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Small S_0–S_1 energy gaps for certain twisted conformations of unsymmetric polymethine dyes: quantum chemical treatment and spectroscopic manifestations

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The AM1–CI (Austin model 1 configuration interaction) method has been used to calculate energy gaps between the ground state (S_0) and the lowest biradicaloid (BR) excited state as a measure for roughly estimating the probability of reaching an S_0–BR conical intersection by bond twisting of one of the bonds along the polymethine chain of unsymmetric cyanine dyes. Invoking qualitative concepts for interpreting the computational data, a pronounced alternation of successive bonds is shown and explained. The magnitude of the S_0–BR energy gap was found to be governed by the position of the corresponding bond with respect to the polymethine chain ends and by the degree of electronic asymmetry of the chain, *i.e.* by the difference in electron donor abilities of its end groups. These results are compared to experimental photophysical data for a series of differently bridged asymmetric cyanine dyes and suggest that the magnitude of the energy gap for a given twisted bond can be modulated by bridge-induced perturbations. Nonreactive low-lying minima caused by the accessibility of several twisted excited-state conformers have to be invoked in order to explain the experimentally observed "inverse-loose-bolt" effect of the nonradiative decay rates and should be taken into account in the treatment of possible pathways of fluorescence quenching and in the design of high-quantum-yield fluorescent dyes.

I. Introduction

The increasingly extensive application of cyanine dyes in the development of new fluorescent materials and fluorescent probes (see, for instance, the surveys in refs. 1 and 2) calls for a deeper insight into the relationship between dye structure and the basic characteristics of the light emitted, and particularly into the variety of fluorescence quenching pathways. Clearly, there are a large number of possibilities for radiationless degradation of the excited-state energy in a cyanine molecule with a reasonably long polymethine chromophore. An efficient experimental and theoretical tool for detecting the most probable fluorescence quenching situations has been developed over the last decade within the framework of the twisted-intramolecular-charge-transfer (or charge-shift) model[3–6] and the more general theory of biradicaloid (BR) states.[7–9]

Starting from this combined approach, all photochemical processes competing with fluorescence in conjugated polyene- or polymethine-type molecules and leading efficiently back to the ground state (S_0) proceed *via* the approach of the excited species towards a hypersurface region with a narrow to vanishing S_0–S_1 energy gap occurring preferentially near a 90° twist around one or more bonds.[10–13] This approach is followed by the efficient radiationless decay through a so-called "conical intersection" or photochemical funnel[7,9] to the close-lying maximum of the corresponding ground-state 90° rotational barrier. In the ground state, either photoisomerization or the return to the original starting material can result. The presence of conical intersections has been substantiated by high-level calculations in protonated Schiff base compounds resembling closely the unsymmetric polymethine dyes studied here.[12,14,15] In this case, reduced S_1–S_0 energy gaps indicate the vicinity of a conical intersection, even if it is not completely reached for a given geometry. In addition to near 90° twisted conformations, conical intersections involve bond-length changes within the main chain and, in some cases, out-of-plane motions of hydrogen atoms or even larger groups.[16,17] Further, the actual accessibility of the conical intersections depends on the details of the potential energy surface, such as S_1 energy barriers between the initial valley and the intersection region.[10] That is why a rigorous treatment implies the complete optimization of the molecule in the excited state.

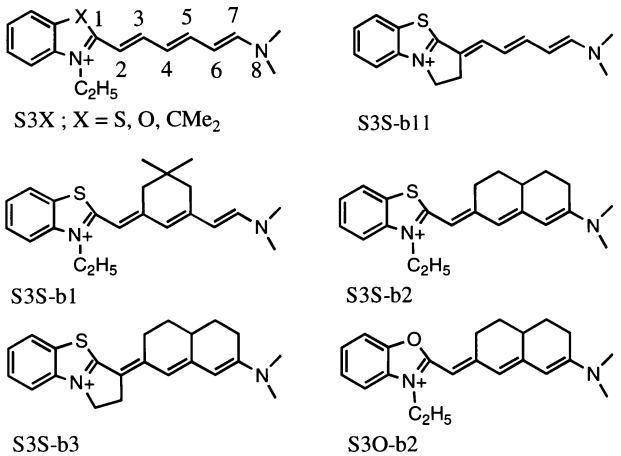
In order to be able to make predictions and interpretations for large molecules, a less demanding method is necessary. We chose to inspect the S_0–S_1 energy gap for the optimized ground-state geometry, *i.e.* the gaps present for the Franck–Condon situation for the various possible twisted conformers, as this should give us at least a rough idea of the probabilities of S_0–S_1 conical intersections. Indeed, a sufficiently small S_0–S_1 energy gap at the optimized S_0 geometry represents a strong indication for its reduction to zero on geometry relaxation in the S_1 state. Moreover, it is the S_0–S_1 gap magnitudes that play a crucial role in the occurrence of conical intersections within a series of analogous compounds provided they have much the same activation barriers to S_1 minima, and it is just the case with the molecules studied in the present work as is shown later (see Section III.3). With the reasoning and reservations outlined above, we can judge the probability for the occurrence of a conical intersection based on the Franck–

Condon geometry and can also assume that the proximity of this geometry to a possible conical intersection is inversely related to the magnitude of the corresponding S_0–S_1 gap.

