Theoretical investigation of the electronic properties of donor–acceptor N-benzylideneanilines and related molecules

John O. Morley
Chemistry Department, University of Wales Swansea, Singleton Park, Swansea, UK SA2 8PP

The dipole moments, transition energies and hyperpolarizabilities of a substituted stilbene, azobenzene and two isomeric–benzylideneanilines containing the 4-dimethylamino-group at one end of the molecule and the 4-nitro-group at the other, have been calculated using a semi-empirical sum-over-states method on structures optimized with the 3-21G basis set. An excellent correlation is found between the calculated and experimental spectra. The azobenzene is predicted to have the largest hyperpolarizability of this series of molecules, followed by the stilbene and N-(nitrobenzylidene)aniline which have comparable values, with the non-planar N-(benzylidene)nitroaniline showing the smallest value.

Introduction

Organic molecules with conjugated π-electron systems are known to exhibit extremely large optical non-linear responses in terms of their molecular hyperpolarizabilities with applications in many current areas of interest such as second harmonic generation (SHG) and linear electro-optic modulation (LEO).[1-3] Both theoretical and experimental studies have shown that large hyperpolarizabilities generally arise from a combination of a strong electron donor and acceptor positioned at opposite ends of a suitable conjugation path. The values obtained are dependent not only on the strength of the donor and acceptor groups but also on the path length between them. Thus, the experimental hyperpolarizability of (E)-4-dimethyl-amino-4'-nitrostilbene (**1a**) is an order of magnitude larger than 4-nitroaniline (**2a**).[4]
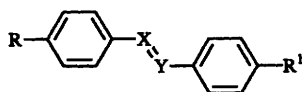
la R = NMe$_2$; X–Y = CH=CH; R^1 = NO$_2$
 b R = NMe$_2$; X–Y = N=N; R^1 = NO$_2$
 c R = NMe$_2$; X–Y = N=CH; R^1 = NO$_2$
 d R = NMe$_2$; X–Y = CH=N; R^1 = NO$_2$
 e R = NH$_2$; X–Y = CH=CH; R^1 = NO$_2$
 f R = NH$_2$; X–Y = N=N; R^1 = NO$_2$
 g R = NH$_2$; X–Y = N=CH; R^1 = NO$_2$
 h R = NH$_2$; X–Y = CH=N; R^1 = NO$_2$
 i R = N(Et)(C$_2$H$_4$OH); X–Y = N=N; R^1 = NO$_2$
 j R = NEt$_2$; X–Y = N=N; R^1 = C(CN)=C(CN)$_2$
 k R = Me; X–Y = CH=N; R^1 = NO$_2$
 l R = Me; X–Y = N=CH; R^1 = NO$_2$
 m R = OMe; X–Y = N=CH; R^1 = NO$_2$
 n R = R' = H; X–Y = CH=N
 o R = R' = H; X–Y = CH=CH
 p R = NMe$_2$; X–Y = C(CN)=CH; R^1 = NO$_2$

Furthermore, the nature of the conjugation path between donor and acceptor groups also contributes to the value[5-8] and recent theoretical studies have suggested that an alkenylene chain positioned between the substituents is far superior to either the corresponding phenylene,[5,6] thienylene,[7] furylene,[7] pyrrolylene[7] or alkynylene chain[8] because the π-electrons are able to move more easily from the donor to the acceptor on excitation.[8]

The insertion of elements other than carbon into a conjugated backbone containing a donor and acceptor group at each end would be expected to have a significant effect on molecular properties such as the ground and excited state dipole moments, electronic transition energies and the hyperpolarizability. Pre-
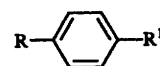
2a R = NH$_2$; R^1 = NO$_2$
 b R = NMe$_2$; R^1 = NO$_2$
 c R = NMe$_2$; R^1 = C(CN)=C(CN)$_2$

liminary calculations on the effect of replacing an ethenylene sp^2 carbon atom in 4-dimethylamino-4'-nitrostilbene (**1a**) by nitrogen, using structures based in part on crystallographic data, indicated that large effects are produced.[9] Thus both the calculated static hyperpolarizabilities, β_0, and frequency dependent values, β_F (at 1.17 eV or 1060 nm) of 4-dimethyl-amino-4'-nitroazobenzene (**1b**) are predicted to be greater than those of the related stilbene (**1a**), which in turn has greater values than those of N-(4-nitrobenzylidene)-4-dimethylamino-aniline (**1c**) with its isomer, N-(4-dimethylaminobenzylidene)-4-nitroaniline (**1d**), showing the smallest values[9] (Table 1).

