Thermal, Optical, and Nonlinear Optical Properties of Tetrafluorinated Donor–Acceptor Benzenes

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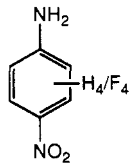
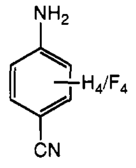
Received March 23, 1993

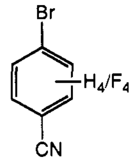
Compatibility of nonlinear optical (NLO) dyes with the generally high temperature (>250 °C) processing steps which may be required for the fabrication of electrooptic devices is of great importance for the commercialization of organic- or polymer-based NLO devices.[1] As part of a project for the development of second-order nonlinear optical chromophores with increased thermal stability, we became interested in the absolute and relative effects fluorination has on the thermal and NLO properties of several chromophores. Replacement of hydrogen by fluorine might be expected to lead to greater (kinetic) oxidative stability due to fluorine's strong electron-withdrawing effect. Fluorination also results in substantial changes in the electronic absorption spectra of many chromophores, but the effect of fluorination on second-order susceptibilities of chromophores had only briefly been investigated.[2] The effect of fluorination on the thermal stability of dyes has not been reported. Ring fluorinated analogs of three para-substituted donor-acceptor benzenes, **1**–**3**, were therefore chosen for this study.



1a,b



2a,b



3a,b

Compounds **1b**, **2a,b**, and **3a,b** are commercially available and were used as received. Compound **1a** was prepared by treatment of pentafluoronitrobenzene with ammonia.[3] Elemental analyses on the halogenated species were variable, in particular for fluorine content, possibly due to incomplete combustion, but all showed sharp melting points, single compounds by TLC, and no discernible contaminants by ^1H or ^{19}F NMR. DSC measurements were taken in sealed capillary tubes to prevent loss of material due to sublimation.[4]

The microscopic second-order susceptibility was measured using the infinite dilution extrapolation procedure which requires concentration-dependent measurements of the macroscopic susceptibility, index of refraction, and dielectric constant.[5,9] This technique approximately accounts for local fields and yields values for the linear polarizability α, the dipole moment μ, and the molecular second-order susceptibility β. The electric-field-induced second-order macroscopic susceptibility was measured using previously described techniques.[5–7] The fundamental beam of 1.59 μm used for EFISH is the third Stokes line produced by pumping a hydrogen-filled Raman cell with the output of a Q-switched frequency doubled Nd:YAG laser. This pumping arrangement produced fundamental beam energies of 1 mJ with pulse widths of 10 ns. Index of refraction measurements were made using a differential refractometer[8] illuminated with a He–Ne laser (λ = 632 nm). Dielectric constants were measured with a capacitance bridge. All measurements were made in dioxane solution at 10^{-2}–10^{-4} weight fraction. The apparatus was calibrated against previous measurements of dioxane and *p*-nitroaniline.[9]

Substitution of hydrogen by fluorine on an aroamtic ring substantially affects the charge distribution within the ring and may complicate the assignment of electronic transitions because of the participation of fluorine π orbitals. Fluorine shows a strong inductive electron withdrawing effect as measured on aliphatic systems (σ_I = 0.50, between CN = 0.56 and Br = 0.44, but not as strong as NO_2, σ_I = 0.65),[10] but is a moderate π donor when attached to an aromatic ring ($\sigma_R°$ = −0.34, the same as −OPh, but weaker than NH_2 = −0.48, and stronger than Br = −0.19).[11] The effect of fluorine substitution on electronic structure and electronic spectra is therefore complex and is made more complex because of conformational changes which may also result from the higher electronegativity and greater size of fluorine relative to hydrogen (van der Waals radii of 1.293 and 1.135 Å, respectively).

Semi-empirical calculations using MOPAC and the PM-3 parametrization method[12] were used to quantify the effect of fluorination on the geometry of **1a**–**3a**, but only in the case of **1b** was a significant change noted. In this case, the nitro group was forced significantly (46° dihedral angle) out of plane with the phenyl ring due to close contacts of the nitro group oxygens with the ortho fluorines, both of which carry partial negative charges. The significant blue shift (see Table I; 37 nm, acetonitrile) of λ_{max} in **1b** can probably be assigned to this change of conformation and the resulting loss of conjugation. However, the measured molecular dipole decreases by only 8% upon fluorination, which may imply that in the ground state of **1a** and **1b** the primary polarization of the molecule is derived from the sigma withdrawing nature of the nitro group (see σ_I = 0.65, previous paragraph).