Evidently, the primarily important challenge in molecular design of highly fluorescent compounds is to reveal which bond twists are associated with most probable conical intersections (smallest S_0–S_1 gaps) and to rule out these ultrafast gateways from the excited to the ground state, *e.g.*, by the corresponding rigidization (bridging) of the conjugated molecule. This methodology as applied to the development of cyanine-based fluorescent probes has given rise to the present and previous[18] work: we intend here to relate the polymethine dye structure and photophysics to the probability of conical intersections by calculating S_0–S_1 gaps for all possible twisted bonds using both the Austin model 1 (AM1) method and rationalizing the results in terms of more simple qualitative models. The computational strategy chosen is related to that used in ref. 19 but in the present work it is performed at a much more sophisticated level; the tools for qualitative treatment, namely, the Momicchioli partitioning model[20] and the long-polymethine-chain approximation,[21–23] which were formerly applied to highly unsymmetric cyanines[19] and to merocyanines with mono-π-atomic end groups,[24] respectively, are used here to treat polymethines with the end groups strongly differing in topology but causing only a slight electronic asymmetry.

The molecules of interest from the series of streptopolymethine cations S3X are depicted in Scheme 1. In addition, some of their bridged derivatives are available (S3S-b11, S3S-b1, S3S-b2, S3S-b3, S3O-b2; see Scheme 1) and their photophysical behaviour was recently reported[18] and can be correlated with the quantum chemical results.

The effect of chemical bridging in the S3S derivatives is rather unusual. Normally, chemical bridging of flexible bonds increases the fluorescence efficiency of dyes, in accordance with the so-called "loose-bolt theory",[25,26] due to a reduction of nonradiative rate constants. This is indeed so if the oxygen derivative S3O and its bridged derivative S3O-b2 are compared, where the fluorescence efficiency increases by a factor of 1.5 (ref. 18). But for the same bridging pattern of the sulfur derivative, the fluorescence efficiency decreases by a factor of 2 from S3S to S3S-b2 (ref. 18). We can call this an "inverse-loose-bolt" effect. Very large inverse-loose-bolt effects have been observed in stilbenoid systems such as 4-dimethylamino-4′-cyanostilbene series.[27–29] In this case, a three-state model involving more than one fluorescent conformer has been put forward. The same model, somewhat extended, can be used to explain the inverse-loose-bolt effect in S3S derivatives.[18] Here, we also want to scrutinize possible alternative explanations, namely (i) possible steric effects due to the more bulky sulfur atom and (ii) bridge-induced changes in magnitudes of S_1 potential barriers on the way to funnels.



Scheme 1

The compounds in Scheme 1 represent unsymmetric polymethines, though their electronic asymmetry in the conjugated chromophore—arising from the better donor character of the heterocyclic moiety than of the dimethylamino group—is slight enough. Nevertheless, the degree of asymmetry suffices for a situation when all the 90° twisted (perp) forms are characterized in the ground state by the localization of two electrons of the broken π-bond on one molecular submoiety (so-called "hole-pair" situation) and in the excited BR state[9] on two different submoieties ("dot-dot" situation). In what follows we will not explicitly consider the case of multiple simultaneously twisted bonds and treat the magnitudes of the S_0–BR gaps only for a single twisted bond, in order to keep a clear general picture resulting from the different possible partitionings of the molecule. If allowance is made for multiple bond twists possibly important for some conical intersections,[30] the regularities concerned should not change qualitatively.

II. Calculation method

All quantum chemical calculations were performed using the AM1 method within the AMPAC program package.[31] Full geometry optimization for the ground-state structure of all species under consideration was performed. For twisted geometries, the corresponding dihedral angle was fixed, and the remaining internal coordinates were fully optimized. Energy gaps between ground and excited state were calculated assuming the Franck–Condon nature of electronic transitions, including configuration interaction (CI) which involved 300–400 singly and multiply excited configurations generated from the central eight molecular orbitals.

III. Results and discussion

1. Ground-state structure and energetics for planar and twisted species

As seen from the computational results of the AM1 method (see Tables 1 and 2), the ground-state geometries of S3S, S3O and S3C are characterized by the alternation of atomic charges and C–C bond lengths along the polymethine chain. As the charge alternation is quite pronounced and the bond-length alternation is rather small, the compounds under study are not far from the ideal polymethine situation, in terms of the triad theory.[32,33] Nonetheless, alternating bond lengths

Table 1 The ground-state alternation of charges on carbon atoms in the polymethine chain of S3S, S3O and S3C (AM1 without configuration interaction)

	Atomic charges							
Compound	1	2	3	4	5	6	7	8 (*N*)
S3S	−0.06	−0.30	+0.08	−0.29	+0.09	−0.35	+0.12	−0.22
S3O	+0.28	−0.33	+0.11	−0.30	+0.10	−0.35	+0.13	−0.21
S3C	+0.19	−0.33	+0.10	−0.30	+0.10	−0.35	+0.13	−0.21

Atoms are numbered as in Scheme 1.

