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Bond-length alternation in symmetrical cyanine dyes

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Abstract

As a probe of transient perturbation of symmetrical cyanine chromophores from their C_{2v} molecular symmetry by displacements along the bond-length alternation coordinate, we have selected hyper-Rayleigh scattering (HRS) spectroscopy. Three of the four members investigated of a homologous series of dithiacarbocyanine dyes exhibit HRS signals in methanol, indicative of hyperpolarizabilities comparable to those of the reference compounds, *m*- and *p*-nitroaniline. The signals disappear in toluene; we infer that the observed hyperpolarizabilities are a property of the solute–solvation shell system. The results suggest significant, albeit transient, bond-length alternation in the ground state.

Semi-empirical molecular orbital calculations (at the AM1 level) are used to model ground state *cis–trans* isomerization in a representative dye. From the calculated energetics and geometries we infer that isomerization locks in the bond-length alternation, enabling isomerization about a low-order bond. According to the generally accepted relaxation scheme for S_1 cyanines, bond-length alternation must likewise be pre-requisite to S_1–S_0 internal conversion. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyanine dyes; Hyper-Rayleigh scattering; Relaxation; Bond-alternation

1. Introduction

1.1. Background

Since its introduction by Goddard and co-workers [1], the bond-length alternation coordinate concept has become a standard component in the quantum chemical description of push–pull linear polyenes, including quadrupolar [2] and octupolar [3,4] systems. It has been invoked by Haran et al. [5] and by Tajkkorshid et al. [6] to rationalize the isomerization of rhodopsin, the first step in the photochemical reaction chain leading to visual signal transduction. Most recently, quantum chemical calculations at the CASSCF level have been invoked [7] to infer barrierless stretching of the polymethine chain as prerequisite to torsional relaxation in photoexcited streptocyanine cations, a monopolar system.

The question of involvement of a bond-length alternation coordinate is critical to the mechanism of relaxation of photoexcited cyanine dyes [7]. Internal conversion, which is usually undesirable from the point of view of the technological applications of these dyes, is generally thought [8–15] to involve torsional relaxation of at least one bond in the polymethine chain, along the pathway leading to the *trans* → *cis* isomerization of the cyanine chromophore, according to the Momicchioli scheme [8–10] for relaxation in cyanine chromophores, shown in Fig. 1. Like the analysis of Robb, Olivucci and co-workers [7], this scheme is based on calculations at the ab initio level on a streptocyanine chromophore.

Our interest is in ascertaining the involvement of relaxation along the bond-length-alternation coordinate in the thermal and photoisomerization of symmetrical cyanine dyes, e.g. *N,N′*-diethyl-2,2′-thiacyanine iodide (DTI), *N,N′*-diethyl-2,2′-dithiacarbocyanine iodide (DTCI), *N,N′*-diethyl-2,2′-dithiadicarbocyanine iodide (DTDCI) and *N,N′*-diethyl-2,2′-dithiaditricarbocyanine iodide (DTTCI). See Fig. 2a.

The DTCI for example can be represented, as in Fig. 2b, as a resonance hybrid, usually thought to posses C_{2v} symmetry, of several contributing structures, of which the mirror-image bond localized structures, I and II, and the quadrupolar structure, III, seem to be most important. The best quantum chemical analyses [8–10,16,17] suggest that the quadrupolar structure is more important in the S_1 state than in S_0. Accordingly bond-length-alternation, i.e. pairing, occurs to vary the relative contribution of I or II in the resonance hybrid. Thus, DTCI in solution or in the gas phase could be envisioned as a fluxional molecule, oscillating between

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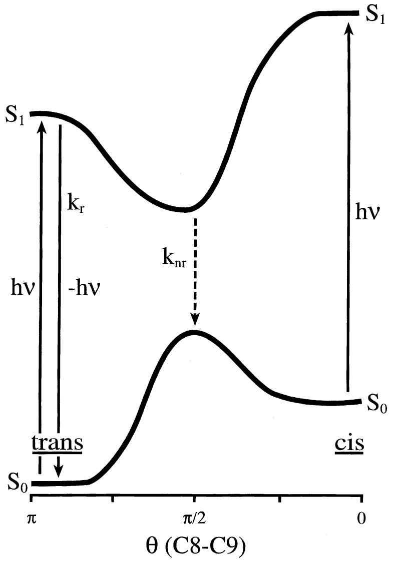

Fig. 1. Energy profiles for isomerization of a generic cyanine chromophore in the S_0 and S_1 states, after [8–12].