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0897-4756/93/2805-1059$04.00/0

Table I. Experimental and Calculated Spectral, DSC, and EFISH Data

	λ_{max}(expt),[a] nm		$\epsilon_{max}/10^3$	λ_{max}(calc), nm	T(DSC),[b] °C	μ,[c] D		β ($\times 10^{+30}$), esu
1a	365	352	14.9	314	379	6.5	7.6	11.8
1b	328	319	9.1	288	336	6.0	7.0	5.5
2a	271	271	23.8	258	>450	6.4	5.9	2.4
2b	275	274	24.5	271	407	6.5	5.8	2.6
3a	240	240	19.3	241	>450	2.5	1.8	2.2
3b	245[d]	240[d]	17.2	250[d]	>450	3.5	1.9	1.35

[a] Experimental spectra measured in acetonitrile and dioxane, respectively. Spectral maxima calculated with 197 configurations (14 C.I. levels) using ZINDO with INDO/S spectroscopic parameters. Initial geometries were obtained using PM3 parameters. [b] Exotherm peak, 10 °C/min, sealed tube; maximum temperature 450 °C to avoid tube failure; no exotherm below 450 °C for **2a**, **3a**, and **3b**, but samples discolor. [c] Measured in dioxane and calculated by PM3. [d] A weak absorption in **3b** was observed at 291 and 293 nm in acetonitrile and dioxane and calculated at 300 nm.

INDO/S[13] calculations were used to evaluate the nature of the lower energy transitions in these molecules. Excellent agreement between the calculated (isolated molecule or gas phase) and observed absorption maxima in 2 and 3 is consistent with the small observed solvatochromism in these molecules. For 2 and 3, which show minimal calculated (PM-3) geometry changes upon fluorination, the effect of fluorination on their absorption spectra is slight (4- and 5-nm red shifts observed in acetonitrile, 9- and 13-nm red shifts calculated, respectively). A more thorough analysis of the calculated spectra shows that additional transitions lower in energy than the principle charge-transfer transition exist in the fluorinated molecules and that longer wavelength cutoffs for second harmonic generation result. This effect is most pronounced in **3b** where a resolved absorbance maximum is observed 46 nm to the red of the higher absorbance charge-transfer band.

In contrast, poor agreement between the calculated and observed spectra for the significantly more solvatochromic *p*-nitroanilines is observed. (The poor agreement for 1 has been noted but not analyzed.[14]) Furthermore, the observed gas phase absorption spectrum of **1a** (λ_{max} = 271 nm)[15] is in poor agreement with the calculated value of 314 nm. Therefore, there is a deficiency in the spectral calculations for **1a** and, by implication, of **1b**. The error may originate in a poor geometry as calculated by the PM-3 method (the NO_2 group is known to be not well represented by parameters optimized for other nitrogen containing groups[16]) or may be due to limitations of INDO/S approach and/or parameters. Further work with ab initio optimized geometry calculations with 3–21G and 6–31G* basis sets did not reduce this error, and we concluded that these errors are due to limitations inherent to the INDO/S approach.

Trends in the microscopic second-order susceptibility, β, upon fluorination are not apparent from the experimental data in every case. The >50% decrease in β that is observed from **1a** to **1b** is consistent with the blue shift combined with the reduced molar absorptivity (oscillator strength) observed in the linear optical spectra upon fluorination. The calculations are in complete agreement: a blue shift accompanied by reductions in oscillator strength and transition dipole. The small increase (10%) in β for **2b** relative to **2a** is consistent with minimal changes in the wavelengths of absorption in the ultraviolet spectra of these molecules. Again the calculations and experiment agree to the within the limits of the experimental techniques and theoretical methods. However, the reason for the substantial decrease in β for molecule **3b** relative to **3a** is not apparent from the observed electronic spectra. Semiempirical calculations reveal the source of the decrease in β however: the change in dipole moment between the ground and excited states is substantially less in **3b** than in **3a**, which when coupled with a significant decrease in oscillator strength is consistent with a reduced hyperpolarizability. The origin of these effects cannot be attributed to conformational changes as in the **1a**/**1b** pair but is attributable to subtle electronic effects that result from fluorine substitution.

Arguably, NLO dyes that are intended for use in polymer systems that require high-temperature processing must minimally be stable toward decomposition in the solid state or melt at the processing temperatures. However, typical small molecules may sublime rapidly at such temperatures, making stability measurements problematic. The solution to this is a sealed-tube capillary with a high sample volume to surface area ratio (such a design was previously applied to measurements of volatile inorganic and organic materials[4]). The maximum temperature we applied was 450 °C to avoid capillary rupture. No failures of the capillaries occurred, and the data obtained were reproducible. This technique could also be applied to the measurement of the thermal properties of mixtures of dyes in polyimide precursors for direct evaluation of potential electrooptical or nonlinear optical materials.

The optical, nonlinear optical, and thermal properties of ring-fluorinated donor–acceptor benzenes were contrasted with their nonfluorinated analogs. The trends observed in the linear and nonlinear optical data can largely be understood with INDO/S calculations, and the observed unexpected significant *decrease* in thermal stability in the fluorinated materials is consistent with the increased susceptibility of fluorinated rings to nucleophilic attack.[3] The sealed-tube DSC technique used here should be widely applicable to studies of the thermal stability of NLO dyes and materials.

Acknowledgment. A portion of this work was performed at Sandia National Laboratories and was supported by the U.S. Department of Energy under Contract DE-AC04-76DP00789. Ab initio calculations were performed by C. M. Rohlfing. D. A. Schneider assisted with ^{19}F NMR spectroscopy.

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