



# Photochemical switching through protonation in merocyanines

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## Abstract

The ground- and excited-state energies for the planar and various 90-degree twisted structures of the merocyanine  $\text{Me}_2\text{N}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{O}$  and its protonated form  $^+\text{Me}_2\text{N}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{OH}$  have been calculated by the AM1 method involving complete geometry optimization. On successively twisting bonds in the polymethine chain, the energies of the resulting twisted forms display a pronounced alternation which is opposite in the ground and the excited state. This trend in computed energy values as well as the reversed alternation pattern for the two types of polymethine compounds can be anticipated from simple qualitative MO considerations and in the topological long-chain approximation. © 1999 Published by Elsevier Science S.A. All rights reserved.

**Keywords:** Merocyanine; Polymethine; AM1 method;  $S_1-S_0$  conical intersections

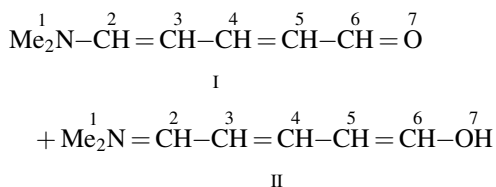
## 1. Introduction

The selectivity and environment-specificity as well as the subpicosecond timescale of the photoisomerizations in long conjugated chains [1,2] are known to be primarily significant in light-driven in-vivo phenomena like vision (see, e.g., [3,4]) and they lead to the question regarding the nature of such isomerization processes. Since many years, the isomerization of ethylenes and small polyenic systems has been understood theoretically [5,6] and shown to involve the possibility of conical intersections, i.e. very close approaches or touchings of  $S_1$  and  $S_0$ . This is especially so, if acceptor and/or donor groups are present. In the more recent literature, several examples are treated where isomerizing systems react via such conical intersections as ultrafast gateways from the excited to the ground state [7]. A general observation is that such outstanding geometries are usually connected with the twisting of bonds, sometimes even with several bonds twisted simultaneously [8]. The highly specific photochemical behaviour of long polymethine chromophores suggests (i) that different twisting coordinates corresponding to the many possible isomerization channels possess conical intersections of different efficiency, and (ii) this efficiency pattern can change depending on protonation, charge environment, medium polarity, etc.

Nowadays the abundant literature is available in which the photoisomerization behaviour of visual pigments and related systems is modelled quantum chemically [9–13]. As shown, the probability for a bond in a conjugated chain to provide a conical intersection on twisting [7,8], i.e. a “funnel” for the excitation energy, is essentially controlled by the corresponding bond order, and it is for this reason, that the photoisomerization pattern is so sensitive to the protonation and other bond-order-altering effects. On the other hand, molecular bond orders, though frequently being a predominant factor, cannot solely account for the photoisomerization selectivity [14,15].

In view of these various viewpoints, we intend here to study the protonation effect on bond “funneling” probabilities in the polymethine chromophore by an all-valence semiempirical method with large CI, and to reveal substantial MO and topological regularities underlying the computational results. We focus on a rather short conjugated donor-acceptor model system enabling all possible twists to be considered. From this standpoint, merocyanine I and its protonated form II are convenient to be compared in terms of energy gaps or funnel efficiency of twisted bonds. As seen, the two conjugated polymethinic species are of the same length (7 atoms) and  $\pi$ -electronic population (8 electrons), one being a merocyanine molecule carrying no charge (I) and the other (II) representing a cyanine cation (because of different core charges of the oxygen atom).

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In a first attempt to classify the efficiency of a conical intersection or photochemical funnel [6] we can take the zero-order energy gap between the ground and the excited state of the perpendicular system, as calculated using quantum chemical methods. Small energy gaps as existence criterion for a funnel were efficiently used in previous studies which investigated e.g. the formaldiminium ion  $\text{H}_2\text{C}=\text{NH}_2^+$  with ab initio methods [16] and found a surface-touching situation suggesting an efficient conical intersection, while the corresponding acroleiniminium ion  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{NH}_2^+$  possesses larger energy gaps.

