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Electronic Tera-Order Stabilization of Photoinduced Metastable Species: Structure of the Photochromic Product of Spiropyran Determined with in situ Single Crystal X-ray Photodiffraction

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The extraordinary stability of the photoinduced red form of a cationic spiropyran ($k \approx 10^{-6}$ s^{-1} in water and $\sim 10^{-6}$ to less than 10^{-8} s^{-1} in the solid state) was employed to obtain in situ X-ray diffraction evidence of its molecular structure. By UV excitation under selected experimental conditions, on average, approximately one third of the cations in a single crystal of spiropyran iodide salt was converted and retained as the red form during the experiment. According to the structure of the mixed crystal, the ring opening, which is due to increased distance between the spiro oxygen and carbon atoms, is associated with slight molecular flattening caused by concurrent out-of-plane shift (11.2(5)°) of the pyranopyridinium half and in-plane shift (4.8(7)°) of the indoline half. The overall geometry change of the cation fits the steric requirements imposed by the ion packing in the crystal and can be viewed as molecular flattening caused by breaking of the spiroconjugation. The structure of the cation confirms that (at least in the case of cationic spiropyrans) the product is confined in the crystal mainly as a zwitterionic resonance structure in cis configuration similar to the (early) transition state. Although the positive charge of the closed form facilitates the ring-opening reaction by moving the reactant closer to the transition state, neither the weakening of the spiropyran C−O bond nor the space provided by the iodide alone can account for the stability of the product. Instead, the density functional theory calculations indicate that the stabilization of the red form of the cationic relative to the neutral spiropyran is thermodynamically controlled, probably through compensation of the charge within the zwitterion by the methylpyridinium group.

1. Introduction

Spiropyrans (SPs) and spirooxazines (SOs) constitute one of the most important and best studied organic photochromic families. They have been exploited for a variety of applications, including materials for self-developing photography, actinometry, displays, transmission-controllable optical elements, and ophthalmic lenses.[1] Having some of the largest two-photon cross-sections among the organic photochromic compounds,[2] a prerequisite for application as memory elements capable of nondestructive readout, the SPs and SOs have become a favorite photoswitching unit for control of properties of composite materials, including polymers and liquid crystals. Some of the recent promising applications are photocontrol of protein conformation and enzyme activity,[3] combination with magnetic ions[4] and luminophores,[5] ion detection,[6] inclusion in host−guest compounds,[7] modification of surface properties and membrane permeability,[8] and incorporation in photoresponsive nanoparticles.[9] Based on the existing pool of physicochemical (mainly spectroscopic) results, it has been accepted that the photochromic reaction mechanism of SPs and SOs represents a 6π 6-atom pericyclic process: ring opening during the photoinduced forward reaction, resulting in a merocyanine (MC) dye-like product and ring closure during the photoinduced or thermally induced reverse reaction. Surprisingly, despite the great importance of these photochromic systems, the creation of the open form has been corroborated only with spectroscopic methods in solution, such as ^{1}H NMR NOE;[10] no direct diffraction evidence for the creation and the atomic-level structure of the MC-like product has been reported yet. The relative ratio of the two possible resonance structures of the MC form, dipolar (zwitterionic) and apolar (quinonic), has also remained unknown. The only X-ray structure of a pure MC form was elucidated from a sample obtained by irradiation of a spirobenzothiopyran solution and subsequent crystallization of the product.[11] However, because in solution the molecules are conformationally flexible, they can react through solvent-assisted pathways, and during the crystallization they are confined to their most stable (*s*-trans, *s*-trans) conformation, the structure of the as-crystallized MC product does not provide insight into the formation and the primary geometry of the as-obtained MC form. In fact, the photochromism of SPs and SOs in the solid state has remained unknown until the recent observation of photochromic activity of microcrystalline powders of catonic SPs and SOs prepared as iodide salts.[12,13] In these structures, such as (SP$^+$)I in Scheme 1, a pyridinium-containing pyran or oxazine system is spiroconjugated with an indoline fragment and charge-balanced by a lattice iodide ion. The stability of the open-ring forms of these compounds is unprecedented (Figure 1B,C). In acetonitrile, the red MC species decays with monoexponential kinetics ($k_1 =$