Table 2 Ground-state bond lengths for all-*trans* forms of S3S, S3O and S3C and their bridged derivatives

Bond	S3S	S3S-b11	S3S-b1	S3S-b2	S3S-b3	S3O	S3O-b2	S3C
12	1.41	*143* + +	1.40 −	1.40 −	*1.42* +	1.40	1.39 −	1.40
23	1.38	1.37 −	1.40 + +	1.40 + +	1.39 +	1.39	1.41 + +	1.39
34	1.40	1.40	*1.41* +	*1.40*	*1.41* +	1.40	*1.40* +	1.40
45	1.38	1.38	*1.39* +	*1.39* +	*1.39* +	1.39	*1.40* +	1.39
56	1.40	1.41 +	1.41 +	*1.40*	*1.41* +	1.40	*1.40*	1.40
67	1.39	1.39	1.38 −	*1.40* +	*1.40* +	1.39	*1.40* +	1.39
78	1.35	1.35	1.35	1.36 +	1.36 +	1.35	1.36 +	1.35

Values in *italics* correspond to the bonds fixed by bridging. Plus or minus signs near bond-length values for bridged compounds respectively point to the lengthening or the shortening of corresponding bonds.

are of importance in the context of possible conical intersections between the ground and the lowest BR state (more space is given to this subject in the next section). As expected from comparison of Brooker's basicities[34] or topological electron donor abilities[21–23] for two end groups of the polymethines under study, the alternation weakens in the series S3S, S3O, S3C, with decreasing electronic asymmetry of their molecules.

As far as bridged S3S and S3O derivatives are concerned, it is notable that the bridging exerts a marked effect only on the bond 23, which is lengthened in the molecules S3S-b1, S3S-b2 and S3O-b2 (see Table 2). All bridged structures deviate only slightly from ideal planarity. This rules out one possible source of the observed "inverse-loose-bolt effect", namely a strong non-valence interaction between the bulky sulfur atom and the closest hydrogens of the cyclic bridge in the case of the benzothiazolium systems which could cause pretwisted ground-state conformers and hence the possibility of a faster approach to the conical intersection for the bridged systems.

Though weak enough, the bond-length alternation induces the heats of formation of the 90° twisted (perp) forms of the molecules to display the corresponding alternating pattern for rotational barrier heights in S_0 as successive bonds in the polymethine chain are twisted (see Fig. 1). Especially S3S shows a rather strong alternation in the ground-state energies of the twisted forms whereas the alternation for S3O and S3C is smaller. In accordance with the effect produced on the bond lengths, bridging of bonds somewhat influences the calculated rotational barriers in the sense that, as a rule, increased bond lengths lead to reduced barriers (*cf.* the data in Tables 2 and 3). The comparison of the heats of formation for the all-*trans* and various mono-*cis* forms leads to the prediction that the compounds under study are likely to represent, in the ground state, a mixture of isomers; especially, the *cis*(2–3) and *cis*(5–6) forms for bridged S3S and S3O derivatives, and the *cis*(1–2) form for S3C appear to be energetically advantageous and can hence be expected to be populated preferentially (see Table 3). It is clear that bridging giving rise to an additional steric hindrance results in an increased thermodynamic preference for the *cis*(2–3) isomer.

2. Occurrence of S_0–BR conical intersections and "funneling" function of bond twists: qualitative models in the interpretation of computational results

(a) Alternation of S_0–BR energy gaps ΔE As seen from Fig. 1, the perp forms of S3S, S3O and S3C exhibit a clear-cut regular alternation not only for the ground-state barriers but also for the energy of the lowest BR state as the bond rotated successively changes its position in the polymethine chain. Thus, an alternating pattern results for the magnitude of the S_0–BR energy gap ΔE (see also Table 4), which is assumed to be inversely followed by the funneling activity of the corresponding bond. As an example, the tendency for access to a conical intersection through bond twisting in the S3S molecule increases in the following series of twisted bonds (for atom numbering, see Scheme 1): 56 (3.16) < 78 (2.79) < 34 (2.55) < 12 (2.47) < 45 (1.74) < 67 (1.65) < 23 (1.47), in accordance with the decreasing S_0–BR energy gaps ΔE (in parentheses, eV). It should be pointed out that the alternation in the BR energy (and hence in the magnitude of the S_0–BR gap) weakens significantly when passing from S3S to S3O and S3C. It is also noteworthy that the energies of locally excited states do not alternate (see Fig. 1).

It can easily be noticed that twistings around formally single bonds (we call them A-type bonds) result in lower ground-state and higher excited-BR-state energies for the corresponding perp forms, whereas formally double bonds (B-

Table 3 Relative energies (kcal mol^{-1}) of planar and twisted ground-state species of the compounds investigated