Importantly, for twist cases considered in the literature, the properties of ground and excited state are always complementary because their electronic structure differs by the localization of two electrons on one submoiety (hole-pair situation) or on two different ones (dot-dot situation) [6]. As I and II are classified with polymethinic chains including an odd number of  $\pi$ -centres, straightforward rules can be applied to determine on which submoiety the electron pair is localized in the ground and the excited state of their molecules. These rules were first formulated by Momicchioli for symmetric cyanine systems in terms of a simple qualitative model for twistings in the conjugated chains [17]. Twist is regarded as a  $\pi$ -decoupling, both fragments possessing an even number of electrons (hole-pair situation). In the ground state, the odd (polymethinic) fragment always has more electronic density (by one electron) than in the excited state. Vice versa, the even (polyenic) fragment gains an extra electron in the excited state. As a result, both fragments in the excited state contain odd numbers of electrons (dot-dot situation). Based on this concept, we partition (by twisting different bonds) the odd polymethinic molecules I and II in all the possible ways and then consider the resulting ground- and excited-state charge redistribution from the energetic point of view. This permits to qualitatively estimate the relative accessibilities of the corresponding resulting perpendicular (perp) structures. In order to keep a clear general picture resulting from the different possible partitionings, we do not consider the possibility of multiple bond twistings which might be important for some conical intersections [8] not affecting, however, the overall qualitative conclusions aimed at.

## 2. Computational method

To determine the relative probabilities for different bonds in these molecules to twist on excitation and to lose the excitation energy acting as photochemical funnels, AM1 calculations [20] using the AMPAC package [21] were

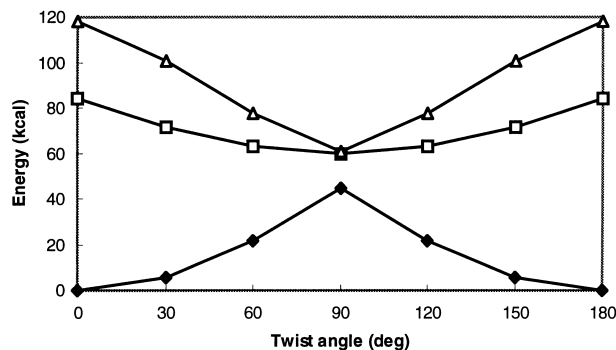
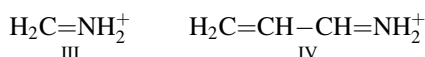


Fig. 1. AM1-calculated  $S_0$ ,  $T_1$ , and  $S_1$  energies (respectively designated by solid rhombic, empty square, and empty triangle markers) versus twist angle, for the N=C bond of the formaldiminium cation III, with 8 MOs involved into the configuration interaction matrix and the geometry specified as in [16] (bond lengths change proportionally with the twist angle).

performed to yield the magnitudes of all possible rotation barriers in the ground state and the depths of the excited-state energy wells for the corresponding 90-degree twisted forms.

In general, the adequacy of the method used for the problem under consideration represents a separate challenge. The quality and reliability of the results for systems I and II have been judged by comparison with smaller model systems, formaldiminium (III) and acroleiniminium (IV) cations, which have been calculated with the same AM1 approach. The potential energy curves are shown in Figs. 1 and 2.



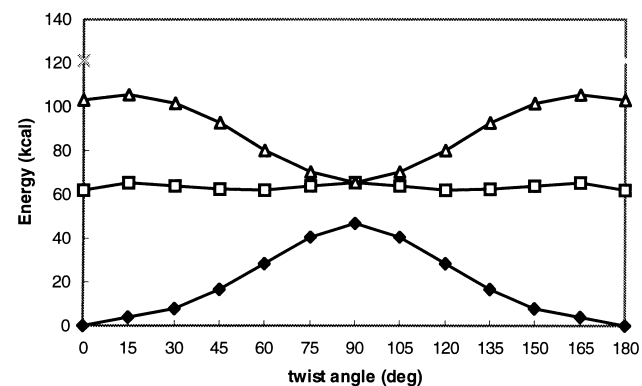
The outcomes can be compared to previous large-scale CI ab initio results [16] (see Table 1). As far as the cation III is concerned, the surface-touching situation (see Fig. 1) as well as the numerical parameters of the potential curves are reproduced, in essence, quantitatively by the semiempirical computational procedure. Equally convincing is the conformity of results provided by the two methods for the twisting of the N=C and the external C=C bonds in the cation

