THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2007, *111,* 2035−2039
Published on Web 02/28/2007

Charge-Transfer Transitions in Twisted Stilbenoids: Interchangeable Features and Generic Distinctions of Single- and Double-Bond Twists

M. Dekhtyar[†] **and W. Rettig***[,‡]

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya str. 5,
Kiev-94, 02094, Ukraine, and Institute of Chemistry, Humboldt University of Berlin, Brook-Taylor-Str. 2,
D-12489 Berlin, Germany

Received: November 17, 2006; In Final Form: February 15, 2007

The charge-transfer transitions relevant to single- and double-bond photochemical twisting have been studied in the framework of the biradicaloid state theory using the AM1 method for a family of donor−acceptor-substituted stilbenoids and a series of sparkle-simulated model stilbenes. Features in common and mutually interchangeable properties for the two transition types as well as their peculiarities are revealed; they are considered in relation to the varied donor−acceptor strength of the substituents, with particular attention given to the occurrence of S_0−S_1 state conical intersections. The difference in critical points at which the conical intersections occur for double-bond and single-bond twisted stilbenoids is shown to be related to the splitting of the cyanine limit of their planar counterparts.

Introduction

The photophysics and photochemistry of stilbenes and related compounds is known to be significantly contributed by light-induced bond twisting.[1,2] Although the parent stilbene possesses two clearly distinct types of bonds, viz. two single bonds and a double bond, and photochemical processes involve mainly double-bond twisting, its donor−acceptor-substituted derivatives or structural analogues exhibit a less-clear distinction between the nature of bonds and, accordingly, between the bond twisting types. As a result, reversal of the twist behavior becomes possible and competing spectroscopic and nonradiative reaction channels emerge on twisting.[3−6] Insight into the nature of electronic states and transitions associated with single- and double-bond twisting is provided by the biradicaloid state theory, which accommodates the two limiting cases (pure single and double bonds) and a diversity of intermediate situations.[7]

The essential concept of the theory is represented in a simple way by the example shown in Figure 1, which elucidates the gradual change from a pure double-bond twist (as in ethylene) to a pure single-bond twist (as in aminoborane). A 90° double-bond twist in a molecule results in π-decoupling and the localization of its spatially separated frontier π-molecular orbitals (MOs) on the different sides of the twisted bond. The corresponding transition, often the S_0−S_1 transition, will therefore be of charge-transfer nature. In the general case, the two MOs differ in energies and in what follows we shall call the lower-lying one “the highest occupied molecular orbital” (HOMO) and the higher-lying one “the lowest unoccupied molecular orbital” (LUMO).[8] The lowest two singlet states can arise either from the singly populated HOMO and LUMO forming the so-called dot−dot (dd) configuration or from the doubly populated HOMO constituting the hole−pair (hp) configuration. The energy difference between the low-lying dd and hp states abbreviated as $\Delta E_{\mathrm{hp-dd}} \equiv E_{\mathrm{hp}} - E_{\mathrm{dd}}$ appears as a sum of the HOMO−LUMO energy gap in the one-electron approximation (correlating with electronegativities of the bond-forming atoms) and the electron−electron interaction energy. In the symmetric or slightly asymmetric case where the

