Stark Spectroscopy of Donor−Acceptor Polyenes: Correlation with Nonlinear Optical Measurements

Gerold U. Bublitz,[†] Rafael Ortiz,[‡] Claude Runser,[§]
Alain Fort,[§] Marguerite Barzoukas,[§] Seth R. Marder,[‡,⊥] and
Steven G. Boxer*[,†]

*Department of Chemistry, Stanford University
Stanford, California 94305
The Beckman Institute, California Institute of
Technology, Pasadena, California 91125
Institut de Physique et Chimie des Matériaux de
Strasbourg, Groupe d'Optique Nonlinéaire et
d'Optoélectronique (UMR 046 CNRS)
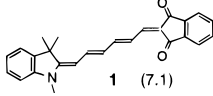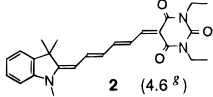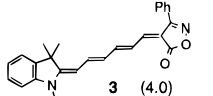67037 Strasbourg Cedex, France
The Jet Propulsion Laboratory,California Institute of
Technology, Pasadena, California 91109
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Many laboratories have sought to understand the molecular properties which enhance second-order nonlinear optical phenomena such as second harmonic generation and electro-optic switching. The second-order nonlinear response $\chi^{(2)}$ of a bulk material depends both on the intrinsic second-order nonlinear coefficient (or first hyperpolarizability) β of the chromophore and some source of alignment which does not possess inversion symmetry. Donor/acceptor polyenes are a versatile class of compounds that have proven to be especially useful to probe the structure−function relationships that control the value of β and other nonlinear optical properties such as the second hyperpolarizability γ.[1] In a simple two-level model, β is proportional to the change in dipole moment $\Delta\mu$ between the ground and first electronic excited state.[2] $|\Delta\mu|$ can be directly[3] determined by measuring the effect of an applied electric field on the absorption spectrum, the Stark effect spectrum. We present results of Stark and EFISH measurements for a series of donor/acceptor polyenes which demonstrate the correlation between optical nonlinearities and $|\Delta\mu|$ along with a large solvent dependence of their electronic structure.

The Stark spectra of compounds **1**−**4** (Table 1) were measured as described in detail elsewhere.[4] For an isotropic, immobilized sample, an applied electric field will broaden and shift an isolated transition due to the change in dipole moment $\Delta\mu$ and change in polarizability $\Delta\alpha$, respectively.[5] Stark spectra for compounds **1** and **4** taken in frozen 2-methyltetrahydrofuran (2-MeTHF), toluene, and ethanol (EtOH) solutions at 77 K are shown in Figure 1, and the results of the analysis of the spectra[5] are summarized in Table 1. In 2-MeTHF, **1** shows large values of both $|\Delta\mu|$ and $\Delta\alpha$, and **2** and **3** show somewhat smaller values.[6] For **4** the Stark spectrum has a very different line shape due to a dominant negative $\Delta\alpha$ and a small $|\Delta\mu|$. Both the absorption and Stark spectra of compounds **1** and **4** show a large solvent dependence. In both cases, a decrease in solvent polarity (toluene) leads to an increase in both $|\Delta\mu|$ and $\Delta\alpha$. On the other hand, in a polar solvent (EtOH) **1** shows a small $|\Delta\mu|$ and negative $\Delta\alpha$, while **4** exhibits negligible $|\Delta\mu|$ and a positive value of $\Delta\alpha$.

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　† Stanford University.
　‡ The Beckman Institute, California Institute of Technology.
　§ Institut de Physique et Chimie des Materiaux de Strasbourg.
　⊥ The Jet Propulsion Laboratory, California Institute of Technology.
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　(5) The change in absorption, ΔA, upon application of an electric field can be decomposed into contributions proportional to the first and second derivative of the molecule's absorption spectrum, which are related to $\Delta\alpha$ and $|\Delta\mu|$, respectively. See ref 4.
　(6) The ΔA spectra for **2** and **3** in 2-MeTHF are similar in line shape but of smaller magnitude than the spectrum for **1**.

Table 1. Values of $|\Delta\mu|$ and $\Delta\alpha$ as determined by Stark Spectroscopy for Compounds **1**−**4**[i]

Compound (pK_A(acceptor)[a])	Solvent[b]	λ^c [nm]	$|\Delta\mu|^d$ [D]	$\Delta\alpha^e$ [Å^3]	region[f]
1 (7.1)	T	676	14	1900	**(A)/B**
	M	692	10	1000	**B**
	E	707	2.5	-50	**C**
2 (4.6[g])	M	671.5	6.0	385	**B/(C)**
3 (4.0)	M	689	5.4	300	**B/(C)**
4 (2.5[g])	T	692.5	8	600	**B**
	M	700.5	2	-300	**C**
	E	694.5	0	325	**(D)/E**[h]