Table 1

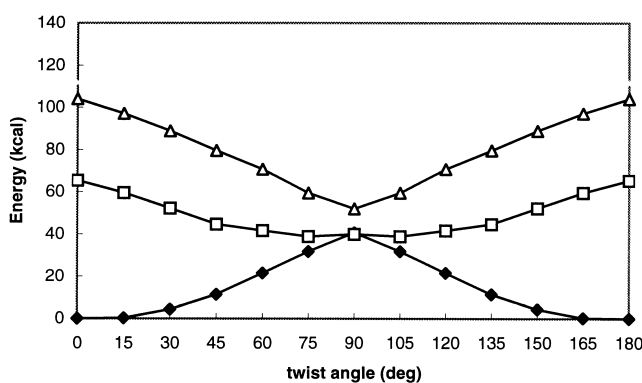
Energy parameters of the  $S_0$  and  $S_1$  potential curves derived by the ab initio [16] and the AM1 methods, for perpendicular geometries of the formaldiminium III and acroleiniminium IV cations, with reference to the planar structures

Energies (kcal)	Formaldiminium III / Acroleiniminium IV					
	Formaldiminium III		Acroleiniminium IV		Bond CC (external)	
	ab initio <sup>a</sup>	AM1	ab initio <sup>a</sup>	AM1	ab initio <sup>a</sup>	AM1
$S_0$ barrier height	80	60	55	50	60	40
$S_1$ well depth	120	70	55	40	50	50
$S_1-S_0$ gap	0	3	20	20	25	10

<sup>a</sup> Data from [16].



a



b

Fig. 2. AM1-calculated  $S_0$ ,  $T_1$ , and  $S_1$  energies (respectively designated by solid rhombic, empty square, and empty triangle markers) versus twist angle for the N=C (a) and external C=C (b) bonds of the acroleiminium cation IV, with 8 MOs involved into the configuration interaction matrix and the geometry specified as in [16] (bond lengths change proportionally with the twist angle).

IV: in these two latter cases, the  $S_1-S_0$  energy gaps substantially differ from zero. On passing from the C=N twist to the external C=C twist, the electronic nature of the ground-state barrier changes from hole-pair to dot-dot, the latter being recognizable by the degeneration of the singlet and triplet states of the perp form (see Fig. 2(a) and (b)). The results provided by the AM1 procedure are thus verified by the comparison with high-quality *ab initio* calculations.

### 3. Results and discussion

As can be seen, both  $S_0$  and  $S_1$  energies of the perp forms of the two polymethinic species, I and II, exhibit clear-cut regular alternation, as the bond twisted successively changes its position in the polymethine chain (see Fig. 3). Importantly, the alternation patterns are opposite for the polymethinic species under consideration. As anticipated, in both cases twistings around formally single bonds (call them A-type bonds) result in lower ground-state and higher

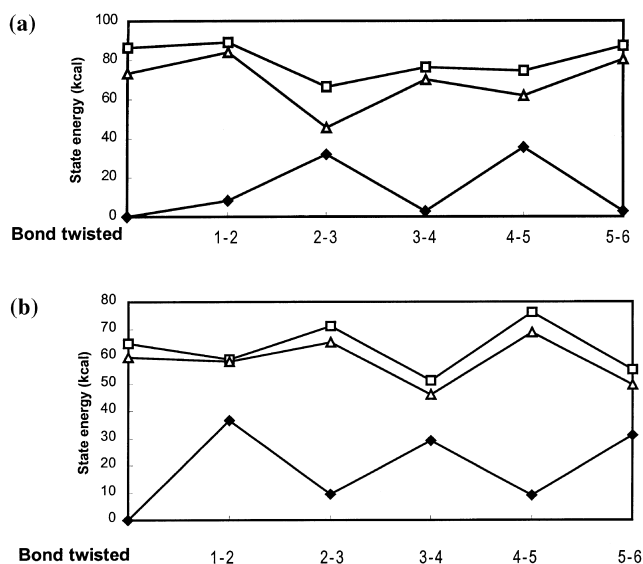


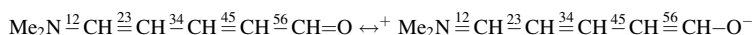
Fig. 3. AM1-calculated  $S_0$  and  $S_1$  energies for the planar and all possible perp forms of I (a) and II (b) with 8 MOs involved into the configuration interaction matrix. Solid rhombic markers designate ground-state energies for structures with the optimized geometries and only a dihedral angle of one (twisted) bond frozen in each case (with the identification of the bond as indicated in the formula). Empty square and triangle markers respectively represent the energies of the charge-transfer excited state calculated for the ground-state Franck-Condon and the relaxed (fully optimized) geometry.