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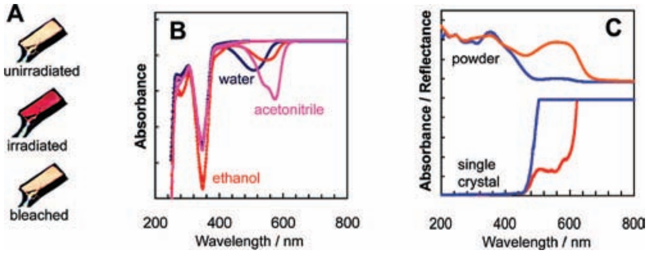
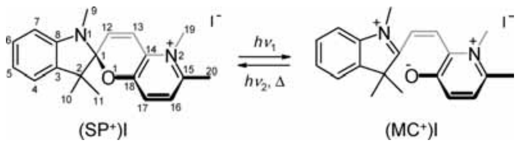


Figure 1. (A) Color change of a $(SP^+)I$ single crystal before and after several seconds exposure to UV radiation and after several minutes of bleaching with visible light. (B) UV radiation-induced changes in the absorption spectra of aqueous (blue trace), ethanol (red trace), and acetonitrile (pink trace) solutions of $(SP^+)I$. (C) UV radiation-induced changes in the reflectivity spectrum of $(SP^+)I$ powder and in the absorption spectrum of $(SP^+)I$ single crystal (blue traces are the spectra before irradiation and orange and red traces represent the spectra after irradiation).

SCHEME 1: Simplified Mechanism of the Photochromic Reaction of the SP Cation in $(SP^+)I$ with Atom Numeration of the Basic Structure



$4.47{\cdot}10^{-5}$ s^{-1}), whereas in ethanol, the decay is biexponential ($k_1 = 2.60{\cdot}10^{-5}$ s^{-1} and $k_2 = 4.11{\cdot}10^{-6}$ s^{-2}), indicating different reaction mechanisms. In aqueous solution, the monoexponential thermal back reaction is extremely slow ($k_1 = 1.72{\cdot}10^{-6}$ s^{-1}). The reversibility of the photochromic reaction in these solvents is confirmed by complete recovery of the spectrum of the closed form, which can be induced by irradiation with visible light. In the solid state, the constants of thermal fading reactions of cationic SPs are on the order of 10^{-6} s^{-1} to less than 10^{-8} s^{-1}.[12]

Recently, Masuhara et al.[14] have demonstrated that if excited by femtosecond laser pulses, neutral SPs and SOs can also exhibit solid-state photochromism. Relative to the MC forms of cationic SPs which are stable for days in the dark, the neutral MCs are of much shorter lifetimes: in the case of weak laser excitation (<1 mJ$\cdot$cm^{-2}), they exist during nanoseconds before decaying to the closed SP form. The extraordinarily large, tera-order-of-magnitude (if the time scales of thermal decay are compared) lifetime extension of the cationic relative to neutral MCs provides a basis to study the mechanism of the photochromic reaction of SPs and SOs at atomic-level resolution with X-ray photodiffraction - a combination of photoexcitation and X-ray diffraction. Here, we report the observation of the ground-state MC structure, which provides the first direct evidence of the reaction mechanism of a SP molecule. The reasons underlying the unusual stability of the colored structure of cationic SPs are substantiated by density functional theory (DFT) calculations.