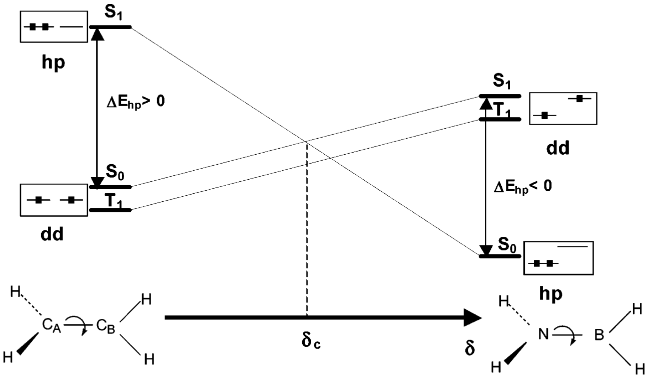


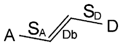
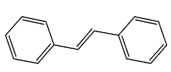
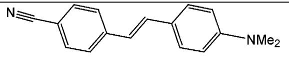
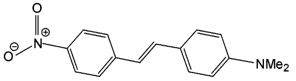
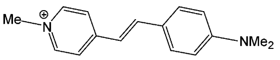
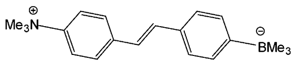
Figure 1. Schematic representation of the biradicaloid state model. For a 90° twisted molecule, the energies and occupation patterns (electronic configurations) of the decoupled frontier MOs localized on D and A are indicated by the bars and points in the boxes. The configurations where both electrons are localized on one moiety are called hole−pair (hp), those where an unpaired electron is situated on both D and A, are called dot−dot (dd). The energies of the lowest two singlet (S_0 and S_1) and of the triplet (T_1) states are correlated with δ, the electronegativity difference of the two MOs involved in the $S_0 \rightarrow S_1$ transition. At $\delta \sim 0$, the dd configuration is lower in energy than the hp one and the opposite is true at $\delta \gg 0$ (the limiting cases are exemplified by ethylene and aminoborane). The dd triplet state is very close to the dd singlet (i.e., to S_0 at the left and S_1 at the right). At a certain critical value, δ_c, an S_0−S_1 intersection occurs and the two states interchange their nature ($\Delta E_{\mathrm{hp-dd}} = E_{\mathrm{hp}} - E_{\mathrm{dd}}$ becomes negative).

---

[*] Corresponding author. E-mail: Rettig@chemie.hu-berlin.de.
[†] Institute of Organic Chemistry, National Academy of Sciences of Ukraine.
[‡] Institute of Chemistry, Humboldt University of Berlin.

10.1021/jp0676484 CCC: $37.00

TABLE 1: Structures, Designations, and Donor−Acceptor Differences for 4,4′-DA-Substituted Stilbenoids as Well as Relevant MO Characteristics

DA-substituted stilbenoids		Energy of the frontier MO on a π-decoupled moiety (eV)		ΔE_{DA}[a] (eV)
Structure 	Designation	E_D HOMO localized on the donor moiety by twisting around S_D	E_A LUMO localized on the acceptor moiety by twisting around S_A	
	S[b]	-11.105 HOMO	1.839 LUMO	-12.944
	DCS	-8.291 HOMO-1[c]	-0.119 LUMO+1[c]	-8.172
	DNS	-6.095 HOMO	-0.740 LUMO+1[c]	-5.355
	DASP	-9.584 HOMO	-5.549 LUMO	-4.035
	SF	-5.895 HOMO	-2.293 LUMO	-3.602

[a] Donor−acceptor difference for a suitably twisted stilbenoid, i.e., energy difference, $E_D - E_A$, between "local-frontier" MOs localized on D and A moieties.[17] [b] The stilbene molecule is slightly dissymmetrized by sparkles. [c] The corresponding "global-frontier" MO is localized on the other molecular moiety.

interelectron interaction governs the sign of ΔE_{hp-dd}, the dd configuration is energetically preferable because repulsion between single electrons occupying HOMO and LUMO is less than that between two electrons both situated on HOMO. For strongly different bond-forming atoms, however, the MO energy gap becomes the prevailing term and the hp configuration proves to be lower in energy because it is now energetically advantageous that both electrons reside on the lower-lying HOMO. At some critical value of the HOMO−LUMO energy difference characterizing the bond polarity, ΔE_{hp-dd} as well as the distinction between single- and double-bond twists vanishes. This point corresponds to a S_0−S_1 conical intersection (COI) occurring near the 90° twisted conformation, which constitutes a channel of ultrafast nonradiative deactivation.[7] Such "photochemical funnels" are significant, in particular, in the primary process of vision.[9−11]

It is the uniformity of single- and double-bond twists that is accentuated by the above-presented model. The message of our communication is to reveal the peculiarities and limitations of this concept in the application to realistic π molecules. Here we exploit it to elucidate not only features in common but also the essential distinctions between the two types of bond twisting. It is also challenging to expand this approach by relating the effects of donor−acceptor (DA) substituents on twisted and on planar species so that the significant phenomena in both structural types can be indicative of each other, thus facilitating search and design of new compounds of interest. For this purpose, the charge-transfer transitions relevant to single- and double-bond twisting have been studied for a family of DA-substituted stilbenoids (for structures and designations, see Table 1) and a series of sparkle-simulated model stilbenes using the AM1 method.[12,13] The relative energies of dd and hp configurations for both twist types were monitored, with particular attention given to the placement of S_0−S_1 COIs. For convenience, we trace S_0−S_1 transition energies in the form of ΔE_{hp-dd} throughout the study so that they can appear both positive and negative.