"I-like" and "II-like" geometries. Such oscillation would couple the carbon–carbon symmetric and asymmetric stretch modes of the polymethine chain [2] which normally occur at ca. 1500 cm^{-1}; so this oscillation might be expected to occur on the vibronic time scale, i.e. femtoseconds [7].

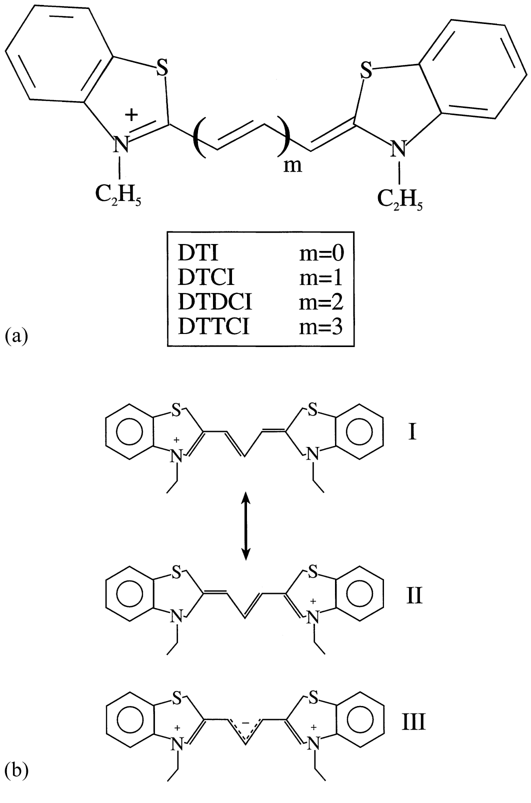

Fig. 2. (a) Dyes used in this study. (b) Monopolar (I and II) and quadrupolar (III) contributing structures to the resonance hybrids corresponding to S_0 and S_1 DTCI.

1.2. Computational studies

In previous work [18],[1] we had found in semi-empirical calculations at the AM1 level that the HOMO of DTCI was doubly degenerate, with orbitals localized primarily on one or the other of the heterocyclic ring systems, as shown in Fig. 3a. The degeneracy could be broken by Jahn–Teller splitting, involving significant bond alternation, with bond-length extrema of 1.33 and 1.50 Å, comparable to those found in the relaxed S_1 states of streptocyanine chromophores [7]. This result suggests that dyes such as DTCI oscillate between bond-alternate structures, as proposed above. Crystal structure determinations [19–21] suggest, however, that this molecule exists in (or close to) a C_{2v} geometry in the solid state.

In order to ensure that these results were not an artifact of the AM1 method, calculations were repeated in the same manner on the five-carbon streptocyanine studied by other groups at higher levels of theory [7–10]. In this case, convergence was obtained for a fully delocalized structure, with a resonance stabilization energy of ca. 15 kcal/mol [22]. The electron density surface for the HOMO of the streptocyanine is shown in Fig. 3b. Thus, we infer that even high level calculations on streptocyanines are not necessarily an infallible guide to the relaxation pathways operating in more complex dyes in this series.