2. Experimental Section

$(SP^+)I$ was prepared by condensation of 3-hydroxy-6-methyl-2-pyridinecarboxaldehyde and 2-methylene-1,3,3-trimethylindoline.[12] The compound is well soluble in water, methanol, ethanol, and acetone, but it is very weakly soluble or almost insoluble in hexane, cyclohexane, and toluene. It was recrystallized in the dark by very slow evaporation from warm aqueous solution (prolonged heating results in partial decay to stable red decay products). Rapid cooling of the solution affords brittle yellow plates which break spontaneously when exposed to light, whereas slow cooling affords regular prismatic crystals. In most crystallization attempts, yellow trapezoid crystal twins were obtained with doubled monoclinic cell, but a few batches contained exclusively long yellow single-crystal prisms of good quality. The UV−vis spectra of the powdered samples were recorded from a KBr matrix in reflectance mode by using a JASCO V-570 spectrometer. The single crystal UV−vis spectra were recorded in transmission mode from unpolished plate-like single crystal with USB4000 spectrometer (Ocean Optics). In all cases, the sample was exposed to unfiltered UV radiation from a 250 W medium-pressure mercury lamp (SP-7, Ushio), and the reversibility was confirmed by bleaching upon storage in the dark or by irradiation with white LED light. The photoreaction kinetics measurements in solution were performed by continuous recording of the absorption spectral maxima in the dark (the data are corrected for solvent absorption). The reversibility of the process was checked by bleaching with visible light. The aqueous solution can be cycled between the two forms at least three times without measurable decay. Unlike the other solvents, the decay kinetics in chloroform was not reproducible and the compound was not completely bleachable, indicating partial decay in this case.

The X-ray data of $(SP^+)I$ were collected (in the dark, at ambient temperature) from a regular yellow prism (270 × 100 × 50 μm) with a SMART APEX diffractometer (Bruker) by using sealed tube source, graphite-monochromated Mo Kα X-rays, and a CCD detector.[15] The structure was solved with direct methods[16] and refined[17] on F_o^2 with all non-hydrogen atoms anisotropic and the hydrogen atoms included as riding. A series of experiments employing various wavelengths, irradiation times, and temperatures were performed on test samples in order to optimize the reactivity and to increase the photoconversion yield in the single crystals. Excitation with pulsed laser light (various powers in the visible region, power between 4 mW and 24 mW in the red region and between 160 μW and 5 mW at 335 nm) was less efficient than that with a polychromatic excitation source. In many cases, the coloration was pale red or brownish, and at higher incident powers, the crystallinity of the samples was occasionally decreased. Therefore, the crystal was exposed during 45 min to polychromatic, nonfocused, heat-filtered cw UV radiation from a medium-pressure mercury lamp (250 W, Ushio SP-7), and the temperature was subsequently decreased to 200 K. Several new peaks appeared around the cation in the difference Fourier map, of which the most apparent were those of height 7.0, 6.9, and 2.2 e/Å^3, the latter being positioned about 1 Å from O1. The temperature was then increased to 298 K, and in order to retain the photoconverted fraction of molecules in the crystal, a second data set was collected during irradiation from the same source at that temperature. A total of 20 019 reflections were extracted from 2500 collected frames of 0.3° width, each measured with an exposure of 20 s, and integrated to obtain 3741 unique reflections of up to $2\theta = 52°$. Assuming that the nonconverted fraction of SP^+ had remained unaffected by the excitation, the distances (but not the coordinates) between the anisotropic atoms of the unconverted fraction of the SP^+ cation were fixed to the respective values in the unirradiated crystal, whereas the secondary photoinduced cation, MC^+, was refined as mixed isotropic−anisotropic model. No attempt was made to split the methyl groups of the indoline ring in any of the structures. The refined structures of the nonirradiated and irradiated crystal are deposited within the CCDC as depositions 668923 and 668924.