excited-state energies for the corresponding perp forms, whereas formally double bonds (B-type bonds), when twisted, give rise to perp forms with a significantly decreased energy gap between the high-lying  $S_0$  and the low-lying  $S_1$  states. In this sense, the ground and the excited states demonstrate complementary alternation pattern, and twisted structures with the largest barriers in the ground state exhibit the strongest energy lowering in the excited state. As a consequence, B-type bonds are evidently more prone to photoisomerization as well as to “funneling” the excitation energy nonradiatively to the ground state. As far as the merocyanine I is concerned, the rotation around bond 23 appears to be the most probable funnel, with the lowest total energy and smallest  $S_1-S_0$  gap.

Causing A-type and B-type bonds to interchange, protonation radically changes the state energy alternation picture. On going to the protonated molecule, II, the smallest  $S_1-S_0$  gap and, accordingly, the highest tendency for nonradiative excited-energy degradation is found for the perp form resulting from the twisting of the neighbouring bond 34. However, it should be noted that the rotations around other B-type bonds (bond 12 and 56) cannot be ruled out from consideration as other possible funnels, since they demonstrate noticeable but not sufficient distinctions in the size of the energy gap as compared to bond 34, the most probable gateway from the excited to the ground state. These slight energy differences can in principle be sensitive to the settings chosen in a given computational procedure and

Table 2

Possible ways of fragmentation and charge redistribution in the perpendicular forms of molecule I:



$\pi$ -Fragment length (number of electrons; charge)						
Bonds twisted	A-type (anti-funnel)			B-type (funnel)		State
	12	34	56	23	45	
Odd fragment	1 (2;0)	3 (4;0)	5 (6;0)	5 (6-)	3 (4;-)	$S_0$
Even fragment	6 (6;0)	4 (4;0)	2 (2;0)	2 (2;+)	4 (4;+)	
Odd fragment	1 (1;+)	3 (3;+)	5 (5;+)	5 (5;0)	3 (3;0)	$S_1$
Even fragment	6 (7;-)	4 (5;-)	2 (3;-)	2 (3;0)	4 (5;0)	

would not be taken too quantitatively. On the other hand, twisted A-type bonds could be designated as “anti-funnels” because they present especially large  $S_1-S_0$  energy gaps.

It is noteworthy that for case I the excited-state dot-dot electronic structure of twisted conformations corresponds to a charge transfer state and is closely related to the well-known twisted intramolecular-charge-transfer states [18,19]. For case II, excitation of twisted structures leads rather to a charge shift than to a separation of charges.

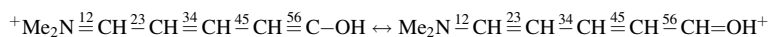
The alternating pattern found for molecules I and II can be interpreted in terms of the above-discussed simple qualitative model, which can account for the origin of the revealed trends in energies for different perp forms. Tables 2 and 3 were constructed based on the principle that upon electronic excitation, an electron is transferred from the odd to the even fragment. These tables present all possible fragmentation modes for I and II, respectively, corresponding to the different perp forms, with the fragment lengths and charges indicated. In each case, fragment charges as specified by the qualitative model are easily correlated with the correspond-

ing limiting valence-bond structure, if the bond broken is identified with a single bond of that structure in the ground state and with a double bond in the excited state, in accordance with the respectively involved hole-pair and dot-dot situations (see Tables 2 and 3).

As seen, fragments produced by twisting around A-type bonds of the molecule I (see Table 2) are uncharged in the ground state, contrary to virtually complete charge separation in the excited state. Twisting around B-type bonds gives rise to the reverse situation: the initially planar molecule with a fraction of charge separation turns into two oppositely charged fragments upon twisting in the ground state whereas no or little charge separation occurs in the excited state. From general considerations, charge separation should be energetically disadvantageous (in the context of Coulomb interactions), and we should expect the perp form energies of I to be arranged as follows: A (12, 34, 56) < B (23, 45) in the ground state and B (23, 45) < A (12, 34, 56) in the excited state, which is the case in terms of the AM1-produced computational data. From this point of view, the increased