Structure	S3S	S3S-b11	S3S-b1	S3S-b2	S3S-b3	S3O	S3O-b2	S3C
all-*trans*	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
tw1–2	5.8	—[a]	7.0	7.2	—	10.4	11.6	8.9
iso1–2	1.3	—	5.4	5.2	—	2.1	5.7	− 0.7
tw2–3	15.1	17.3	11.7	10.5	12.8	13.9	9.1	12.3
iso2–3	0.4	−0.8	−0.2	−0.3	−0.8	1.5	0.0	5.9
tw3–4	10.8	9.7	—	—	—	12.8	—	12.4
iso3–4	1.4	2.8	—	—	—	1.6	—	1.3
tw4–5	15.7	17.6	—	—	—	14.6	—	14.5
iso4–5	1.3	1.2	—	—	—	1.2	—	1.4
tw5–6	10.7	9.7	7.7	—	—	12.2	—	12.0
iso5–6	0.9	1.1	− 0.7	—	—	0.9	—	0.8
tw6–7	14.6	16.1	15.5	—	—	13.8	—	13.6
iso6–7	2.9	2.9	7.5	—	—	2.9	—	1.0
tw7–8	11.4	10.6	10.0	9.5	8.8	12.8	10.7	12.6

[a] Dashes indicate no value due to bridging of the bond.
The label iso n–(n + 1) indicates a planar isomer with the corresponding bond twisted by 180° (to the *cis* side), and the label tw n–(n + 1) indicates the perp structure twisted by 90° around the same bond. The numbers give the barriers [for tw n–(n + 1)] and isomerization energies [for iso n–(n + 1)] (from AM1 ground-state optimization without configuration interaction). The numbering n is defined in Scheme 1.

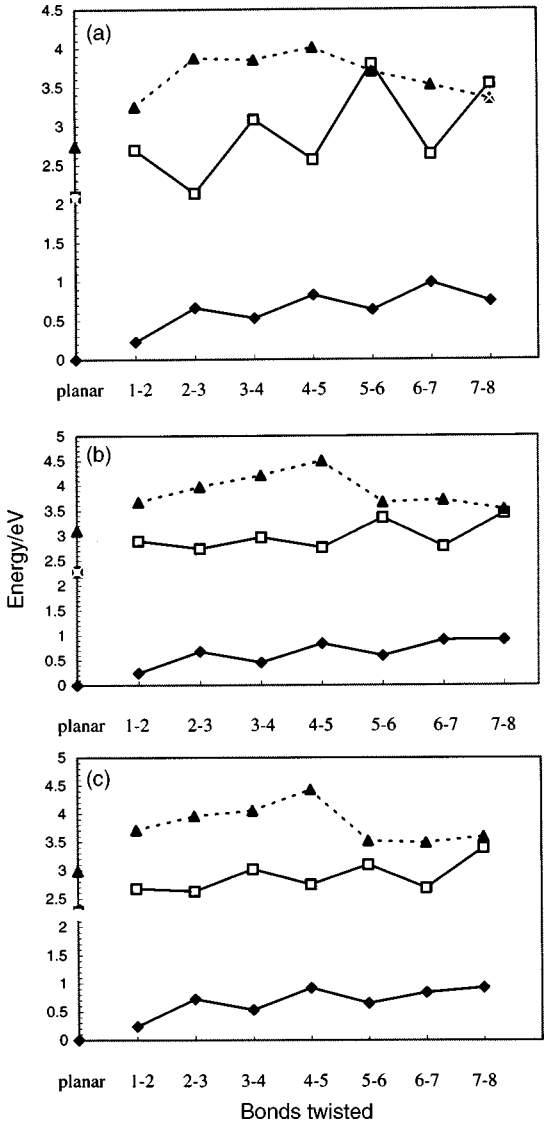


Fig. 1 AM1-calculated energies of the ground, BR excited, and locally excited states for the planar and all possible perp forms of (a) S3S, (b) S3O, and (c) S3C. Filled rhombic markers designate ground-state energies for structures with the optimized geometries and one (twisted) bond frozen in each case; open square markers represent the energies of the BR excited state calculated with the assumption of a Franck–Condon $S_0 \rightarrow$ BR transition (*i.e.*, for the equilibrated ground-state geometry); and filled triangle markers indicate the lowest locally excited state.

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 (BR) states. In this context, B-type bonds are evidently more liable to photoisomerization as well as to

Table 4 Magnitudes of the S_0–BR energy gaps (eV) for perp forms of S3S, S3O and S3C

Twisted bond	S3S	S3O	S3C
Planar	2.10	2.28	2.28[a]
12	2.47	2.65	2.44
23	1.47	2.06	1.91
34	2.55	2.51	2.49
45	1.74	1.92	1.83
56	3.16	2.76	2.45
67	1.65	1.87	1.85
78	2.79	2.53	2.47

[a] S_0–$S_1(\pi\pi^*)$ transition energies in the planar conformation.

"funneling" the excitation energy to the ground state through a conical intersection. In this connection, it should be stressed that it is not so much the bond order of the various bonds in the planar species (not to mention the formal single/double bond assignment, which is based only on the most stable valence structure as shown in Scheme 1) that primarily determines the magnitude of the S_0–BR energy gap. The bond order as a main criterion of the bond funneling efficiency appears especially unlikely, as far as S3X compounds are concerned, taking into account the negligible bond-length alternation.

(b) Energy estimates based on the partitioning model of bond twists. Here we show that the primary reason for the regularity revealed is comprehensible even in terms of molecular topology, *i.e.* it is sufficient to manipulate bond parities with respect to end groups and their qualitative characteristics accounting for their difference in electron withdrawing or donating power (*e.g.*, Brooker basicities[34] or electron donor abilities[21–23] as widely used in cyanine chemistry).