All theoretical calculations were performed at the supercomputer center of the National Institute for Materials Science (Tsukuba). The molecular geometries were optimized without restraints, and the stationary points were checked for minima by subsequent harmonic vibrational analyses. The synchronous transit-guided quasi-Newton method was used to locate the transition structures. The choice of the basis set was based on its success to model the substituent effects in a previous study;[18] diffuse functions were added to the non-hydrogen atoms of all modes to account for eventual charge effects in the cationic structure.

3. Results and Discussion

Well-diffracting long prismatic single crystal specimens of $(SP^+)I$ were selected among many batches of twins obtained by recrystallization from water.[12] Similarly to solutions and microcrystalline powders, UV excitation of the yellow single crystals causes rapid change of their color to violet-red, accompanied by a decrease of the 350 nm absorption and evolution of a red MC^+ band at 560 nm (Figure 1). The red color is remarkably stable for days in the dark, but it can be bleached completely by several minutes of irradiation with continuous-wave visible light, confirming that the solid-state reaction is a reversible photochromic process. The structure of the yellow crystal before the irradiation conforms to the spiro-conjugated form SP^+ (Scheme 1). The pyranopyridinium half is planar, except for the average position of O1 which deviates slightly (0.06 Å) from the plane. The indoline half is bent at N1−C2 (29.8(2)°), and the planar and bent indoline parts are quasiperpendicular to the pyranopyridinium plane (86.0(2)° and 87.0(2)°). Because of the $n-\sigma^*$ orbital interaction between the unshared electron pair of N1 and the antibonding orbital of the C1−O1 bond, the latter (1.462(5) Å) is longer than usual (1.41−1.43 Å).[19]

Excitation of the 350 nm transition of the same $(SP^+)I$ crystal with polychromatic nonpolarized continuous-wave UV light induced change of reflection intensities and strongly enhanced the anisotropy of the atomic displacement parameters of the cation. The structure refinement of the excited crystal improved considerably by fitting of the difference electron density of the cation with a two-component model, the second component corresponding to the open MC form. Figure 2A represents the two components, SP^+ and MC^+, with the respective occupancies refined on F_o^2 to ~67.6 and 32.4%. The structure of the mixed crystal $(SP^+)_{0.68}(MC^+)_{0.32}I$ shows simultaneous shifts of both halves of the cation, out-of-plane (11.2(5)°) of the pyranopyridinium half and in-plane (4.8(7)°) of the indoline half.[20] The associated molecular distortion is reflected in decreased interplanar angles between the planar and bent portions of the indoline part relative to the pyranopyridinium half, from 86.0(2) to 80.8(9)° and from 87.0(2) to 81.4(6)°. The overall change of cation geometry can be viewed as flattening caused by breaking of the spiroconjugation and tendency for increased intramolecular conjugation. The observed changes of the cation geometry are consistent with the ion packing (Figure 2B): because of the stacking along the 2_1 axis (normal to the plane of Figure 2B), the indoline half is only capable of in-plane sliding, whereas owing to the offset by the iodine ions, the pyranopyridinium half is less hindered for out-of-plane shift.