It should be noted that both the concept represented in Figure 1 and the model employed by us are to a certain extent simplistic because they do not consider a number of COI features as, for instance, the facts that a COI is rather a region than a point between the zwitterionic (hp) and covalent biradicaloid (dd) states, and that it involves changes not in a single internal coordinate but in a set of them,[14−16] and so forth. Thus, the approaches of this kind can hardly elucidate the details of COIs occurring in nonpolar molecules, for example, in unsubstituted stilbene. At the same time, we use the idea of Figure 1 in relation to some energetic COI regularities that can be comprehended even at this level of approximation. In particular, we show that the model used allows tracing the position of COI for double- and single-bond twisting in the series of donor−acceptor-substituted polar conjugated molecules

Following the approach reported previously,[17] the donor−acceptor difference of a stilbenoid molecule, ΔE_{DA}, is found as the difference between the frontier MOs completely localized on the corresponding molecular moieties (HOMO on the D and LUMO on the A) due to the twist of the appropriate bond (see Table 1). This quantity is rather close to that defined in terms of HOMO and LUMO of the respective individual molecules, DH and AH.[18] Accordingly, this parameter characterizes a given pair of end substituents in the stilbene molecule and can serve as a measure of asymmetry of electronic distribution resulting from donor−acceptor effects: it decreases in absolute magnitude, as the substituent-induced molecular polarity (asymmetry) rises. The donor−acceptor difference thus refers to the whole stilbenoid molecule and is a global parameter. For comparison with the biradicaloid state model, another parameter is also used to correlate the results. This is the energy difference between MOs involved in a given CT transition of the twisted molecule, that is, the HOMO−LUMO energy gap of the moieties on either side of the twisted bond considered, ΔE_{HO-LU}. Clearly, this parameter is a local one with respect to the molecular scale because it refers to a certain bond twist within a stilbenoid molecule.

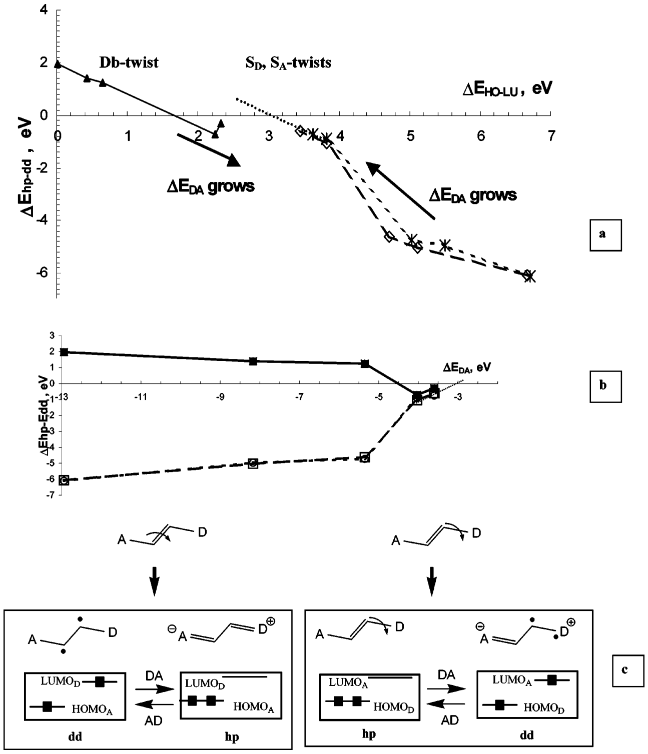


Figure 2. ΔE_{hp-dd} for the double-bond (solid line, Db) and single-bond twists (broken lines with diamonds for S_D and with asterisks for S_A) vs (a) ΔE_{HO-LU}, a parameter similar to δ, which characterizes the polarity of the twisted bond and (b) ΔE_{DA}, a characteristic of the global molecular polarity. For a: critical values of ΔE_{HO-LU} are ~1.65 eV for the double-bond twist and ~3 eV for S_D and S_A twists; for b: the respective values on the ΔE_{DA} scale are about −4.5 and −3 eV. (c) A diagram elucidating the different direction of the charge-transfer transition due to the different localization of the transition-relevant MOs for double- and single-bond-twisted species. The direction (donor-to-acceptor electron transfer or vice versa) is given by the labels AD and DA next to the arrows designating the transitions between the dd and the hp states.