Table 3

Possible ways of fragmentation and charge redistribution in the perpendicular forms of molecule II:



$\pi$ -Fragment length (number of electrons; charge)						
Bonds twisted	A-type (anti-funnel)			B-type (funnel)		State
	23	45	12	34	56	
Odd fragment	5 (6;0)	3 (4;0)	1 (2;0)	3 (4;0)	5 (6;0)	$S_0$
Even fragment	2 (2;+)	4 (4;+)	6 (6;+)	4 (4;+)	2 (2;+)	
Odd fragment	5 (5;+)	3 (3;+)	1 (1;+)	3 (3;+)	5 (5;+)	$S_1$
Even fragment	2 (3;0)	4 (5;0)	6 (7;0)	4 (5;0)	2 (3;0)	

tendency for B-type bond rotations to act as photochemical funnels becomes evident.

On the other hand, the statement about complete charge separation valid within the simple topological model can hardly hold in the framework of a method which allows for interelectronic interactions on the all-valence basis and hence suggests that there is no complete  $\pi$ -decoupling in a perp form. Thus, the realistic electron-density distribution between fragments proves to involve no integer-electron charges: these are “adjusted” so that odd fragments are slightly electron-excessive in comparison with the topological picture, which somewhat lowers the resulting energy of all twisted structures but causes no significant changes in their relative energy advantages.

The energy alternation pattern for the molecule II can be interpreted essentially on the same basis, with the positive charge location on the nitrogen or on the oxygen atom in the valence-bond resonance structure serving as energetic discriminator (as was done, for instance, in [22]). As rotations around A-type bonds imply a positively charged nitrogen (energetically advantageous situation) in the ground state and a positively charged oxygen (disadvantageous situation) in the excited state and rotations around B-type bonds result in the reverse picture (see Table 3), the perp form energies are expected to be arranged as follows: A (23, 45) < B (12, 34, 56) in  $S_0$  and B (12, 34, 56) < A (23, 45) in  $S_1$ , in conformity with the results of the AM1 calculation.

Interestingly, the protonation-induced change in the alternation pattern for the  $S_1$ – $S_0$  gap for molecules I and II can be modelled in terms of LUMO–HOMO energy differences within another topological approach, the long polymethine chain approximation [23]. Energies of HOMO and LUMO, respectively localized on odd (polymethinic) and even (polyenic) fragments,  $Z_{\text{HOMO}}$  and  $Z_{\text{LUMO}}$ , appear as functions of the number of methine units in the fragment,  $n$ , and of two effective parameters of its end group, the electron donor ability,  $F$ , and the effective length,  $L$  (see Eq. (1)).

$$Z_{\text{LUMO}} = 2\pi F / (n + 1 + L) \quad (1)$$

$Z_{\text{HOMO}}$  is specified by the same expression, with  $(F-1)$  substituted for  $F$ ; in the case of even  $n$ ,  $F$  should be increased by 1/2 [23]. The parameter  $F$  characterizes the shift of the energy gap of a polymethine chain and  $L$  accounts for the narrowing of the gap under the action of a conjugated group attached to the chain end. For a simple case presented by monoatomic end groups, as in compounds I and II,  $F$  and  $L$  are expressible in terms of the corresponding Coulomb,  $\alpha$ , and resonance,  $\beta$ , integrals:

$$F = \frac{1}{2} + \frac{1}{\pi} \arctg(\alpha/\beta), \quad L = \frac{1}{1 + (\alpha/\beta)^2} \quad (2)$$

Finding the energy difference between LUMO of the even fragment and HOMO of the odd fragment which result from every possible twist, we can roughly estimate the corresponding funnelling efficiency.