1.3. Experimental strategy

As an experimental probe, we selected hyper-Rayleigh scattering (HRS). The HRS is an incoherent spectroscopy for measurement of second harmonic generation by molecules in condensed phases [4,23]. The HRS signal may arise from an instant anisotropy that breaks the symmetry of the probe molecule and its solvation shell, i.e. symmetry reducing perturbations [24]. It should be ideally suited to probe the possible fluxionality of a nominally C_{2v} molecule between extreme structures of C_1 symmetry. As an incoherent spectroscopy, HRS does not require a coherent excitation source and allows second harmonic signals to be observed with pump powers of the order of 0.05–5 W [25]. Its signal is a measure of the molecular hyperpolarizability, β, which, in turn, has been shown to depend critically on the degree of bond alternation in molecules which have internal charge transfer (ICT) excited states [26].

In HRS, the measured signal, the second harmonic intensity, $I(2\omega)$, may be expressed as

$$I(2\omega) = G(N_\mathrm{s}\beta_\mathrm{s}^2 + N_\mathrm{a}\beta_\mathrm{a}^2) I(\omega)^2 \tag{1}$$

where G is a proportionality constant, reflecting signal collection efficiency, etc. N designates the number density of the solvent (subscript s) or solute (subscript a) [4,23]. The observable product, $G\beta_\mathrm{a}^2$, is often called the quadratic

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[1] Structural parameters from [19–21] were used to provide the starting geometry for the calculations reported in [18].