In what follows, we compare the behavior of the values ΔE_{hp-dd} and the reasons behind it for the transitions associated with both types of bond twisting (see the solid lines in Figure 2a and b and the left-hand panel in Figure 2c for double-bond twists, whereas the broken lines and the right-hand panel in the respective illustrations represent the single-bond twists).

The most significant feature in common for the two types of bond twisting is the fact that the S_0-S_1 transition energies for symmetric and slightly asymmetric stilbenoids (i.e., having large negative values of ΔE_{DA}) are rather large but they progressively decrease, approaching each other with rising donor−acceptor difference until the minimum (COI) at the corresponding critical value of ΔE_{DA} is passed. Thus, both solid and broken lines in Figure 2a and b tend to cross the zero line in going from symmetric and slightly asymmetric species like stilbene, DCS, and DNS to strongly asymmetric DASP and SF. In this context, the central scheme of the biradicaloid state model is exemplified especially well by the behavior of the S_0-S_1 curve for double-bond twisted DA stilbenoids in relation to ΔE_{HO-LU}, the local molecular asymmetry (polarity) of the central double bond (see Figure 2a). Furthermore, the single- and double-bond twists are also similar in that the direction of the S_0-S_1 transition is D → A before the COI is reached and changes to A → D after this point is passed (see Figure 2c).

At the same time, some inherent features of either twist type are preserved in any region of the ΔE_{DA} scale (see below), which demonstrates that the double and single bonds in twisting do not merely interchange on both sides of the COI but retain a certain part of their identity, contrary to what might be inferred from the formal treatment of the concept illustrated by Figure 1.

First, the localization of the MOs relevant to the S_0-S_1 transition is different for the two twist types. As far as double-bond twisted species are concerned, the LUMO is localized on the D and the HOMO on the A moiety, whereas single-bond twists are characterized by the reverse MO localization (see Figure 2c). As a result, the nature of the S_0-S_1 transition differs for the two twist types. For double-bond twists in the pre-COI region, the D → A electron transfer is realized through a descent of an electron from the higher-lying LUMO to the lower-lying HOMO and corresponds to a switch from the nonpolar or slightly polar dd to the highly polar hp configuration; in the post-COI region, the A → D electron transfer is the HOMO → LUMO move up of an electron corresponding to the hp → dd switch. The S_0-S_1 transitions in single-bond twisted molecules exhibit the corresponding mirror-like features: in the pre-COI region, the D → A electron transfer is the HOMO → LUMO move up of an electron and at the same time the hp → dd switch, the dd case being much more polar than hp; in the post-COI region, the A → D electron transfer is the LUMO → HOMO descent which implies the dd → hp switch.

Second, the HOMO−LUMO energy gap relevant to the S_0-S_1 transition changes oppositely for the two twist types with growing DA strength of the terminal substituents: it rises for double-bond twists (acceptors lower the HOMO and donors raise the LUMO energy thus pulling them further apart) and diminishes for single-bond twists (donors raise the HOMO and acceptors lower the LUMO thus pushing them closer to each other), see Figure 2a and c. In other words, the scales of the local bond polarity (ΔE_{HO-LU}) and the global molecular polarity (ΔE_{DA}) change in the same direction for double bonds and oppositely for single bonds. That is why the line of ΔE_{hp-dd} plotted against ΔE_{HO-LU} and ΔE_{DA} goes in the same direction for double-bond twists and is sloped oppositely for single-bond twists (cf. the slopes of the solid and broken lines in Figure 2a and b).