First, we invoke a previously reported[20] simple qualitative model of twisting in polymethine molecules including an odd number of π-centres which takes into account some substantial features of the theory of biradicaloid states.[3–6,9] For a closed-shell amino-terminated polymethine cation consisting of $2k + 1$ π-atoms and, accordingly, $2k + 2$ π-electrons, a 90° twist is regarded as a π-decoupling, both fragments possessing an even number of electrons ("hole-pair" situation[9]). To satisfy this closed-shell condition posed on each of the two fragments in the ground state of the perp form, the number of electrons should be the same as the number of atoms for the polyene fragment and should exceed the number of atoms by 1 for the polymethine fragment. Thus, the former should carry the positive charge, and the latter should be neutral. On excitation, the polymethine fragment donates and the polyene fragment gains one electron so that the open-shell ("dot-dot"[9]) situation with odd numbers of electrons results for both of them.

In the light of this concept, the partitioning of an odd polymethine molecule in all the possible ways followed by the consideration of the resulting ground- and excited-state charge redistribution permits the relative energies of the resulting perp structures to be qualitatively estimated (as was done, for instance, in refs. 19 and 24). As an energy discriminator, it is natural to use the asymmetry of molecular end groups in terms of their electron donor ability, *i.e.*, in their ability to be charged positively. For a symmetric polymethine cation treated in the framework of the same twisting model, some second-order effects like electron–electron interactions become important and dictate the relative advantage of certain bond twists in the ground and excited state.[35]

Table 5 presents all possible fragmentation modes for the polymethine compounds under consideration, with the fragment lengths and charges indicated. In each case, charge redistribution specified upon twisting is easily correlated with a certain limiting valence-bond structure.

The electron donor ability of the 2-benzothiazolyl group is known to be higher than that of the dimethylamino group. Therefore, rotations around type-A bonds imply the positive charge to be located on the nitrogen of the heterocycle in the ground state and on the nitrogen of the amino group in the excited state, and rotations around type-B bonds result in the reverse picture. Thus, the positively charged heterocycle appears to provide a more energetically advantageous situation, which results in the following energetic arrangement: A (12, 34, 56, 78) < B (23, 45, 67) in the ground state and B < A in the excited state, as is also found in the AM1-provided calculation data [see Fig. 1(a)].

From the topological point of view, the most important distinction between type-A and type-B bonds consists in their

Table 5 Possible ways of fragmentation and charge redistribution in the S3X molecule (X = S, O, C) in the ground and the lowest BR states

$$> {}^{+}N_{Het}{=}C{-}C{=}C{-}C{=}C{-}C{=}C{-}NMe_2 \leftrightarrow > N_{Het}{-}C{=}C{-}C{=}C{-}C{=}C{-}C{=}NMe_2^{+}$$

	Fragment length (number of electrons; charge)								
	Type-A bonds					Type-B bonds			
	Bond twisted =	12	34	56	78	23	45	67	State
Even fragment length	(with N_{Het})	2 (2; +)	4 (4; +)	6 (6; +)	8 (8; +)	(with NMe_2)	6 (6; +)	4 (4; +)	2 (2; +)	S_0
Odd fragment length	(with NMe_2)	7 (8; 0)	5 (6; 0)	3 (4; 0)	1 (2; 0)	(with N_{Het})	3 (4; 0)	5 (6; 0)	7 (8; 0)	
Even fragment length	(with N_{Het})	2 (3; 0)	4 (5; 0)	6 (7; 0)	8 (9; 0)	(with NMe_2)	6 (7; 0)	4 (5; 0)	2 (3; 0)	S_1 (BR)
Odd fragment length	(with NMe_2)	7 (7; +)	5 (5; +)	3 (3; +)	1 (1; +)	(with N_{Het})	3 (3; +)	5 (5; +)	7 (7; +)	

different disposition with reference to the ends of the donor–acceptor terminated polymethine chromophore (quasilinear conjugated chain). Focusing, for example, on the donor end (the nitrogen atom of the heterocyclic residue), we can specify type-A and type-B bonds as those separated respectively by an even and an odd number of bonds from the terminal bond involving the donor atom, N_{Het}–C. As regards the position of type-B bonds in the chain of the all-planar conformation, they can be called, following the former nomenclature, bonds *conjugated* with this selected terminal bond. (Likewise, type-A bonds are those *conjugated* with its acceptor counterpart, Me_2N–C.)

Interestingly, the above qualitative model is consistent with the AM1 method, not only in the resulting alternation pattern of the energy gap between the closed-shell S0 and the BR excited state, with the evident energetic preference of type-B bond twists (23, 45 and 67) regarding the access to conical intersections on twisting, but also in a number of significant points which refer to the behaviour of frontier electronic levels and electronic redistribution associated with bond twists. Thus, it is very illustrative to inspect the alternation of energies (although rather small) for the HOMOs (populated by an electron pair) which are localized in turn on the fragments containing the dimethylamino group Me_2N (a relative acceptor) and the heterocyclic residue (a relative donor), as the twist "moves" along the chain (see Table 6). The former situation, *i.e.* HOMO localized on the acceptor part, is realized for type-A bond twists and naturally results in lower ground-state energies, whereas the localization of the HOMO on the donor part associated with type-B bond twists leads to increased ground-state energies. At the same time, LUMOs which accept an electron on excitation are alternately localized on donor-containing (type-A bond twists) and acceptor-containing fragments (type-B bond twists) and have, accordingly, high and low energies (see Table 6). However, energy alternation appears in this case rather as a tendency than as a rule.