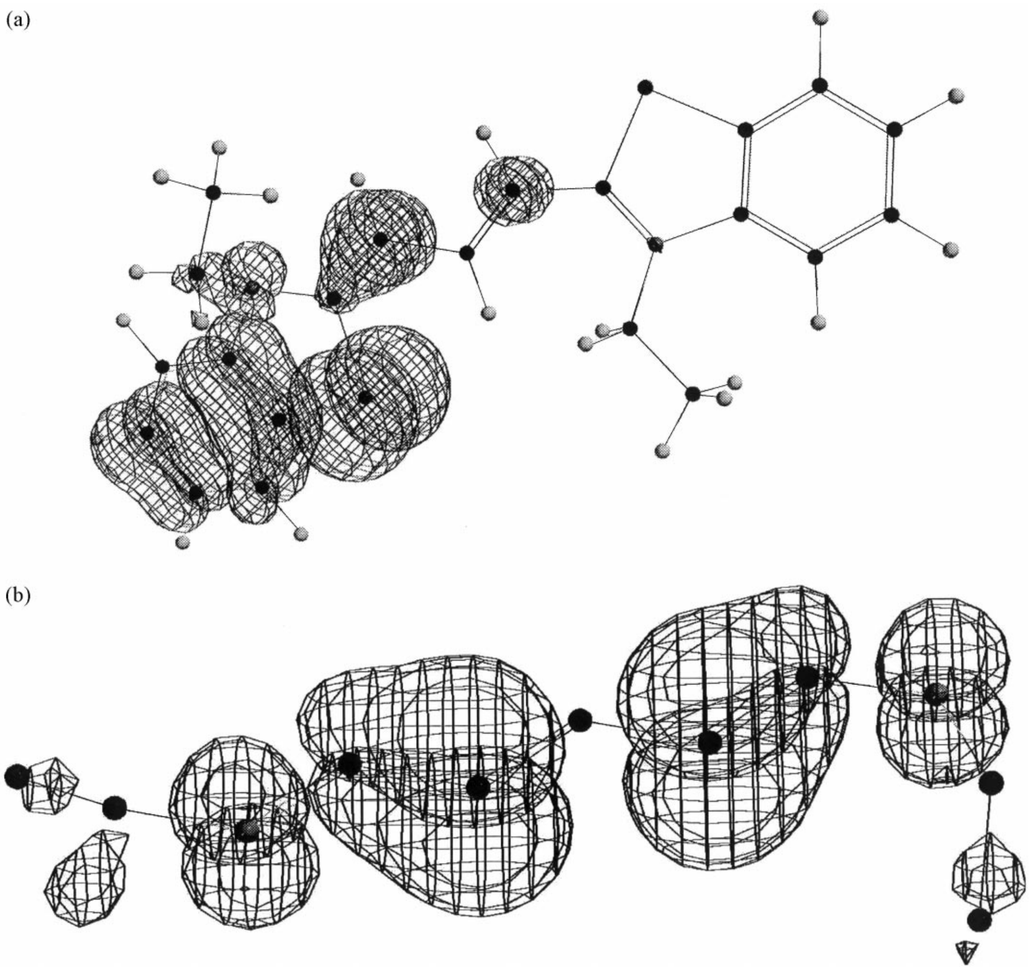

Fig. 3. Electron density surface for: (a) one of the degenerate HOMO's of DTCI from AM1 calculation [18]; (b) the HOMO of the five-carbon streptocyanine cation.

coefficient. In practice the first term of Eq. (1) also includes contributions from adventitious scattered second harmonic radiation.

2. Experimental detail

2.1. Materials

Dyes were products of commerce and used as received: DTI and DTTCI (Aldrich Chemical Co., Milwaukee, WI); DTCI (H. W. Sands Co., Jupiter, FL); and DTDCI (Eastman Kodak Co., Rochester, NY). Control compounds, *p*-nitroaniline (PNA) and *m*-nitroaniline (MNA), were likewise obtained from Aldrich Chemical Co., and were of >99% purity. Spectrograde methanol and toluene (Spectra Products, Gardena, CA) were used for preparation of solutions.

2.2. Methods

The optical path for detection of HRS is shown in Fig. 4. Light from a 150 W Xe arc lamp is passed through a grating monochromator, set to 900 nm with a 2 nm bandpass (except for measurement of the HRS of DTI, where 960 nm was used), and a chopper. The pump beam impinges on a solution sample in a 1 cm quartz cuvette. Scattered radiation is detected at right angles to the pump beam by a Hamamatsu model 933 photomultiplier with lock-in amplification, through a second monochromator tuned to the second harmonic wavelength, 450 nm (480 nm for DTI to avoid re-adsorption of the second harmonic). The signal is ratioed to that of a photomultiplier monitoring the pump beam, in order to minimize the noise arising from time-based fluctuations in lamp output. A polarizing filter was placed in the optical path between sample and detector to minimize the contribution to the signal to second harmonic of the fundamental (a) passed by the first monochromator, and (b) generated off the optical surfaces of the instrumentation.

In practice, HRS was detected as follows. A 2.5 ml portion of the solvent (spectrograde methanol or toluene, Aldrich Chemical Co.) was placed in the sample cuvette. Aliquots (usually 10 μl) of a 1 mM solution of the dye were then added, and the signal recorded after each. A minimum of three replications of each experiment was required to provide

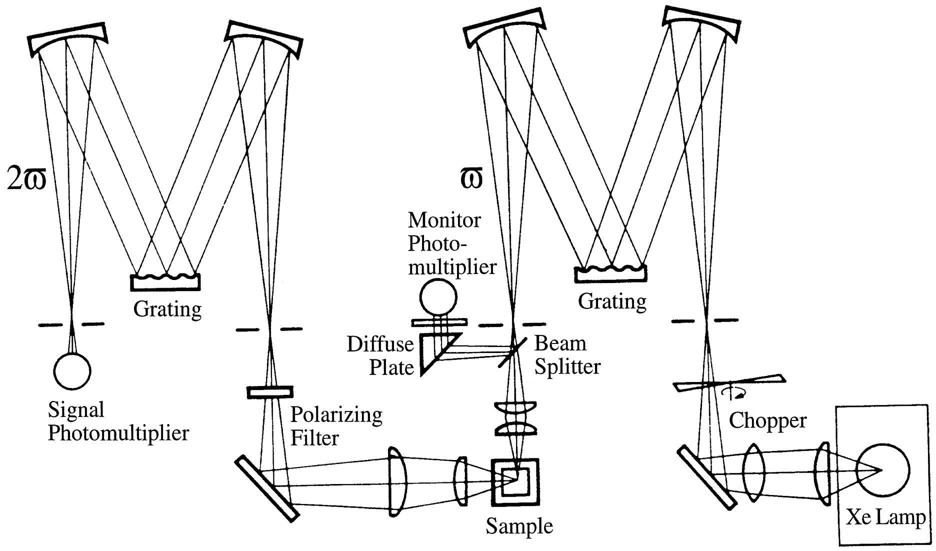

Fig. 4. Optical scheme for detection of HRS.