Another significant point of distinction between the two types of bond twisting is the different COI position: as seen from Figure 2a and b, the value ΔE_{hp-dd} goes to zero at ΔE_{DA} ~ −4.5 eV (ΔE_{HO-LU} ~ 1.6 eV) for double-bond twists and at ΔE_{DA} ~ −3 eV (ΔE_{HO-LU} ~ 3 eV) for single-bond twists (though neither of the single-bond twists involves the occurrence of the COI within the range of compounds considered, a notion of where the crossing point should be is given by extrapolation of the corresponding practically merging broken lines). Thus, for the S_0-S_1 COI to occur, a smaller degree of molecular asymmetry is needed for double-bond-twisted than for single-bond-twisted species. This distinction reflects the difference in the corresponding bond orders in the prototype compound, stilbene: the origins of the lines ΔE_{hp-dd} for double-bond and single-bond twists are seen from Figure 2a and b to be differently distant from the abscissa. A smaller critical value of ΔE_{DA} for a double-bond twist is essentially attributable to a much lower S_0-S_1 transition energy in double-bond-twisted stilbene (~2 eV) in comparison to the energy of the first charge-transfer transition in the same single-bond-twisted molecule (~6 eV). In turn, this distinction arises from opposite π-decoupling effects on the excitation energy for twisted single and double bonds (see, e.g., refs 1 and 4). Indeed, a formal double bond has a higher bond order in the ground than in the excited state and that is why π-decoupling (e.g., via twisting) raises the

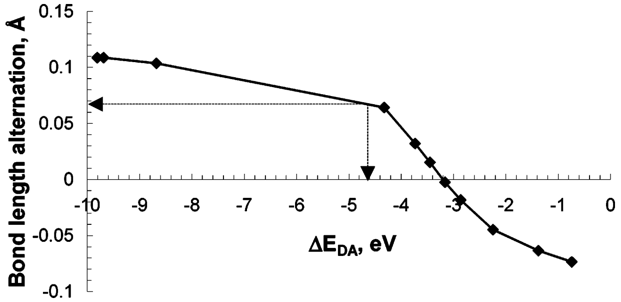


Figure 3. Bond length alternation for the series of model (sparkle-simulated) *planar* stilbenoids of varied polarity. The alternation was calculated as the difference of the mean single bond and the double-bond length.[17] The cyanine limit (i) is found at the ΔE_{DA} value of about −3.2 eV. The arrows point at the cyanine limit (iii) found previously for the same family of “realistic” stilbenoids at $\Delta E_{DA} \sim -4.6$ eV and bond length alternation about 0.07 Å.[17]

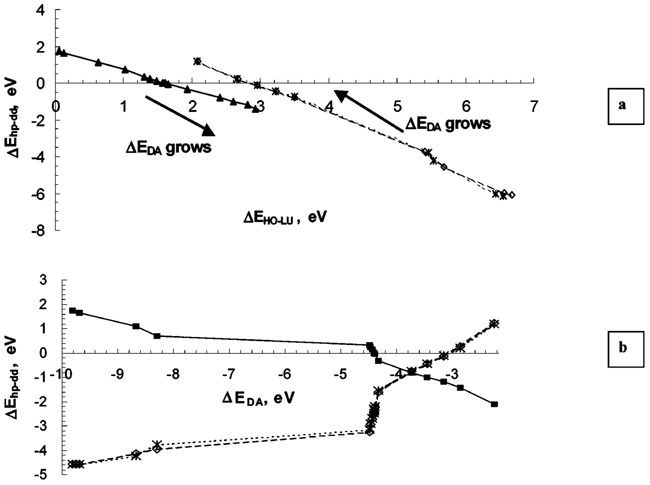


Figure 4. ΔE_{hp-dd} for the double-bond and single-bond *twisted species* for sparkle-simulated stilbenoids plotted vs ΔE_{HO-LU} (a) and ΔE_{DA} (b) (for designations see Figure 2a and b). For a: critical values of ΔE_{HO-LU} are ~1.6 eV for the double-bond twist and ~2.9 eV for S_D and S_A twists. For b: the respective critical values of ΔE_{DA} are ~−4.5 eV and ~−3 eV.

energy of the S_0 state more than that of S_1 giving rise to a decreased S_0-S_1 gap as against the conjugated (planar) situation. Vice versa, a formal single bond is characterized by a lower bond order in the ground than in the excited state; as a result, π-decoupling leads to the S_1 state being raised in energy more than S_0 and hence to an increased S_0-S_1 gap.

