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Comment on "On Saltiel's isopolarizability approach and its applicability to diphenylpolyenes" by J. Catalán Chem. Phys. Lett. 635 (2015) 56-59

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Abstract

This is in response to Catalán's objection to our use of isopolarizability conditions in the resolution of the absorption and fluorescence spectra of the s-cis and s-trans all-*trans*-1,6-diphenyl-1,3,5-hexatriene (*ttt*-DPH) conformers and the resolution of the fluorescence spectrum of the s-trans conformer to $2^1A_g \rightarrow 1^1A_g$ and $1^1B_u \rightarrow 1^1A_g$ spectra. Contrary to Catalán's assertion, we did not assume identical solvatochromic and thermochromic responses of *ttt*-DPH, to medium changes. Those responses depend on a complex combination of factors that can differ from molecule to molecule.

Key words: Medium Polarizability, Diphenylpolyenes, Conformers, Spectral Resolution

1 Introduction

The lowest energy electronic transitions in the one-photon absorption spectra of the planar all-s-trans conformers of all-*trans*- α,ω -diphenylpolyenes, $\text{Ph}(\text{C}=\text{C})_n\text{Ph}$, are due to the $1^1B_u \leftarrow 1^1A_g$ transitions.[1,2] Those transitions are also responsible for the fluorescence spectra of *trans*-stilbene and *trans,trans*-1,4-diphenyl-1,3-

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butadiene, *tt*-DPB, but, starting with *ttt*-DPH, the fluorescence spectra of the higher polyenes are dominated by the $2^1A_g \rightarrow 1^1A_g$ transitions of all-s-trans conformers that are one-photon forbidden, two-photon allowed in absorption [1,2]. Also, the λ_{exc} dependence of the fluorescence spectra revealed contributions of higher energy s-cis conformers to the absorption and fluorescence spectra of *ttt*-DPH [3] and *tt*-DPB [4-6]. The initial resolution of s-cis and s-trans *ttt*-DPH conformer fluorescence spectra was carried out separately at each T and was based on the λ_{exc} dependence of observed spectra [3]. Application of singular value decomposition (SVD) to spectrothermal matrices that reflect increased s-cis conformer contributions with increasing T , does not easily yield pure conformer spectra because each conformer spectrum, being subject to nonlinear T induced changes, is a moving target. Well documented T induced changes are spectral shifts that depend linearly on medium polarizability, $\alpha = (n^2-1)/(n^2+2)$ [7-9], and broadening due to increased population of higher vibrational energy levels at higher T s. Adding to the complexity is the dependence of the shifts on the oscillator strength of the electronic transition. In the case under consideration, the main component in the fluorescence of *st*-DPH is almost independent of solvent polarizability because it is due to the forbidden $2^1A_g \rightarrow 1^1A_g$ transition that borrows transition probability through vibronic coupling with the $1^1B_u \rightarrow 1^1A_g$ transition [10]. In contrast, the other two components, the thermally activated $1^1B_u \rightarrow 1^1A_g$ fluorescence and the fluorescence from *sc*-DPH depend strongly on solvent polarizability [9-11]. We resolved spectrothermal fluorescence [12] and absorption matrices [13] of *ttt*-DPH by employing isopolarizability conditions to minimize differential polarizability induced shifts, and by compensating for thermal broadening. Catalán ignored our detailed response [13] to his criticism [14] of the use of isopolarizability conditions in resolving the fluorescence spectra, and has extended his critique [15] to our resolution of conformer specific absorption spectra [13]. This response we trust will clear up any confusion.

2 Misconceptions

Catalán's opening statement "The isopolarizability approach of Saltiel et al. relies on the assumption that the bathochromic effect found in the solvatochromism and thermochromism of polyenes merely echoes the polarizability of the solvent" [15] is incorrect. The very opposite is true. Our spectral resolution approach relies on the differences between solvatochromic and thermochromic responses [13].

Ignoring a large body of experimental and theoretical evidence [1,2,16], Catalán rejected the well-established Hudson-Kohler $1^1B_u/2^1A_g$ model for diphenylpolyene fluorescence [17,18]. He contends that "The spectral emissions of α,ω -diphenylpolyenes can be ascribed to the presence of several different molecular structures in their excited electronic state. One, 1^1B_u , is directly produced by light absorption in the all-trans form of the α,ω -diphenylpolyene; the other, C_s , is generated by rotation about a terminal single bond in 1^1B_u . Both structures emit light via dipole-allowed transitions." [18] Catalán allows for contributions from s-trans and s-cis conformers in the fluorescence spectra, but assumes that the s-cis conformers are generated from excited s-trans conformers in violation of

Havinga's nonequilibration of excited rotamers, NEER, principle [19]. Ignored is the dependence of the fluorescence spectra of *tt*-DPB [4-6] and *ttt*-DPH [3,12] on λ_{exc} that confirms their adherence to the NEER principle. Excitation to the 1^1B_u state reverses single/double bond order in the diene and triene moieties converting readily equilibrating ground state conformers into nonequilibrating excited state isomers. The complex *T* dependence of *ttt*-DPH fluorescence Catalán ascribes to thermally induced participation of different molecular geometries produced by equilibration in the 1^1B_u state when, in fact, such equilibration is a ground state phenomenon and there is, in addition, the *T*-dependent dual $1^1\text{B}_u/2^1\text{A}_g$ emission from the *st*-DPH conformer, an excited state phenomenon.