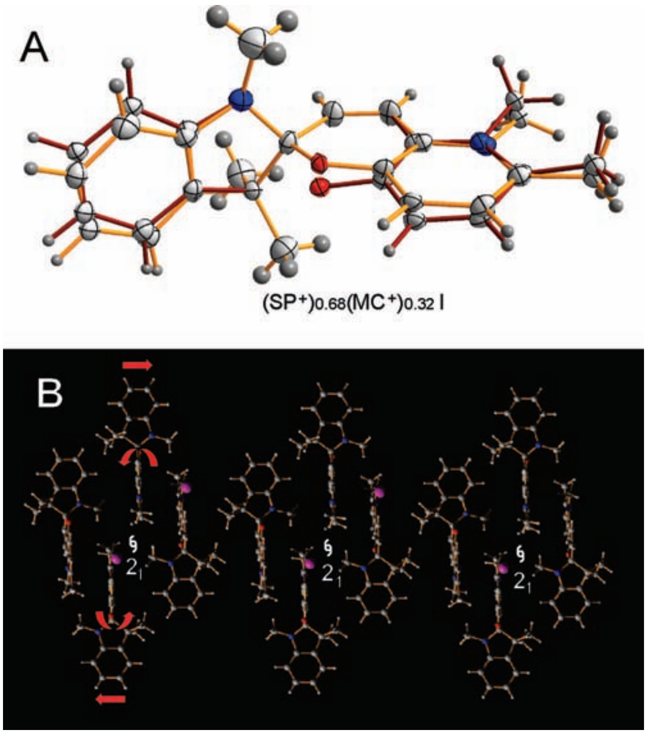


Figure 2. (A) ORTEP-type diagram of the molecular structure of the disordered cation in the mixed crystal $(SP^+)_{0.68}(MC^+)_{0.32}I$ obtained by UV irradiation of a $(SP^+)I$ crystal, showing the two components, SP^+ (beige bonds) and MC^+ (brown bonds). (B) Molecular packing in the crystal before excitation, viewed along the *b* axis. The arrows indicate the positional shifts of the two molecular halves accompanying the conversion of the SP form to the MC form, in-plane shift of the indoline half and out-of-plane shift of the pyranopyridinium half.

The eventual predominance of the zwitterionic over the neutral resonance structure in the hybrid MC form of SPs and SOs has been one of the major issues of discussion in the past.[1] The structure of the MC^+ cation in the mixed crystal confirms that (at least in the case of cationic SPs) the MC form exists mainly as zwitterion in *cis*-C12−C13 configuration. A similar zwitterionic MC structure can be suggested for the solution state on basis of the observed dependence of its absorption maximum and the decay kinetics on the solvent polarity (Figure 1B). The most apparent evidence is provided by the C18′−O1′ distance of 1.34(3) Å, which is closer to typical $C(sp^2)-O$ bond in phenols (1.362 Å) than to $C(sp^2)=O$ in cyclohexanones (1.211 Å).[21] The resonance structure of the MC^+ cation in $(SP^+)_{0.68}(MC^+)_{0.32}I$, quantified with the aid of the bond length alternation model,[18] yields value of −0.025 on the scale of −0.1 to +0.1 for pure zwitterionic and neutral structures, respectively. Inspection of the geometry of the pyridinium ring of MC^+ shows that bonds C14′−C18′ and C16′−C17′ of MC are shorter than C17′−C18′, in support of the zwitterionic resonance structure. After the spiroconjugation of the SP form has been broken by excited-state C1−O1 dissociation, probably during an early transition state,[18] the ground-state MC form is created through molecular flattening and increased separation between the spiro-oxygen and the spiro-carbon.

The second important question to be answered by the structure of the MC^+ form is the remarkable extension of its lifetime in the case of cationic SPs and SOs relative to their neutral counterparts, which appears as solid-state photochromic activity. Three possible reasons have been suggested in previous works:[12,15] increased volume around the pyranopyridinium half caused by the charge-directed molecular packing, weakening of the C1−O1 bond of the SP form by the electron-pulling effect of the pyranopyridinium moiety, and stabilization of the open form by the positive charge of the methylammonium functionality. The insensitivity of the photochromic activity of cationic SPs and SOs on the nature of the counteranion indicates that