Furthermore, the idea of an integer positive charge "migrating" between two end groups in successive bond twists, however simplified it appears in the context of the qualitative model used, can be traced even in a much more realistic AM1-based picture of electronic distributions. Indeed, the lack of an electron on one of the two end groups can be recognized in the somewhat lowered calculated negative charge on the corresponding nitrogen atom (*cf.* charge localizations on fragments, Table 5, and charge on the nitrogen atoms, Table 6).

The above parallels are not unexpected taking into consideration that the S0 and the lowest BR state of twisted S3X molecules are mainly contributed by the electronic configurations involving only the frontier π-MOs. At the same time, this specificity justifies the application of the very simple qualitative π-model to the compounds of interest. It can be argued that the bond length (bond order) for any bond, and hence the corresponding ground-state rotational barrier, is essentially determined by the bond position in the chain, the chain length, and the difference in electron donor abilities of chain end groups. The same independent factors govern the magnitude of the S_0–BR energy gap for the respective bond twist.[3] These arguments provide much space for qualitative predictions on the probabilities of S_0–BR conical intersections and consequently on positions and efficiencies (S_0 barrier heights, gap magnitudes) of possible photochemical funnels, as far as terminally substituted conjugated chains are concerned. Instead of the mentioned primary factors—bond position, chain length and difference in electron donor ability (the latter are sometimes difficult to measure)—related characteristics may be used. As an example, the difference in electron donor abilities of chain ends can be rather adequately represented (for constant chain length) by the bond-length alternation[36] (as was done, *e.g.*, in the study of nonlinear optical properties of polymethine compounds.[37]

Table 6 Charges q on nitrogen atoms of the heteroatomic (N_{Het}) and the dimethylamino (NMe_2) end groups in the ground state together with frontier MO energies for the planar and all-perp forms of S3S, as calculated by AM1; frontier MO localizations on the fragment containing the donor (N_{Het}) or the acceptor (NMe_2) are parenthesized[a]

Structure	$q(N_{Het})$	$q(NMe_2)$	HOMO /eV	LUMO /eV
Planar	−0.1	−0.2	−10.42	−4.7
12	−0.1	−0.3	−10.19 (NMe_2)	−4.53 (N_{Het})
23	−0.2	−0.2	−10.11 (N_{Het})	−5.24 (NMe_2)
34	−0.1	−0.3	−10.15 (NMe_2)	−5.06 (N_{Het})
45	−0.2	−0.1	−9.84 (N_{Het})	−5.11 (NMe_2)
56	−0.1	−0.3	−10.42 (NMe_2)	−4.98 (N_{Het})
67	−0.2	−0.1	−9.87 (N_{Het})	−4.49 (NMe_2)
78	−0.1	−0.4	−10.93 (NMe_2)	−5.2 (N_{Het})

[a] A tendency to alternate (though rather slightly) can be traced for all the quantities listed. The lack of an electron on one of the two end groups, *i.e.* a localized integer positive charge (within the π-approximation), leads to a somewhat lowered negative charge on the corresponding nitrogen atom (*cf.* charge localizations in Table 5). Accordingly, in the cases when the electronic density is higher on the nitrogen of the heterocycle (relative donor) than on the dimethylamino group (relative acceptor), the HOMO energy rises somewhat and LUMO, as a rule, lowers.

(c) Application of the long-polymethine-chain approximation. Starting from the same partitioning model of bond twist, we invoke a topological approach, the long-polymethine-chain approximation,[21–23] in order to account for alternating patterns in the energetics of the ground and excited state for S3S, S3O and S3C. The magnitudes of the S_0–BR gap are modelled in terms of energy differences between spatially separated frontier MOs. The energies of HOMO and LUMO, respectively localized on odd (polymethine) and even (polyene) fragments, Z_{HOMO} and Z_{LUMO}, are 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, as given by:

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

Z_{HOMO} is specified by the same expression, with $(F - 1)$ substituted for F; in the case of an even number n of methine groups, F should be increased by 1/2 (ref. 22). The parameter F characterizes the shift of the energy gap as a whole (the same energetic displacement of the HOMO and LUMO levels) for a polymethine chain under the action of a conjugated end group attached to it, and L accounts for the narrowing of the gap caused by this end group. For the end groups contained in the polymethine compounds concerned, the parameters F and L (as taken from refs. 28 and 29) are listed in Table 7.

By determining 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 magnitude of the S_0–BR energy gap and hence the corresponding funneling efficiency. Thus, the HOMO–LUMO gaps calculated for every possible twist (partitioning of the molecule into two fragments) in S3S, S3O and S3C are alternating series as displayed in Fig. 2. As seen, the alternation patterns are qualitatively consistent with the AM1-based results, type-B bond twists appearing as potential funnels, in contrast to type-A bond twists.

