecular wire was imperceptibly changed from replacement of a central ring proton by a nitro group.[5] One of the alternative theoretical models posited to rationalize the conductivity of phenylene−ethynylenes and a weak dependence on the substitution involved resonant tunneling through the central ring as a barrier.[10] Another assumed an influence of molecular vibrations on the conductance.[11] Both models imply that conductance depends primarily on the internal conformational twist of the aromatic rings. Time-resolved picosecond resonance Raman spectra ($\lambda_{ex} = 267$ nm) of 1,4-bis(phenylethynyl)benzene examined conformational and structural details in the ground- and the excited states.[12] Since the phenyls of the phenylene−ethynylene chromophore have a low rotational potential barrier in the ground state and a higher barrier in the excited state,[13] photoexcitation was presumed to provide transient control over conformation. An observed red-shift in the −C≡C− vibrations suggested a weakening of the triple bond.

To test electron communication in conjugated phenylene−ethynylenes, we have synthesized compounds capable of producing "long-lived"[14] single-electron species, and studied these by transient absorption spectral methodologies (see Figure 1). Thus, 1,4-bis(2-[4-*tert*-butylperoxycarbonylphenyl]ethynyl)benzene (**1**) and *tert*-butyl-4-(2-{4-[2-(4-phenyloxycarbonylphenyl)-1-ethynyl]phenyl}-1-ethynyl)peroxybenzoate (**2**) upon excitation by a 10-ns laser pulse at 355 nm, rapidly form aroyloxyl radicals **3** and **4**, and these can be studied by time-resolved IR (TRIR) spectroscopy,[15] see Chart 1. An observed red-shift in their −C≡C− vibrational frequencies and an intensity increase following excitation indicates substantial concomitant changes in molecular structure, proposed to result from changes in triple bond character due to the formation of a partial cumulene-like structure resulting through delocalization of the free electron. This allows comparison of the radical species observed to the excited singlet state of the phenylene−ethynylene chromophore.

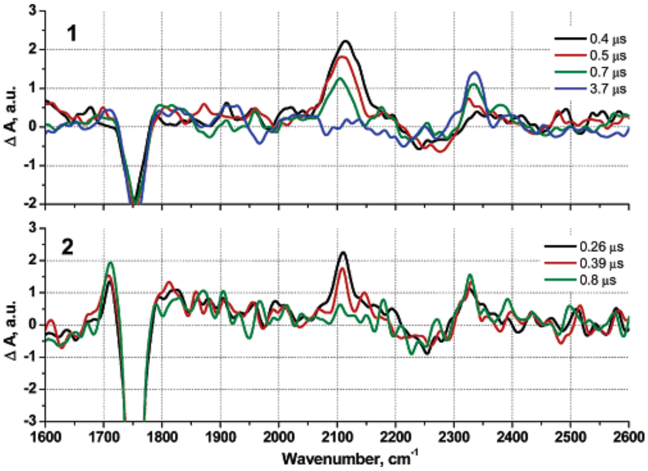
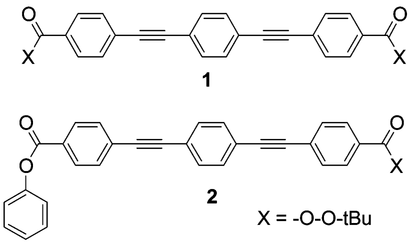


Figure 1. Time evolution of transient FTIR spectra of **1** and **2** acquired after 355 nm laser pulse.

Chart 1 Structures of Peroxyesters **1** and **2**

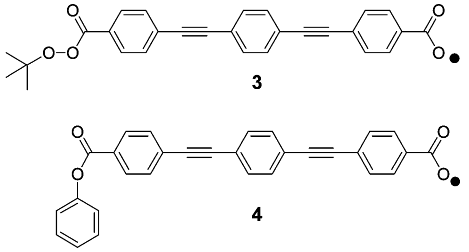


The only stable products of photolysis of **1** and **2** were 1,4-bis(4-chlorophenylethynyl)benzene and carbon dioxide. TRIR spectra of chloroform solutions of **1** and **2** after the 355-nm laser pulse featured ground-state depletion around 1750 cm^{-1}, transient absorption around 2112 cm^{-1}, and formation of a stationary absorption at 2335 cm^{-1} (see Supporting Information for details).