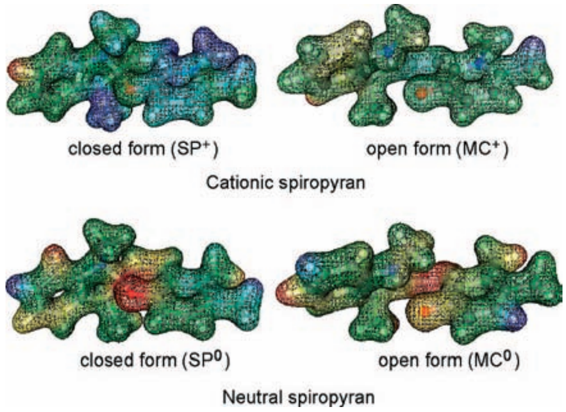


Figure 3. Electron density isosurfaces of the closed (SP^+) and open (MC^+) forms of the cationic SP and of the closed (SP^0) and open (MC^0) forms of its neutral isoelectronic analogue, color-coded with the electrostatic potential. The structures were optimized at the B3LYP/6-31+G(d) level. The potential increases from red (most negative), to yellow and green, and to blue (most positive).

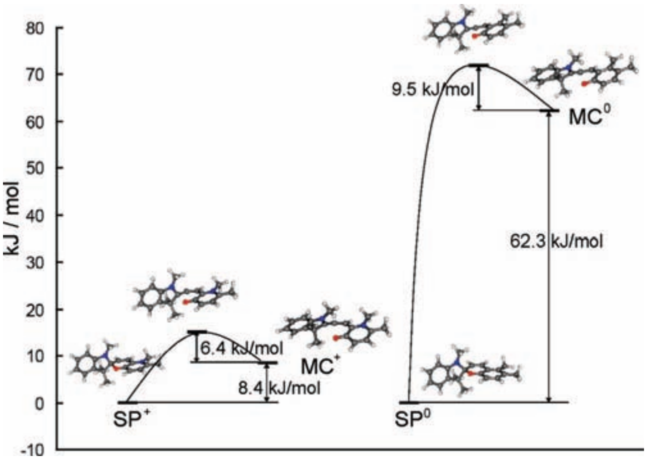


Figure 4. Ground-state B3LYP/6-31+G(d)//B3LYP/6-31+G(d) energies of the open forms (MC^+ and MC^0) and transition states for the ring opening−closing reaction, relative to the respective closed forms (SP^+ and SP^0).

anion-related steric factors are not of primary importance for the solid-state photochromism.[12] The structural similarity of the closed and open forms and the small volume increase (+0.5%) observed in the present study substantiate such considerations, demonstrating that the photochromic reaction $SP^+ \rightarrow MC^+$ does not require a large structural change. Instead, the stabilization is probably caused by the strong electron-withdrawing effect of the methylpyridinium group. To check this hypothesis, the geometries of SP^+ and MC^+ and of their isoelectronic neutral analogues SP^0 and MC^0, in which atom N2 has been substituted with carbon, were fully DFT-optimized at the B3LYP/6-31+G(d) level.[22] The C1−O1 bond of the theoretical SP^+ structure is 0.054 Å longer than that of SP^0.[23] Although the positive charge of the closed form clearly facilitates the forward ring-opening reaction by moving the reactant SP^+ closer to the (early) transition state on the reaction coordinate of the ring-opening reaction, the weakening of the C1−O1 bond alone does not seem to be the main reason for the stability of the product MC^+. The electrostatic potential plots (Figure 3) show that the negative charge positioned on the spiro-oxygen O1 of the closed form of SP^0, which shifts to the bridge in the open form MC^0, is balanced by the positive charge of the quaternary ammonium atom in the closed form SP^+ and especially, in the structure of the open form MC^+. Consequently, the cationic open form MC^+ is stabilized by the uniform charge distribution induced by the extra positive charge.