data suitable for analysis, along with estimates of confidence limits for the values obtained thereby. Thus, in terms of Eq. (1)

$$I_{\mathrm{obs}} = \left(\frac{I(2\omega)}{I(\omega)^2} - GN_{\mathrm{s}}\beta_{\mathrm{s}}^2\right) = GN_{\mathrm{a}}\beta_{\mathrm{a}}^2 \qquad (2)$$

where $G\beta_{\mathrm{a}}^2$ can be determined by least-squares fitting of the experimental data. As a result of this rearrangement, any adventitious second-order signal, e.g. diffracted fundamental which may have passed the polarizing filter, is included with second harmonic generated from the solvent. At the beginning of each run, the signal detector was set to zero to eliminate any contributions to I_{obs} from these sources.

Two criteria were met to confirm that the observed signals were, indeed, HRS: (1) the amplitude of the observed signal was directly proportional to the concentration of added solute as predicted by Eq. (2), i.e. the quadratic coefficient was independent of solute concentration; and (2) the output radiation was monochromatic, distributed over a bandpass comparable to the pump beam slit width. Conformance with Eq. (2) confirmed that our strategy for excluding adventitious second harmonic signals was, in fact, successful.

Values of β are estimated relative to that of PNA in methanol as standard, taken as 30×10^{-30} esu [27]. Measurement of the quadratic coefficient for a substance for which β is known effectively determines the collection efficiency factor, G, in Eq. (2), and allows it to be solved directly for β in the cases of interest.

3. Results and discussion

3.1. HRS experiments

The values of $G\beta_{\mathrm{a}}$ obtained for six compounds, the four dyes and the two standards, probed in methanol, were derived from analysis of the HRS signal data according to Eq. (2), as shown in Fig. 5, and are given in Table 1, along with estimates of β. The estimate of β obtained thereby for MNA is somewhat larger than the best literature value, 10×10^{-30} esu [27]. The HRS response of DTTCI was not detectable under our conditions.

The commonly used two-level expression [27,28] for β is

$$\langle\beta\rangle = 3r^2\Delta\mu\left\{\frac{E_{\mathrm{op}}^2}{|2[E_{\mathrm{op}}^2-(h\omega)^2][E_{\mathrm{op}}^2-4(h\omega)^2]|}\right\} \qquad (3)$$

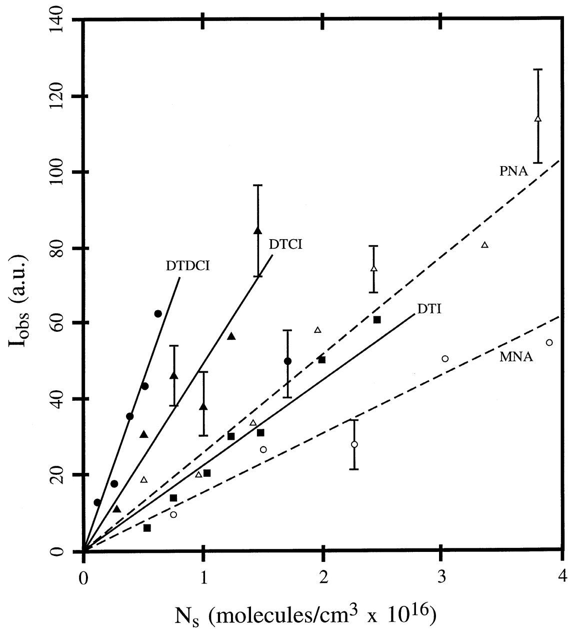

Fig. 5. Dependence of HRS signal on concentration of PNA, MNA, DCI, DTCI, and DTDCI in methanol. Closed symbols and solid lines: cyanine dyes; open symbols and dashed lines: reference compounds. Error bars are representative.