[a] pK_A value of the free acceptor end group. [b] T, toluene; M, 2-MeTHF; E, EtOH. [c] Absorption maximum in the given solvent. [d] Experimental error ±10%. [e] Experimental error ±20%. [f] Assignments are based on comparison of the results obtained from the Stark spectra and the model prediction (*cf.* Figure 2)—see text. The brackets stand for "shifted toward", i.e., **2** and **3** in 2-MeTHF are displaced from limit **B** toward **C**. [g] pK_A value of the dimethyl form. [h] Agreement between model and data is not good enough to exactly locate the position of **4** in EtOH.[4] [i] Experiments were carried out in frozen glasses at 77 K.
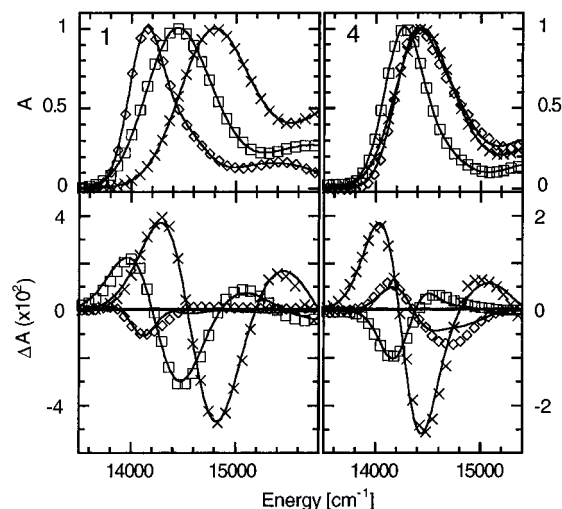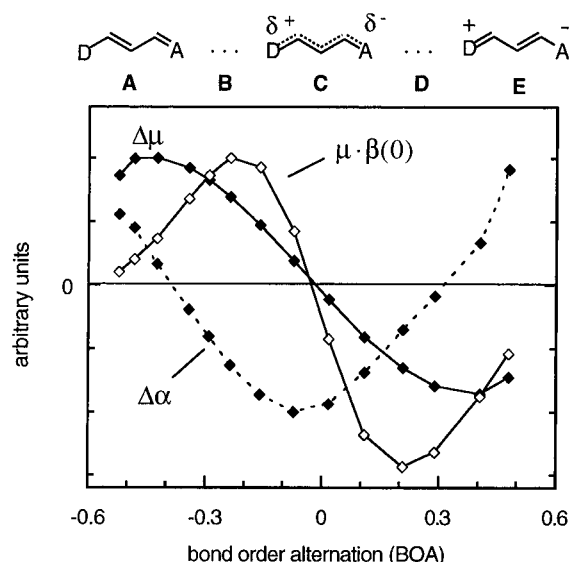

Figure 1. Absorption spectra (top panels) and ΔA (Stark) spectra (bottom panels) for compounds **1** (left) and **4** (right) taken at 77 K in frozen glasses of toluene (crosses), 2-MeTHF (squares), and EtOH (diamonds). All spectra were scaled to a peak absorbance of unity and a field strength of 1×10^6 V/cm to ease comparison between different spectra. The solid line superimposed on each spectrum gives the result of the simultaneous best fits of the A and ΔA data from which $|\Delta\mu|$ and $\Delta\alpha$ are obtained.[5]

Table 2 gives values of $\mu\cdot\beta(0)$ for **1**−**4** measured in eight different solvents as well as the position of the peak of the room temperature absorption spectrum in these solvents.[7] All four compounds show clear changes in their nonlinear optical response, spanning a positive peak in $\mu\cdot\beta(0)$ as the solvent polarity (as measured by the E_T^N scale[8] −*cf.* Table 2) increases. While for **1** the value of $\mu\cdot\beta(0)$ only decreases slightly for high solvent polarities, for **4** it already starts to decrease at low solvent polarity and crosses through zero at a solvent polarity corresponding to DMF. **2** and **3** show an intermediate dependence of $\mu\cdot\beta(0)$ on the solvent polarity.

In order to compare the results of the two experimental methods we need a theoretical framework that can account for both the substituent and solvent dependence of the electronic

Table 2. Solvent Dependent $\mu\cdot\beta(0)$ Values[a] (Units of 10^{-48} esu) for **1**−**4** and the Corresponding Wavelength of the Lowest Energy Absorption Maximum[c]

	Solvent [E_T^N]							
	dioxane [0.164]	THF[b] [0.207]	CHCl$_3$ [0.259]	CH$_2$Cl$_2$ [0.309]	acetone [0.355]	DMF[b] [0.404]	DMSO[b] [0.444]	EtOH [0.654]
1	1055 (621)	1365 (644)	1530 (662)	1630 (660)	1660 (660)	1410 (684)	1290 (696)	(687)
2	1235 (618)	(634)	1430 (650)	1555 (650)	1610 (647)	1180 (662)	925 (668)	75 (661)
3	1645 (620)	1855 (651)	1970 (668)	2005 (672)	1905 (668)	(680)	880 (685)	(677)
4	1550 (661)	1620 (679)	1595 (688)	1465 (690)	920 (684)	-20 (691)	-675 (695)	(688)