The ground-state energy diagrams of the cationic and neutral SPs are represented in Figure 4. The persistence of the red cationic species is supported by the thermodynamic stability of the open relative to the closed form: whereas MC^0 is placed 62.3 kJ·mol^{-1} above SP^0 on the potential energy hypersurface, the MC^+ form is only 8.4 kJ·mol^{-1} less stable than the SP^+ form. It should be noted that actually, the ground-state barrier of the thermal back reaction (the energy difference between the open form and the transition state) of the MC^+ form (6.4 kJ·mol^{-1}) is smaller than that of the MC^0 form (9.5 kJ·mol^{-1}), which would imply faster kinetics of the bleaching reaction. The observed stability of the red cationic form indicates a thermodynamically rather than kinetically controlled process. The structure of the MC^+ form in the crystal of SP^+, where the oxygen is closer to the spiro-carbon than in the theoretical structure calculated on an isolated molecule in vacuum,[23] shows that the MC^+ form is confined in the crystal to a structure which is more similar to the transition state than the difference expected for an isolated molecule. This means that the energy plots in Figure 4 are probably flatter on the MC side. The thermodynamic stabilization of the open form in such case, which can be ultimately traced back to the electronic effects of the positive charge, may dominate over the kinetic factors.

In conclusion, the first direct observation of the product of the 6π 6-atom pericyclic reaction underlying the photochromism of SPs and SOs showed that the ground-state open form has a geometry similar to that of the closed form but slightly flattened, obtained by the shift of both halves of the molecule in different directions. In the case of cationic SPs, the open form exists in the solid state mainly as zwitterionic resonance structure. The tera-order extension of the lifetime of the product, which is responsible for the observed solid-state photochromism, is due to stabilization of the open-ring MC-like structure by electronic effects from the positively charged pyranopyridinium system.

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Supporting Information Available: Plots of the relevant molecular orbitals (Figure S1) and Cartesian coordinates of the optimized structures (Tables S1−S6). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Guglielmetti, R. In *Photochromism, Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amstredam, 2003; p 314. (b) McArdle, C. B., Ed. *Applied Photochromic Polymer Systems*; Blackie: London, 1992; p 1. (c) Crano, J. C., Guglielmetti, R. J., Eds. *Organic Photochromic and Thermochromic Compounds*; Plenum Publishing: New York, 1999; Vol. 2. (d) Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741–1753. (e) Akimov, D. A.; Zheltikov, A. M.; Koroteev, N. I.; Magnitskii, S. A.; Naumov, A. N.; Sidorov-Biryukov, D. A.; Sokolyuk, N. T.; Fedotov, A. B. *Quant. Electron.* **1998**, *28*, 547–554. (f) Konorov, S. O.; Sidorov-Biryukov, D. A.; Bugar, I.; Chorvat, D., Jr.; Chorvat, D.; Zheltikov, A. M. *Chem. Phys. Lett.* **2003**, *378*, 630–637.

(2) Konorov, S. O.; Sidorov-Biryukov, D. A.; Bugar, I.; Chorvat, D., Jr.; Chorvat, D.; Zheltikov, A. M. *J. Raman Spectrosc.* **2003**, *34*, 1013–1017.

(3) (a) Zahavy, E.; Rubin, S.; Willner, I. *J. Chem. Soc., Chem. Commun.* **1993**, 1753–1755. (b) Willner, I.; Katz, E.; Willner, B.; Blonder, R.; Heleg-Shabtai, V.; Bückmann, A. F. *Biosens. Biolectron.* **1997**, *12*, 337–356.

(4) (a) Bénard, S.; Léaustic, A.; Rivière, E.; Yu, E.; Clément, R. *Chem. Mater.* **2001**, *13*, 3709–3716. (b) Bénard, S.; Rivière, E.; Yu, P.; Nakatani, K.; Delouis, J. F. *Chem. Mater.* **2001**, *13*, 159–162. (c) Aldoshin, S. M.; Sanina, N. A.; Minkin, V. I.; Voloshin, N. A.; Iskorskii, V. N.; Ovcharenko, V. I.; Smirnov, V. A.; Nagaeva, N. K. *J. Mol. Struct.* **2007**, *826*, 69–74.

(5) Tomasulo, M.; Kaanumal, S. L.; Sortino, S.; Raymo, F. M. *J. Org. Chem.* **2007**, *72*, 595–605.