Table 1
Hyper-Rayleigh Scattering (HRS) response at 450 nm of selected cyanine dyes and reference compounds[a]

Compound	Solvent	$G\beta_a^2$	β ($\times 10^{30}$ esu)
Reference compounds			
PNA	Methanol	$(1.7 \pm 0.35) \times 10^6$	30[b]
PNA	Toluene	$(0.8 \pm 0.2) \times 10^6$	(20 ± 5)
MNA	Methanol	$(0.95 \pm 0.18) \times 10^6$	(22 ± 4); 10[b]
Cyanine dyes			
DTI[c]	Methanol	$(1.3 \pm 0.3) \times 10^6$	(26 ± 6)
DTCI	Methanol	$(3.1 \pm 0.4) \times 10^6$	(40 ± 5)
DTCI	Toluene	$(-1.0 \pm 0.3) \times 10^6$	
DTDCI	Methanol	$(5.6 \pm 0.8) \times 10^6$	(54 ± 8)
DTTCI	Methanol	$(-0.4 \pm 0.3) \times 10^6$	≤ 5

[a] All values determined in this work except as noted.
[b] Values from [27].
[c] Detected at 480 nm.

where r is the transition dipole, evaluated from the absorption spectrum in the usual manner, $\Delta\mu$ the change in dipole moment between ground (S_0) and first excited (S_1) states, E_{op} is the energy of the principal optical transition, and $\hbar\omega$ is the photon energy of the probe radiation. Strictly speaking, Eq. (3) is applicable only insofar as the hyperpolarizability is associated with a charge-transfer electronic transition [28], hence, its quantitative applicability to the dyes of interest is problematical. However, Eq. (3) shows that significant values of $\Delta\mu$, along with large values of r, are prerequisite to levels of β such as those reported in Table 1.

The origin of a significant value of $\Delta\mu$ is not immediately obvious, as the cyanine dye cation is a monopole when not paired with its counterion. Solvent separation of dye cation and iodide counterion is likely in a polar solvent such as methanol. We propose that the dipole, which couples with the optical field of the pump radiation and is reflected in $\Delta\mu$, arises by interaction of the transient asymmetric charge distribution in the dye cation, associated with bond alternation, with its surrounding solvation shell, i.e. it is a property of the dye-solvent system. This point of view derives from that of Fromherz [29], who describes solvatochromism of cationic dyes in terms of a monopole–dipolar sphere model. To test this idea, we repeated the experiments on PNA and DTCI and DTDCI in the less polar solvent, toluene. Under these conditions, we would not expect to see a significant HRS response from either dye. Data from the experiments on PNA and DTCI are shown in Fig. 6 and also given in Table 1. No signal was observed from DTDCI under these conditions.

There is some effect of solvent in the non-linear optical response of PNA. However, in the case of DTCI in toluene, the non-linear response disappears. The small negative value of the quadratic coefficient observed in this case reflects, we believe, absorption by dye of solvent scattered radiation in the second harmonic bandpass. In summary, our results appear to confirm both the transient structural perturbation of the DTI, DTCI and DTDCI chromophores from C_{2v} symmetry, along the bond alternation coordinate.