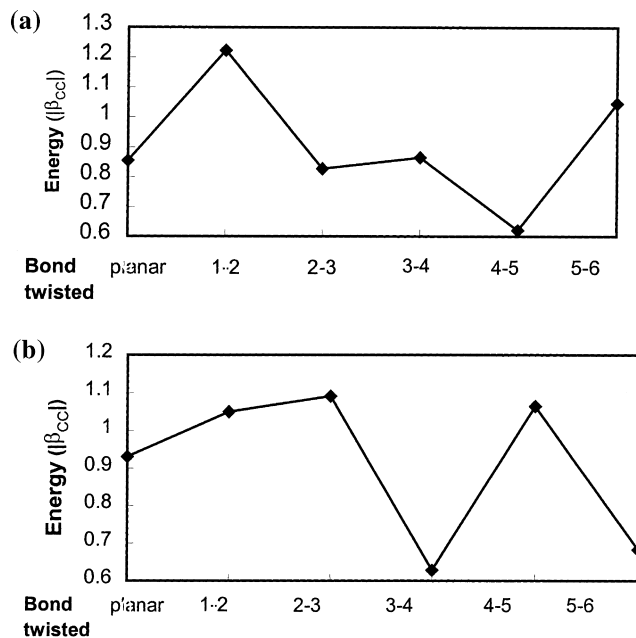


Fig. 4. Variations in the  $S_1$ – $S_0$  energy gap (calculated as the LUMO–HOMO energy difference) for the planar and all possible perp forms of I (a) and II (b) within the long-polymethine-chain approximation. ( $\alpha_{\text{N}} = -0.9$  and  $\alpha_{\text{O}} = -0.5$  for compound I, and  $\alpha_{\text{N}} = -0.9$  and  $\alpha_{\text{O}} = -2$  for compound II; energies are measured in units of  $\beta_{\text{ccl}}$ ).

Within the Hückel approximation, compounds I and II possessing an equal number of  $\pi$ -centres and  $\pi$ -electrons, are distinguishable only due to different core charges of the oxygen atom. For the uncharged merocyanine I, the core charges of the nitrogen and the oxygen atoms amount to +2 and +1, and in the molecule of the protonated form II either core charge is equal to +2. Correspondingly, it is natural to assume the  $\alpha_{\text{O}}$  to  $\alpha_{\text{N}}$  ratio to be smaller than unity in compound I and to exceed unity in compound II. By varying Coulomb integrals in going from compound I to II, it is possible to simulate the change in the bond alternation pattern and hence in the photochemical behaviour occurring on protonation. For instance, with the Coulomb integrals for N and O chosen as  $-0.9$ ;  $-0.5$  in molecule I and  $-0.9$ ;  $-2$  in molecule II, and the resonance integrals for N–C and O–C bonds put equal to that for a C–C bond in the polymethine chain, i.e.  $-1$  (all parameters are given in the units of  $\beta_{\text{ccl}}$ ), the LUMO–HOMO gaps calculated by Eqs. (1) and (2) for every possible twist (partitioning of the molecule into two fragments) result as an alternating series shown for compounds I and II in Fig. 4(a) and (b). As seen, the alternation patterns for the neutral merocyanine I and its protonated form II are opposite, in qualitative conformity with the AM1-based results.

#### 4. Conclusions

Different bonds in the compounds under consideration are characterized by dramatically differing tendencies for non-

radiative degradation of the excited-state energy. A pronounced alternation pattern for perp-structure energies associated with the successive twisting of bonds in the polymethine chain suggests that formally double bonds are mainly expected to be active in photochemical funneling and should be paid special attention if nonradiative losses of the excited-state energy are to be controlled. Importantly, the opposite energy alternation pattern found for merocyanines and their protonated forms can be rationalized and predicted within the framework of simple qualitative models, by the relative energies of the valence-bond resonance structures and in the context of the long-chain approximation. On this basis, relative energies for various perp forms can be estimated and any bond in an unsymmetric polymethine compound can unambiguously be classified as leading to “funnels” or “antifunnels”. These approaches may also be helpful for the understanding of the isomerization process in vision. For instance, proton translocation and/or deprotonation, as discussed in the vision process [6], can radically alter the isomerization pattern and activate or deactivate different bonds with respect to nonradiative deexcitation.

Furthermore, these qualitative considerations can be applied in the primary stage of designing high-efficiency fluorescent dyes, as they enable to distinguish between bond leading to efficient conical intersections by twisting and other bonds connected with a total lack of conical intersection. Only the former type of bonds should be rigidly fixed in order to avoid nonradiative losses, and highly fluorescent cyanine-type chromophores with only partial molecular bridging can be constructed on this basis [14].

At the same time, slight energy differences between relative “funneling” tendencies within each of the two twisting types are evidently governed by some second-order factors (e.g., Coulomb interelectronic interactions which were shown to play the crucial role for the energy alternation pattern of symmetric polymethines [15]) and are not accounted for by the topological arguments. Thus, a refined comparison of funneling probabilities should be based on a calculation on the all-valence level.

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