Catalán's statements: "All polyenes were in their most stable (all-*trans*) and no formation of any other isomers during the cooling process was found. This results in considerably simplified analyses because of the absence of stereo isomers potentially formed at temperatures above room temperature according to Saltiel et al." [15] are confusing because they do not distinguish between conformers and geometric isomers. Conformers and geometric isomers occupy shallow [12] and deep [20] free energy minima on a free energy surface, respectively. DPH geometric isomers do not interconvert in S_0 because rotations about double bonds are subject to large activation barriers [20]. However, each DPH geometric isomer exists as a mixture of conformers in S_0 because conformer equilibration involves rotation about essential single bonds [12]. The spectral broadening inducing population of higher torsional modes in a conformer or in a flexible molecule, such as *trans*-stilbene, with increasing *T* is not equivalent to conformer formation, as Catalán assumes [21]. In references [3,12,13] we studied pure *ttt*-DPH, exclusively. We showed that it exists as a mixture of *s-trans,s-trans* and *s-trans,s-cis* conformers, Scheme 1, and resolved their fluorescence and absorption spectra.

3 Response

There is no doubt that in most solvents, the lowest energy transition in the fluorescence spectrum of *st*-DPH corresponds to the forbidden $2^1\text{A}_g \rightarrow 1^1\text{A}_g$ transition. The thermally activated $1^1\text{B}_u \rightarrow 1^1\text{A}_g$ transition normally appears as a shoulder on the high energy side of the *st*-DPH fluorescence spectrum. The order of those two states can be reversed because, with increasing solvent polarizability, the 1^1B_u state is stabilized much more than the 2^1A_g state. State reversal was achieved for *ttt*-DPH in CS_2 at 77 K [11]. It was also achieved in solution by alkyl substitution in the rigid analogue of DPH, all-*trans*-diindanylidene-2-butene (*stiff*-5-DPH), Scheme 2 [22]. Solvent induced $2^1\text{A}_g/1^1\text{B}_u$ state order reversal also occurs in *tt*-DPB although fluorescence in solution, in this case, is due exclusively to the allowed $1^1\text{B}_u \rightarrow 1^1\text{A}_g$ transition [23,24]. Also relevant is *trans,trans*-1-phenyl-4-(1-pyrenyl)-1,3-butadiene which exhibits dual fluorescence from states of B_u and A_g parentage [25]. Here too, changing solvent polarizability leads to state order reversal and the use of isopolarizability conditions eliminates differential shifts of allowed and forbidden fluorescence transitions [25].

Isopolarizability conditions were imposed in our resolution of $2^1A_g \rightarrow 1^1A_g$ and $1^1B_u \rightarrow 1^1A_g$ fluorescence spectra to minimize, or even eliminate, the differential shifts of the spectra corresponding to those transitions. Maintaining a constant energy gap between the 2^1A_g and 1^1B_u states has the added benefit of keeping the coupling of the two states constant. A look at the resolved emission spectra should convince the reader of the success of the resolution [12]. The resolved $1^1B_u \rightarrow 1^1A_g$ fluorescence spectrum bears the expected mirror image resemblance to the $1^1B_u \leftarrow 1^1A_g$ absorption spectrum and the resolved *sc*-DPH fluorescence spectrum agrees well with spectra derived independently at different T s in the same medium [3]. Similarly, the resolved *sc*- and *st*-DPH absorption spectra obtained under isopolarizability conditions agree well with those obtained using shifting and broadening compensation routines without imposing isopolarizability [13].

Figure 6 of Catalán's paper [15] is not relevant to our studies in which only *n*-alkane fluid solutions were employed, in the 284-374 K range. In that Figure three disparate solvents were used to show that the positions of the 0-0 bands of all-*trans*-diphenyloctatetraene at T s with similar indices of refraction differ. 3-Methylpentane, the one hydrocarbon in the set, at 77 K, a T well below its m.p. (110.3 K [26]), as a glass or a solid, presents Shpol'skii like conditions to the solute [27]. Even the rate of cooling can significantly alter the appearance of a solute spectrum in such cases [28,29]. Finally, it is not surprising that the rigid *trans*-stilbene ("tSc") and anthracene respond to polarizability changes in the same way. It is because of its rigidity that tSc was first exploited for mechanistic purposes in our laboratory [30].

4 Conclusion

Catalán's objection to our use of isopolarizability concerns differences in the solvatochromic and thermochromic responses of *ttt*-DPH and other members in the series to medium changes. He attributes those differences to T -induced molecular structure changes and overlooks the fact that it was precisely the major molecular structural change that was addressed in our resolution of *st*- and *sc*-DPH conformer spectra. In preparing spectral matrices for SVD analyses we also compensated for spectral broadening, thereby addressing structural changes associated with population of higher amplitude vibrational modes with increasing T . Our resolved spectra exactly reproduced the thermochromic responses of the experimental fluorescence and absorption spectra.

Simply imposing the expected thermodynamic change on the relative contribution of *st*- and *sc*-DPH conformer spectra with increasing T , produces an apparent shift in the mixture spectra (see the Supporting Information in [13]) that augments the solvatochromic shift. Finally, as we have also pointed out, the imposition of T -dependent spectral broadening alone, on the contributing conformer spectra can give the appearance of a thermochromic shift [13].

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6 References

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Scheme 1. Conformer equilibria in *tt*-DPB and *ttt*-DPH.

Scheme 2. *stiff*-5-DPH

Graphical abstract (Synopsis)

Resolved *ttt*-DPH fluorescence and absorption spectra from [12] and [13], respectively.