Ground-state absorption bleached within the instrument response time (ca. 30 ns) giving rise to the 2112 cm^{-1} absorption. This transient band decayed concomitantly with the growth of carbon dioxide absorption at 2335 cm^{-1}, indicating species providing this absorption to be direct precursors of carbon dioxide. Purging oxygen through the solution did not decrease the lifetime of the 2112 cm^{-1} transient, a result consistent with the expected slow trapping of aroyloxyl by molecular oxygen. The lack of reactivity of the observed transient to oxygen excludes its assignment to the triplet excited state, while the lifetime of the singlet excited state of the

10.1021/ja053120l CCC: $30.25

Chart 2 Structures of Radical Intermediates (**3** and **4**) Formed after Photolysis of **1** and **2**



3

4

phenylene−ethynylene chromophores is too short[13] to be observed on the time scale of the TRIR experiment. Thus, the kinetic data[16,17] allow unambiguous assignment of the 2112 cm^{-1} transient to the absorption of aroyloxyl radicals **3** and **4** (see Chart 2).

The presence of the two functional groups in **1** could lead to formation of diradical species due to stepwise cleavage of both oxygen−oxygen bonds of both peroxide moieties. The rapid absorption of two photons can be expected at the high energy fluxes of pulsed laser excitation. To establish if biradical or monoradical transient species are formed after photolysis of **1**, we found the amount of carbon dioxide formed relative to amount of the starting peroxyester decomposed within one laser pulse. Although TRIR produced a significant systematic error and an accurate value of this ratio could not be obtained, a more definitive way to prove structure of the radical was to compare the TRIR spectra of **1** with monofunctionalized peroxyester **2** which can produce only monoradical species. The similarity of TRIR spectra as a result of photolysis of **1** and **2** unambiguously assigns the transient species to monoradicals **3** and **4** respectively.

Significant IR absorption at 2112 cm^{-1} in **3** and **4** suggests this infrared transition to be more allowed in the radical species compared to the parent. While the weak IR absorption corresponding to the internal acetylene vibration mode in **2** was observed around 2218 cm^{-1}, no IR absorption in this spectral region was observed in **1**. The lowered symmetry of the radicals leads to an increase in the transition dipole moment of the acetylene vibration. In addition to the increased intensity, the energy of the $-\mathrm{C}{\equiv}\mathrm{C}-$ vibration in **3** and **4** decreased by about 100 cm^{-1} relative to that of **1** and **2**. The decrease in the IR vibration frequency can be predicted by DFT analysis (B3LYP 6-31G*) of aroyloxyl radical (observed $\nu_{-\mathrm{C}\equiv\mathrm{C}-} = 2112\ \mathrm{cm}^{-1}$; calculated[18] $\nu_{-\mathrm{C}\equiv\mathrm{C}-} = 2126\ \mathrm{cm}^{-1}$. See SI for details).

The DFT analysis reveals that this shift takes place only in a state possessing $^2\mathrm{B}_1$ symmetry. A $^2\mathrm{B}_2$ state lying in the proximity of the $^2\mathrm{B}_1$ does not show such a shift.[19] Nonadiabatic population of the higher-energy metastable $^2\mathrm{B}_1$ state observed by TRIR is anticipated after excitation of **1** and **2** by the 355-nm laser pulse.

Steady-state EPR experiments of dinitrene diradical species have demonstrated no delocalization of free electrons through the phenylene−ethynylene bridge,[20] contrary to transient experiments allowing the probe of transient species immediately after the laser flash in their nonequilibrated high-energy states.

Interestingly, the presence of free electron conjugated with the central phenylene−ethynylene chromophore induces structural changes similar to those resulting from an electronic excitation of 1,4-bis(phenylethynyl)benzene to the S_1 state as observed by time-resolved Raman spectroscopy[12] or electronic excitation of Pt acetylide complex to the T_1 state as measured by TRIR.[21]

In summary, our TRIR measurements demonstrate that a free electron conjugated with the phenylacetylene core is substantially delocalized. The fingerprint shift of acetylene bond absorption evidences extensive transmission of free electron density throughout the π-system in metastable $^2\mathrm{B}_1$ state of aroyloxyl radical. Further details will appear in the full paper.