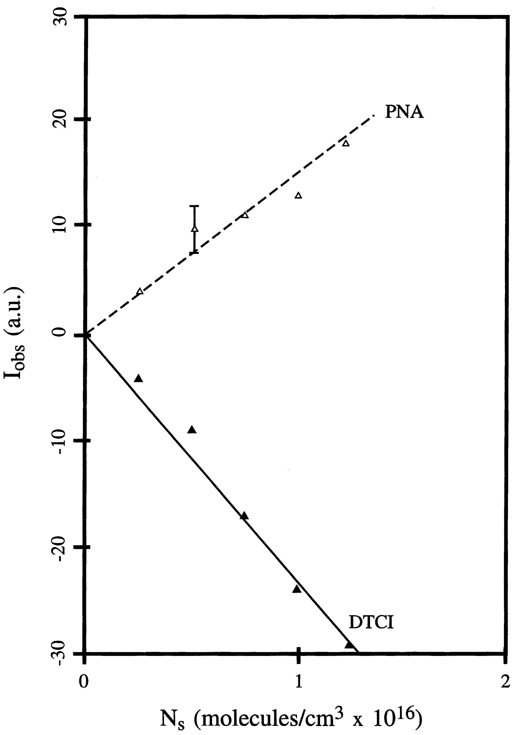

Fig. 6. As Fig. 5 for PNA and DTCI in toluene.

3.2. Computational studies

In order to support involvement of bond alternation in the relaxation of photoexcited cyanine dyes of technological interest, we computationally profiled the energetics of the *trans–cis* isomerization in the ground state of DTCI. This analysis is relevant to the mechanism of excited state relaxation insofar as the Franck–Condon principle requires that geometries of S_0 and S_1 species be identical at the instant of photoexcitation, and again at the funnel of Fig. 1, where internal conversion occurs. Semi-empirical quantum chemical calculations were carried out at the AM1 level, and coupled with MMFF structure optimization in the SPARTAN 4.0 environment [30].

Heats of formation, ΔH_f, were calculated at 15° increments of rotation about the central bond of the polymethine chain in the bond alternate structure of DTCI. The length of this bond in the minimum energy ground state structure for *trans*-DTCI is 1.51 Å. Results are shown in Fig. 7. The geometry of the structure at the midpoint of isomerization, i.e. a torsional angle of 90°, is shown in Fig. 8. The enthalpy of activation for the ground state isomerization process was found to correspond to a barrier height of 13 kcal/mol relative to the *cis*-isomer, in good agreement with experimental values [31,32], which show significant solvent dependence. It occurs at a torsional angle of ca. 95°. The reported solvent dependence is consistent with varying degrees of bond alternation, coupled to varying degrees of solvent stabilized charge localization in one or the other of the dye's heteroaromatic rings.

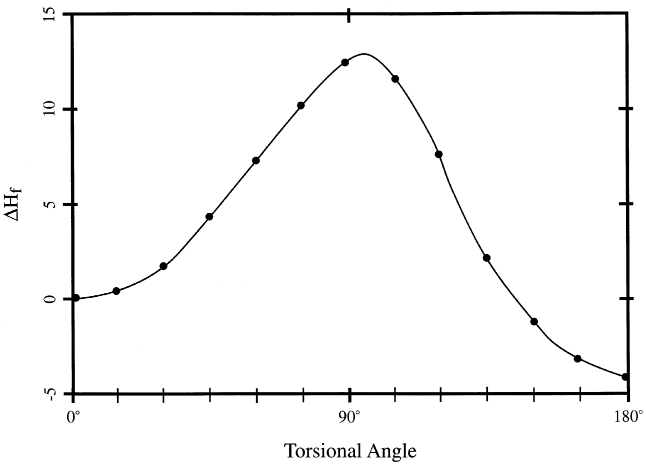

Fig. 7. Energy profile for geometrical isomerization in the polymethine chain in the ground state DTCI from AM1 calculation.

For comparison, similar calculations for isomerization about the adjacent, higher-order bond, of bond length 1.33 Å, in the bond alternate structure of DTCI were carried out. We thus obtained a clearly unrealistic estimate of the enthalpy of activation, ca. 45 kcal/mol for the ground state isomerization process, with the barrier occurring at a torsional angle of only 45°. These results implicate a high degree of bond alternation at the point of internal conversion of photoexcited cyanine dye, which should occur, structurally, close to the maximum for ground state isomerization.