[a] $\mu\cdot\beta(0)$ values were determined using 1.907 μm fundamental radiation and were corrected for dispersion using the two level model.[2] The cubic contribution to the signal was neglected. The estimated precision in $\mu\cdot\beta(0)$ is ±15%. [b] THF, tetrahydrofuran; DMF, dimethylformamide; DMSO, dimethyl sulfoxide. [c] In brackets, units of nm. The polarity of the solvents increases from left to right as indicated by their E_T^N values[8] [in brackets].

Figure 2. Calculated trends in the values of $\Delta\mu$, $\Delta\alpha$, and $\mu\cdot\beta(0)$ with changing ground-state structure of donor/acceptor polyenes derived from the results of ref 13. The top part of the figure shows limiting structures of donor/acceptor polyenes for different values of BOA (see text).

structure of donor/acceptor polyenes. The effects of the electron donating and accepting end groups on the electronic structure of the bridging polyene can be modeled by the simple picture shown above Figure 2. With increasing donor and/or acceptor strength as well as with increasing solvent polarity the ground-state structure of the bridge should change from an unperturbed polyene (**A**) toward a cyanine-like fully delocalized structure (**C**), and for even stronger donors/acceptors or higher solvent polarity, toward the limit of an again localized but charge-separated structure (**E**). A useful concept to quantitate these effects is the average bond order alternation (BOA) between adjacent bonds in the bridge also illustrated in Figure 2. A number of computational studies of donor/acceptor polyenes exist which correlate the molecule's electronic parameters (e.g., μ, α, β, and γ) with its structure.[1,9−14] Figure 2 shows the

calculated variation of the experimentally accessible parameters $\mu\cdot\beta(0)$ (EFISH), $\Delta\mu$ (Stark), and $\Delta\alpha$ (Stark) between the limits **A**−**E**.

1−**4** differ only in their electron acceptor end group, the strength of which (i.e., its capability to stabilize a negative charge) can be approximated by the pK_A value of the corresponding free acid (*cf.* Table 1). Comparing the obtained $|\Delta\mu|$ values and the variations in $\Delta\alpha$ with the model predictions in Figure 2, these molecules can be assigned with respect to the limits **A**−**E**. **1** having both moderately strong donor and acceptor end groups can be expected to be in region **B** which agrees with the measured values of $|\Delta\mu|$ and $\Delta\alpha$ in 2-MeTHF. The decreased values of $|\Delta\mu|$ and $\Delta\alpha$ for **2** and **3** agree with the expected results for compounds with increased acceptor strength and a structure somewhat closer to limit **C**. The results for **4** in 2-MeTHF place it close to the cyanine limit **C**. For both **1** and **4** changing the solvent to the less polar toluene moves the structure toward limit **A**, while in the highly polar EtOH it shifts toward limit **E**.

EFISH measurements were done in fluid solution because motion of the molecules is needed to achieve orientation. The Stark spectra were taken in frozen solution precisely to avoid this complication. In order to compare the results of the two types of measurements the quantitative differences in the solvent matrix between the two experiments have to be taken into account. It is well-known that the polarity of a solvent increases with decreasing temperature,[8,15] mainly due to an increase of the dipole−dipole interactions between solvent and solute.[16] The exact degree of this increase in polarity will depend on the nature of both the solvent and the solvated molecule. The best comparison for the studied molecules thus should be the position of their own absorption maxima (*cf.* Tables 1 and 2). Using this reasoning the data suggest that the results obtained in frozen 2-MeTHF glasses should be compared with those obtained in DMF or DMSO at room temperature,[17] and the observed trends in $\mu\cdot\beta(0)$ and $\Delta\mu$ are then in very good agreement. This provides direct experimental evidence for the correlation of the decreasing optical nonlinearities in regions **B** and **C** with a decrease in $|\Delta\mu|$, as predicted by the two level approximation.[18] Finally, the negative $\Delta\alpha$ observed for compound **4** is in accord with theoretical predictions and the observation of negative γ for cyanine-like molecules[1,13,14] although the observed values of $\Delta\alpha$ are much less negative than predicted.[4]

(7) $\mu\cdot\beta(0)$ is the scalar product of the ground-state dipole moment μ (= μ_g) with the vectorial component of the static hyperpolarizability tensor $\beta(0)$. Values for $\mu\cdot\beta(0)$ as obtained from the EFISH measurements are being reported since μ is not known for these molecules and is also expected to depend on the solvent. $\Delta\mu$ is the difference dipole moment between the ground and excited state, i.e., $\Delta\mu = \mu_e - \mu_g$.

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