Acknowledgment. We thank Dr. John Cable for fruitful discussions. D.E.P. is grateful to the McMaster Endowment for support in the form of a Fellowship.

Supporting Information Available: Synthesis and characterization of compounds **1** and **2**; kinetic details of TRIR experiments; ground-state FTIR of **1** and **2**; DFT calculations details on phenylacetylenecarbonyloxyl radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Center for Photochemical Sciences Contribution #558.
(2) Creager, S.; Yu, C. J.; Bamdad, C.; O'Connor, S.; MacLean, T.; Lam, E.; Chong, Y.; Olsen, G. T.; Luo, J.; Gozin, M.; Kayyem, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1059.
(3) Zhou, C.; Deshpande, M. R.; Reed, M. A.; Jones, L., II; Tour, J. M. *Appl. Phys. Lett.* **1997**, *71*, 611.
(4) Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550.
(5) Donhauser, Z. J.; Mantooth, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W., Jr.; Rawlett, A. M.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303.
(6) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 3015.
(7) Magyar, R. J.; Tretiak, S.; Gao, Y.; Wang, H.-L.; Shreve, A. P. *Chem. Phys. Lett.* **2005**, *401*, 149.
(8) Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. R.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1997**, *119*, 10563.
(9) Biswas, M.; Nguyen, P.; Marder, T. B.; Kundkar, L. F. *J. Phys. Chem. A* **1997**, *101*, 1689.
(10) Cornil, J.; Karzazi, Y.; Bredas, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 3516.
(11) Olson, M.; Mao, Y.; Windus, T.; Kemp, M.; Ratner, M.; Leon, N.; Mujica, V. *J. Phys. Chem. B* **1998**, *102*, 941.
(12) Beeby, A.; Findlay, K.; Low, P. J.; Marder, T. B.; Matousek, P.; Parker, A. W.; Rutter, S. R.; Towrie, M. *Chem. Commun.* **2003**, 2406.
(13) Beeby, A.; Findlay, K.; Low, P. J.; Marder, T. B *J. Am. Chem. Soc.* **2002**, *124*, 8280.
(14) The extensive delocalization of free electron increases the lifetime of produced radical species sufficiently to be detected with available transient techniques. Time resolution of the current TRIR instrument is ca. 30 ns. For more details on experimental setup see ref 15.
(15) For detailed description of the TRIR setup see: Fedorov, A. V.; Danilov, E. O.; Merzlikine, A. G.; Rodgers, M. A. J.; Neckers, D. C. *J. Phys. Chem. A* **2003**, *107*, 3208.
(16) Aroyloxyl radicals generally do not react with oxygen as opposed to carbon-centered radicals. For example see: Chateauneuf, J.; Lusztyk, J.; Ingold K. U. *J. Am. Chem. Soc.* **1988**, *110*, 2877.
(17) The concentration of oxygen in chloroform ($\sim 10^{-2}$ M) was sufficient to quench carbon-centered radicals ($k_q \approx 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$), assuming diffusion-controlled quenching reaction. For reaction rates of carbon-centered radicals with oxygen, see: *CRC Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989.
(18) Scaled by a factor of 0.96.
(19) The energy of the $^2\mathrm{B}_1$ state is 25.7 kcal/mol higher than that of $^2\mathrm{B}_2$. $\nu_{-\mathrm{C}\equiv\mathrm{C}-}$ ($^2\mathrm{B}_2$) = 2217 cm^{-1}; $\nu_{-\mathrm{C}\equiv\mathrm{C}-}$ ($^2\mathrm{B}_1$) = 2126 cm^{-1}
(20) Serwinski, P. R.; Lahti, P. M. *Org. Lett.* **2003**, *5*, 2099.
(21) Cooper, T. M.; Blaudeau, J.-P.; Hall, B. C.; Rogers, J. E.; McLean, D. G.; Liu, Y.; Toscano, J. P. *Chem. Phys. Lett.* **2004**, *400*, 239.

JA053120L