These peculiarities call for relating the S_0-S_1 COI in twisted species to the so-called “cyanine limit” in their planar counterparts. The “cyanine limit”, or “ideal polymethinic state”, is known as a situation occurring for a quasi-linear conjugated chain,[19,20] and can be characterized, for simplicity, by the following three bond-length-related criteria: the bond-length alternation should vanish both in the ground (i) and in the excited state (ii) and thus it should not change on excitation (iii). It was previously found for the stilbenoid series under study that because of the aromatic rings present conditions i−iii are no longer equivalent: condition i is not realized within the investigated ΔE_{DA} interval; condition ii can in principle be ruled out for this family; but the criterion of equal bond-length alternations in the ground and excited state (iii) can be used.[17] The latter occurs at $\Delta E_{DA} \sim -4.6$ eV, that is, at roughly the same point as the suggested S_0-S_1 COI for double-bond twists. This remarkable proximity may be attributable to the following fact: the cyanine limit as defined by condition iii just implies the situation in which the structural parameters of the conjugated chain (in terms of bond-length alternation) are much the same in the ground and the excited state, which is to a considerable extent indicative of the S_0 and S_1 closeness in energy for a planar structure, whereas a COI implies the same for a twisted species. Within a qualitative framework, the point of occurrence of the cyanine limit in planar systems can therefore serve as a guiding mark in the search for COIs of twisted species.

Alternatively, the cyanine limit (i) for the DA stilbenoids is found to be at about −3.2 eV (see Figure 3), much the same ΔE_{DA} value as that needed for the COI of single-bond twists to take place. To establish this regularity, we invoked sparkle simulation of DA-substituted stilbenoids, which provides ΔE_{DA} strengths beyond the values accessible by the substituents used here.[21]

The energies of the charge-transfer transitions in sparkle-simulated species with double- and single-bond twists, if plotted in the form of ΔE_{hp-dd} versus ΔE_{HO-LU} and ΔE_{DA} (see Figure 4a and b), manifest the same general trends and almost the same characteristic values as their counterparts with real substituents (cf. Figures 4a and 2a, and 4b and 2b.[22] The consistent similarity between the results obtained for the two object series suggests the adequacy of the sparkle modeling involved and therefore enables some plausible predictions to be made for not yet existing (and even not yet quantum-chemically studied) molecules based on the data for their sparkle-simulated counterparts. To exemplify, turn to Table 2 in which some essential characteristics are listed for realistic and sparkle-simulated DA stilbenoids. As seen, the lacking data on the ground-state bond length equalization (the cyanine limit (i)) as well as on the occurrence of the S_0-S_1 COI in single-bond-twisted species can to a good accuracy be reproduced on the basis of those obtained in sparkle simulations.

To conclude, some properties of the single- and double-bond twists in stilbenoids are common or interchangeable by varying

TABLE 2: Characteristics of DA-Substituted Stilbenoids and Their Sparkle-Simulated Counterparts: The Conditions for the Occurrence of the Cyanine Limits (i) and (iii) in Planar Systems and the Criteria of S_0-S_1 COI for Systems Twisted around Single (S_A and S_D) and Double Bonds (Db)

planar systems							twisted systems					
occurrence of the cyanine limit	ΔE_{DA}, eV		bond length alternation, Å				ΔE_{DA}, eV		bond length alternation, Å		ΔE_{HO-LU}, eV	
	“real” stilbenoids	sparkle simulation	“real” stilbenoids	sparkle simulation			“real” stilbenoids	sparkle simulation	“real” stilbenoids	sparkle simulation	“real” stilbenoids	sparkle simulation
(i)	*a*	−3.2	*a*	0	occurrence of the conical interesection	S_D, S_A twist	*a*	−3.2	*a*	0	*a*	2.9
(iii)	−4.6[b]	*c*	−0.07[b]	*c*		Db twist	−4.5	−4.5	0.065	0.065	1.65	1.6

[a] Cannot be reached within the stilbenoid family under study. [b] Based on the previously reported data.[17] [c] Excited-state geometry optimization was not performed for sparkle-simulated compounds.

the molecular polarity but some features represent the generic attributes of each twist type. The occurrence of the cyanine limit for the planar structure is supposed to be indicative of the probable dd−hp state intersection in the twisted form, as the cyanine limit transforms, in a sense, into a COI via twisting. Accordingly, it is plausible that the splitting of the occurrence conditions for S_0-S_1 COIs in single- and double-bond twisting may be related to the diversification of the cyanine limit in the corresponding planar molecules (caused, as shown previously,[18] by the end-group effects), but this relation remains to be understood and requires further investigation.