The degree of alternation can also be rationalized in terms of the topological parameter F. To determine the ability of an end group to push or pull π-electrons within the polymethine chromophore, it is reasonable to consider its effect on the position of the energy gap of the chain with respect to the Fermi level. Using the accepted formalism,[22,23] it can be estimated by $\{2F\}$ (curly braces denote taking the fractional part of a number). The intermediate value 0.5 corresponds to frontier MOs symmetrically embracing the Fermi level and hence to the absence of a pronounced acceptor or donor character of the end group; whereas values falling into the ranges from 0 to 0.5 and from 0.5 to 1 are, respectively, associated with low-lying (acceptors) and high-lying (donors) energy gaps and accordingly HOMO and LUMO energies, the acceptor or donor properties increasing with the deviation of $\{2F\}$ from 0.5. From this point of view, the difference between end groups in their value $\{2F\}$ can be a measure of the electronic asymmetry of a polymethine compound. As seen from Table 7, the electronic asymmetry, and hence the bond order and the S_0–BR energy alternation, should decrease in the series S3S, S3O, S3C, which is computationally observed in the AM1-produced results.

Evidently, elucidation of small effects, as for instance the difference in S_0–BR energy gaps for different bonds within each class of bond twists, is beyond the power of the qualitative approach exploited here. In contrast, the energy gap magnitudes resulting from the AM1 calculation (see Fig. 1) suggest a marked preference for the 2–3 bond twist ($\Delta E = 1.47$ eV, see Table 4) with respect to a potential conical intersection as far as compound S3S is concerned. More importantly, this twist leads to an excited BR state only slightly higher in energy than the corresponding $S_1(\pi\pi^*)$ state of the planar structure; the corresponding conical intersection can therefore be expected to be thermally reachable. This greatly adds to the probability of a funneling through 2–3 bond twist. As anticipated from the decreased electronic asymmetry of the molecules S3O and S3C, the calculated energy distinctions between various type-B bond twists for either compound become hardly noticeable. The smallest energy gaps for S3O and S3C are, respectively, associated with the 6–7 (1.87 eV) and 4–5 (1.83 eV) bond twists. Accordingly, in the molecular design of highly fluorescent dyes based on the polymethines studied, it is reasonable to rule out the twisting possibilities (for instance, by bridging) for all type-B bonds, 2–3, 6–7 and 4–5, which presumably provide an easy access to photochemical funneling of the excitation energy.

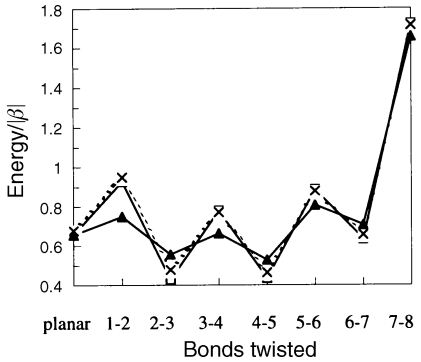


Fig. 2 Variations in the S_0–BR energy gap (calculated as the HOMO–LUMO energy difference) for the planar and all possible perp forms of S3S (empty squares), S3O (crosses), and S3C (filled triangles) within the long-polymethine-chain approximation. (For Coulomb and resonance integrals of heteroatoms and heterobonds, see the caption to Table 7; energies are measured in units of $|\beta_{CC}|$.)

Table 7 Electron donor ability, F, and effective length, L, for 2-benzothiazolyl (BTZ), 2-benzoxazolyl (BOZ), indolenyl (Ind) and dimethylamino end groups

Effective end group parameter	End group			
	BTZ (S3S)	BOZ (S3O)	Ind (S3C)	Me_2N
F	0.84	0.82	0.75	0.19
$\{2F\}$	0.68	0.64	0.50	0.38
L	2.23	1.95	2.25	0.31

(For the nitrogen atom: $\alpha_N = -1.0$ in all heterocycles and $\alpha_N = -1.5$ in the substituted amino group; $\beta_{NC} = -1$ in all cases. For the sulfur atom in S3S: $\alpha_S = -0.7$; $\beta_{CS} = -0.5$. For the oxygen atom in S3O: $\alpha_O = -2$; $\beta_{CN} = -0.7$. Coulomb and resonance intergrals are measured in units of $|\beta_{CC}|$).

3. Excited-state energetics of bridged derivatives

Certain trends in the spectral and photophysical behaviour of the bridged S3X derivatives (S3S-b11, S3S-b1, S3S-b2, S3S-b3 and S3O-b2) can be expected on the basis of their ground-state structures and the rotational barriers (see Tables 2–4). An additional rationale for such an S_0-based treatment is provided by our recent experimental results,[18] which suggest that S_1 potential surfaces are characterized by rather small (comparable to the thermal energy k_BT) barriers on the way to the 90°-perp-twist well, which are in addition similar for all the compounds studied. Thus, based on the ground-state bond length and rotational barriers, one can infer that for none of the S3S derivatives does the bridging pattern rule out the 23 bond twist, which is the most probable twist for the possible conical intersection between the excited state and the ground

state of the perp form. As mentioned in Section III.1, the incorporation of a bridge mainly affects just the length of the 2–3 bond, which itself remains unbridged, with the corresponding twist able to furnish, according to computational evidence, an efficient radiationless pathway for electronic deexcitation, especially for sulfur-containing compounds. For three of the four bridged S3S derivatives (S3S-b1, S3S-b2 and S3S-b3), this bond is notably lengthened, and for the fourth derivative (S3S-b11) it is somewhat shortened as compared to the parent molecule S3S (see Table 2). Correspondingly, the ground-state rotational barriers for the 23 bond in the first three molecules are found to be lower than those for S3S, in contrast to the last case (see Table 3).