(6) (a) Inouye, M.; Ueno, M.; Kitao, T. *J. Am. Chem. Soc.* **1990**, *112*, 8977–8979. (b) Tanaka, M.; Nakamura, M.; Abdussalam Salhin, M. A.; Ikeda, T.; Kamada, K.; Ando, H.; Shibutani, Y.; Kimura, K. *J. Org. Chem.* **2001**, *66*, 1533–1537.

(7) Iyengar, S.; Biewer, M. C. *Chem. Commun.* **2002**, 1398–1399.

(8) (a) Willner, I. *Acc. Chem. Res.* **1997**, *30*, 347–356. (b) Willner, I.; Rubin, S.; Shatzmiller, R.; Zor, T. *J. Am. Chem. Soc.* **1993**, *115*, 8690–8694. (c) Garcia, A. A.; Cherian, S.; Park, J.; Gust, D.; Jahnke, F.; Rosario, R. *J. Phys. Chem.* **2000**, *104*, 6103–6107.

(9) Zhu, M.-Q.; Zhu, L.; Han, J. J.; Wu, W.; Hurst, J. K.; Li, A. D. Q. *J. Am. Chem. Soc.* **2006**, *128*, 4303–4309.

(10) Nakamura, S.; Uchida, K.; Murakami, A.; Irie, M. *J. Org. Chem.* **1993**, *58*, 5543–5545.

(11) Hirano, M.; Osakada, K.; Nohira, H.; Miyashita, A. *J. Org. Chem.* **2002**, *67*, 533–540.

(12) Bénard, S.; Yu, P. *Adv. Mater.* **2000**, *12*, 48–50.

(13) Bénard, S.; Yu, P. *Chem. Commun.* **2000**, 65–66.

(14) (a) Suzuki, M.; Asahi, T.; Masuhara, H. *Phys. Chem. Chem. Phys.* **2002**, *4*, 185–192. (b) Asahi, T.; Suzuki, M.; Masuhara, H. *J. Phys. Chem.* **2002**, *106*, 2335–2340. (c) Suzuki, M.; Asahi, T.; Takahashi, K.; Masuhara, H. *Chem. Phys. Lett.* **2003**, *368*, 384–392.

(15) *SMART-NT, SAINT-Plus-NT, and SADABS*. Bruker AXS Inc.: Madison, WI, 1999.

(16) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

(17) Sheldrick, G. M. *SHELX97. Programs for Crystal Structure Analysis.* University of Göttingen: Germany, 1997.

(18) The BLA value is calculated as $[d(\mathrm{C1{-}N2}) + d(\mathrm{C12{-}C13}) + d(\mathrm{C14{-}N2})]/3 - [d(\mathrm{C1{-}C12}) + d(\mathrm{C13{-}C14}) + d(\mathrm{N2{-}C15})]/3$, according to the atom labels in Scheme 1. Sheng, Y.; Leszczynski, J.; Garcia, A. A.; Rosario, R.; Gust, D.; Springer, J. J. *Phys. Chem.* **2004**, *108*, 16233–16243.

(19) (a) Aldoshin, S. M.; Nikonova, L. A.; Smirnov, V. A.; Shilov, G. V.; Nagaeva, N. K. *J. Mol. Struct.* **2005**, *750*, 158–165. (b) Aldoshin, S. M.; Nikonova, L. A.; Shilov, G. V.; Bikanina, E. A.; Artemova, N. K.; Smirnov, V. A. *J. Mol. Struct.* **2006**, *794*, 103–109.

(20) The dihedral angles are calculated on the disordered portions.

(21) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1987**, S1–S19.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004.

(23) Testing of various model chemistries and comparison with the previous optimizations (e.g., refs. 10, 18) showed that the absolute value of the C1−O1 bond length depends strongly on the used method/basis set, and therefore, it is not directly comparable with the solid-state data. In this work, for comparison, we used only the relative difference between the values of the charged and the neutral species calculated with the same method/basis set.

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