Insofar as photoexcitation may trap a cyanine dye molecule close to one *extremum* of its oscillation on the bond alternation coordinate, the relaxation process may not be activated, as proposed in [7] for the longer chain members of the streptocyanine series. An activation barrier, however, might be encountered if excitation trapped the molecule at the midpoint of the oscillation, i.e. in C_{2v} geometry. Experimentally, this situation should be reflected in a distribution of relaxation times, the distribution presumably becoming broader with increasing chromophore chain length.

If bond alternation is pre-requisite to rotational relaxation of cyanine dyes, then adiabatic isomerization, as proposed by Momicchioli [8–10] is a violation of the so-called NEER principle [33,34]. Accordingly, non-NEER relaxation processes in solution are expected to be gated by solvent relaxation [33]. A stepwise bond alternation–rotational isomerization relaxation pathway, as proposed by Schlegel and co-workers [7], is thus consistent with the solvent dependence of relaxation kinetics in the cyanine dyes, as reported by a number of experimentalists [11–15,31,32].

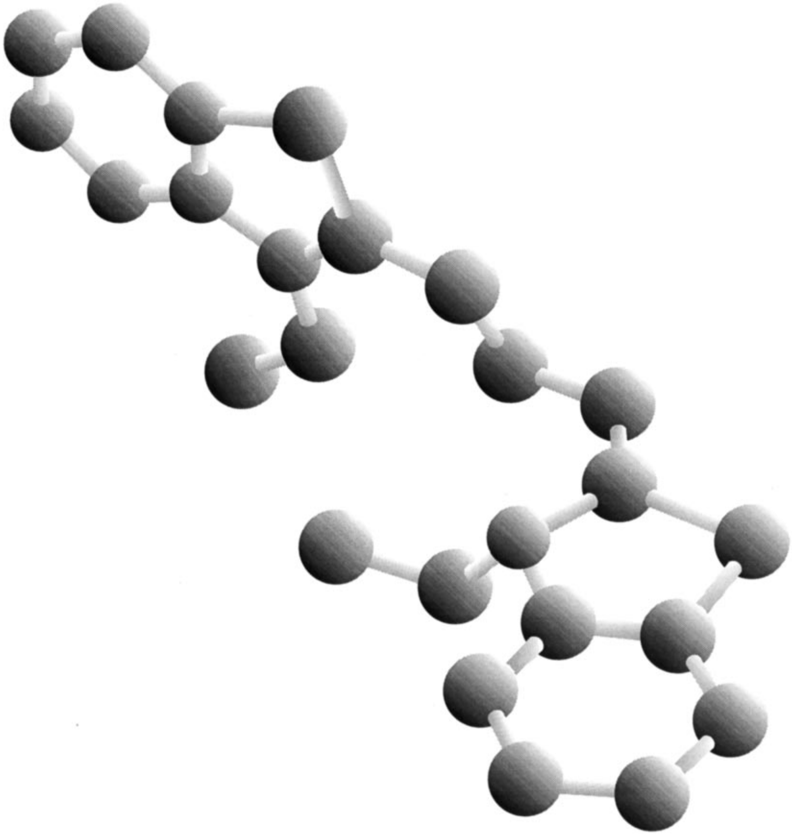

Fig. 8. Minimum energy (AM1-MMFF) geometry for ground state DTCI at the midpoint of its *cis–trans* isomerization pathway: central bond torsional angle of 90°.

4. Conclusions

As a probe of transient perturbation of symmetrical cyanine chromophores from their C_{2v} molecular symmetry by displacements along the bond-length alternation coordinate, we have selected hyper-Rayleigh scattering (HRS) spectroscopy. Three of the four members investigated of a homologous series of dithiacarbocyanine dyes exhibit HRS signals in methanol, indicative of hyperpolarizabilities comparable to those of the reference compounds, *m*- and *p*-nitroaniline. The signals disappear in toluene; we infer that the observed hyperpolarizabilities are a property of the solute–solvation shell system. The results suggest significant, albeit transient, bond-length alternation in the ground state.

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