Acknowledgment. We are grateful to the Deutsche Akademische Austauschdienst (DAAD) and the Deutsche Forschungsgemeinschaft (DFG, within SFB 448) for support of this work by travel grants to M.D.

References and Notes

(1) Klessinger, M.; Michl, J. *Excited States and Photochemistry of Organic Molecules*; VCH Publishers, Inc.: New York, 1995.

(2) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. In *Organic Photochemistry*, Chapman, O. L., Ed.; Marcel Dekker, Inc.: New York, 1971; Vol. 3, Chapter 1, pp 1−113.

(3) Rettig, W.; Majenz, W.; Herter, R.; Létard, J. F.; Lapouyade, R. *Pure Appl. Chem*. **1993**, *65*, 1699.

(4) Rettig, W. Charge Transfer in Self-Decoupling π Systems. In *Modern Models of Bonding and Delocalization*; Liebman, J.; Greenberg, A., Eds.; VCH Publishers: New York, 1988; pp 229−282.

(5) Van der Meer, M. J.; Zhang, H.; Rettig, W.; Glasbeek, M. *Chem. Phys. Lett*. **2000**, *320*, 673.

(6) Sczepan, M.; Rettig, W.; Tolmachev, A. I.; Kurdyukov, V. V. *Phys. Chem. Chem. Phys*. **2001,** *3*, 3555.

(7) Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; J. Wiley & Sons, Inc.: New York, 1990.

(8) The MO designations used here are not the proper terms in the usual sense applied to ground-state occupation pattern because ground states in the present model can have an open-shell character and hence involve “unoccupied” molecular orbitals.

(9) Rettig, W. *Angew. Chem., Int. Ed. Engl*. **1986**, *25*, 971.

(10) Bifone, A.; de Groot, H. J. M.; Buda, F. *J. Phys. Chem. B* **1997**, *101*, 2954.

(11) Sinicropi, A.; Migani, A.; De Vico, L.; Olivucci, M. *Photochem. Photobiol. Sci.* **2003**, *2*, 1250.

(12) Dewar, M. J.; Zoeblich, E.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3202.

(13) AMPAC 6.0 and AMPAC 6.55, Semichem, Inc.; Shawnee, KS, 1997.

(14) Ohmine, I. *J. Chem. Phys.* **1985**, *83*, 2348.

(15) Amatatsu, Y. *Chem. Phys. Lett.* **1999**, *314*, 364.

(16) Amatatsu, Y. *Chem. Phys. Lett*. **2003**, *369*, 673.

(17) Dekhtyar, M.; Rettig, W. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1602.

(18) Rettig, W.; Dekhtyar, M. *Chem. Phys.* **2003**, *293*, 75.

(19) Daehne, S. *Science* **1978**, *199*, 1163.

(20) (a) Dyadyusha, G. G.; Ushomirskii, M. *Teor. Eksp. Khim.* **1989**, *25*, 266. (b) Dyadyusha, G. G.; Ushomirskii, M. *Theor. Exp. Chem.* **1989**, *25*, 243.

(21) By embracing a stilbene molecule by two opposite charges (“sparkles”) of increasing magnitude, a gradual rise of the donor−acceptor difference in a model stilbenoid was induced. Ground-state geometry optimization was performed for a series of thus modeled DA stilbenoids to provide the bond lengths in the ΔE_{DA} range from −9.8 to −0.8 eV. In so doing, the sparkles were rigidly positioned on both sides of the stilbene molecule distant by 2.7 Å from the 4,4′-atoms on the CH bond lines and varied in the range of ±0.05e to ±2e.

(22) The step-like sections on the lines correspond to a jump in the DA properties of the substituents when the local HOMO of the D and the LUMO of the A become the global frontier MOs of the molecule; the congested points thus represent merely a ΔE_{DA}-scale-induced computational effect.