As expected, the calculated S_0–BR gap magnitudes are inversely related to the ground-state rotational barriers and for the series of S3S-b1, S3S-b2, S3S-b3 and S3S-b11 respectively amount to 3.12, 2.80, 2.85 and 1.38 eV. These values would suggest, in comparison with that for S3S (1.47 eV), lowered funneling probabilities and hence *increased* quantum yields and *longer* fluorescence lifetimes for the first three compounds and the reverse effect for the last compound. However, the experimentally observed fluorescence for all four members of the series was characterized by *lower* quantum yields and *shorter* decays than for the corresponding unbridged molecule.[18] It can therefore be assumed that the bridge-induced perturbation of the S3S molecular geometry which leads to a somewhat increased S_0–BR energy gap (due to the lengthened 23 bond) cannot be the cause of the observed inverse-loose-bolt effect. This indirectly supports the alternative explanation using the model of multiple emitting states.[18] In the unbridged molecule, some of the relaxation paths lead to fluorescent states; if this relaxation is connected with bond twisting (fluorescent BR states, as for example evidenced in the stilbene series[27–29] or in some stilbazolium and pyridinium dyes,[2,38,39] molecular bridging leading to a rigidized structure can suppress the fluorescent states with twisted conformation, increasing the remaining possibility to reach the funnel connected with the bond 2–3 twisting.

The situation can also be viewed from another angle. Given rather small activation barriers similar for all the bridged derivatives, the kinetic differences found can be accounted for by different pre-exponential factors, which are larger for the bridged than for the unbridged species. Enhanced rate constants with unchanged Arrhenius slopes would be expected for a model where a random walk on an energy-flat surface is necessary to reach a conical intersection. Such a model has been treated theoretically in a stochastic kinetic approach ("staircase model" of Bagchi[40,41]) and applied to systems showing dual fluorescence.[42] There, it was shown that a reduced diffusion length leads to enhanced rates on potential surfaces with no barrier. In our case, the bridged derivatives are expected to possess a reduced dimensionality, which will restrict the energy-flat space available for diffusional motion. This leads to a higher probability of reaching the conical intersection even if small (but similar) barriers are present.

IV. Conclusions

Different twisting coordinates associated with various possible isomerization channels in the molecules studied correspond to the approach to conical intersections of different efficiency, with a well-defined alternation in the polymethine chain being of significance. As shown, qualitative expectations on the S_0–BR gaps can with good reason be based even on the ground-state geometry provided by semiempirical AM1 calculations or alternatively on some simple topological considerations, since the substantial energetic features resulting from both approaches are clearly comparable.

Thus, it is seen that the S_0–BR gaps, which are small enough to represent geometries close to a conical intersection, result especially from twists of the bonds conjugated with the donor end of the donor–acceptor substituted polymethine chain (type-B bonds). These bonds appear as formal double bonds in the valence-bond structure shown in Scheme 1 and are distinguished by a slightly shorter bond length as compared to their counterparts conjugated to the acceptor chain end (type-A bonds). The latter are harmless with respect to intramolecular fluorescence quenching and hence can remain flexible enabling a designer of fluorescent dyes to avoid the tedious task of bridging them all chemically.

The second factor that governs, together with the bond position, the probability of reaching a conical intersection for a given bond twist is the electronic asymmetry of the conjugated chain, *i.e.* the difference in electron donor ability of the two chain end groups. It is responsible for bond orders and the height of the ground-state rotational barrier as well as the size of the S_0–BR energy gap. In the molecules S3X, the probability of conical intersections decreases regularly with molecular electronic asymmetry from S3S to S3O and S3C.

The calculated energetics and experimental photophysical data for S3S and its bridged derivatives, if compared, suggest that the S_0–BR energy gap is not the only factor responsible for the experimentally observed fluorescence quenching in a given molecule. Thus, in spite of calculated increased S_0–BR energy gaps in bridged derivatives of S3S, an "inverse-loose-bolt" effect is experimentally observed for these compounds. Since, contrary to possible expectations, a ground-state twisting of the 2–3 bond due to a non-valence interaction of the bulky sulfur atom with the hydrogen atoms of the bridge can be ruled out, as also can be the different bridge effect on S1 potential barriers, the only plausible explanation for the increased fluorescence quenching of the bridged S3S compounds is provided by the three-state model, which involves further twisting coordinates not leading to a conical intersection. The possibility for population of such twisted and fluorescent species in the unbridged molecule S3S can therefore enhance the fluorescence efficiency by reducing the probability of reaching the nonradiative funnel. In other words, the bridge-induced reduction of the S1 potential surface dimensionality restricts the energy-flat space available for a random walk of an excited-state species and thus causes a higher probability for its reaching a conical intersection.

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