These results, however, contradict PPP calculations[10] which suggest that the closely related N-(4-nitrobenzylidene)-4-amino-aniline (**1g**) has a greater hyperpolarizability than the corresponding 4-amino-4'-nitrostilbene (**1e**). More recent results at the CNDO/S level on the same molecules support our preliminary findings of the reverse order for structures **1a** and **c**, with **1e** calculated to be greater than **1g**,[11,12] but also suggest that the stilbene **1e** has a much larger hyperpolarizability than 4-amino-4'-nitroazobenzene (**1f**)[11,12] in apparent contradiction with our results on the corresponding dimethylamino-derivatives **1a** and **b** (Table 1). All three methods, however, predict that the N-(4-aminobenzylidene)-4-nitroanilines (**1d** and **h**) have the smallest values.[9-12]

Experimental data from electric field induced second harmonic generation (EFISH) shows that the stilbene **1a** has a larger static hyperpolarizability, β_0, and frequency dependent value, β_F (at 1356 nm) than the benzylideneaniline **1c**.[4] However, the EFISH results also suggest that the stilbene **1a** has a larger β_0 value than the azobenzene **1b** on the basis of the value obtained for 4-(N-ethyl-N-hydroxyethylamino)-4'-nitro-azobenzene (**1i**), though the frequency dependent β_F values at 1356 nm are reversed and support the calculated results. This reversal may be due to a greater resonance enhancement effect for the azobenzene **1i**, which absorbs at 508 nm and is therefore closer to the second harmonic of 678 nm than the stilbene **1a** which absorbs at 452 nm,[4] or a genuine substituent effect.

The experimental EFISH β_0 results for the complex azobenzene **1i**, equal those obtained for 4-amino-4'-nitroazobenzene (**1f**)[4] and imply that the N-ethyl-N-hydroxyethylamino-group exerts no additional effect over that of the amino-group. This

Table 1 Calculated and experimental hyperpolarizabilities and spectra of donor–acceptor stilbenes, benzylideneanilines, azobenzenes and aniline

Molecule	Calculated[a]			Experimental data			
	β_{PPP}[b]	$\beta_{CNDO/S}$[c]	$\beta_{CNDOVSB}$[d]	β[e]	β[f]	λ[g]	λ[h]
1a			42.7	52	105	420	430
b			59.6			447	479
c			38.9	37	77	438	445
d			28.1			387[i]	405[j]
e	248.0	202.8					
f		132.0		47	103		
g	371.0	135.3					
h	77.0	31.8					
i				47	125		
j				154	390		
2a	35.3			9	12		
b				12	21		
c				26	78		

[a] β is the calculated hyperpolarizability (in units of 10^{-30} cm^5 esu^{-1}). [b] Ref. 10. [c] Refs. 11 and 12. [d] Zero field results from ref. 9. [e] Zero field results from ref. 4. [f] Frequency dependent results at 0.914 eV (1356 nm) from ref. 4. [g] Absorption maxima in cyclohexane from ref. 10. [h] Absorption maxima in ethanol from ref. 20. [i] Absorption maxima in hexane from ref. 20. [j] Absorption maxima in dichloromethane from ref. 20.

result is surprising as the replacement of the amino-group by the closely related dimethylamino-group would be expected to produce a significant enhancement of the hyperpolarizability of the simple azobenzene 1f in a similar way to the experimental increase from 9 to 12 (in units of 10^{-30} cm^5 esu^{-1}, throughout) noted by the EFISH technique in moving from 4-nitroaniline (2a) to N,N-dimethyl-4-nitroaniline (2b).[4] Because the EFISH method generates the vector component of the hyperpolarizability along the direction of the molecular dipole moment, the presence of a terminal electronegative oxygen atom in one of ethyl-groups produces a local dipole, which at best will be positioned approximately orthogonal to the main charge transfer axis and at worst may be opposed to it, resulting in a vector value which will be somewhat less than that which is theoretically possible along the charge transfer axis alone. This argument is supported also by the experimental data on 4-(N,N-diethylamino)-4'-tricyanovinylazobenzene (1j) where the β_0 value is over three times larger than that of 4-(N-ethyl-N-hydroxyethylamino)-4'-nitroazobenzene (1i) whereas only a factor of two would be expected from comparable data on 4-(N,N-dimethylamino)-4'-tricyanovinylbenzene (2c) and 4-(N,N-dimethylamino)-4'-nitrobenzene (2b) where the β_0 value increases from 12 to 26.[4] All this evidence therefore suggests that the β_0 value of 4-dimethylamino-4'-nitroazobenzene (1b) is likely to be greater than that of the corresponding stilbene 1a.

The studies reported here are an extension of previous theoretical work [9] to further evaluate the effect of heteroatoms placed in the conjugation path of substituted donor–acceptor diarenes. In these more exact studies designed to clarify previous confusing theoretical results, all the molecular structures were optimized at both the semi-empirical and *ab initio* levels and their hyperpolarizabilities calculated using the CNDOVSB method.[13]

Method of calculation

All calculations of both the static and frequency dependent hyperpolarizabilities (at 0.914 eV or 1356 nm) were carried out using the CNDOVSB method [13] which involves an initial configuration interaction treatment between ground and excited state wave functions and then evaluation of the tensor from a perturbation expansion involving the transition moments and transition energies between the ground and singly excited states.[14] All 27 components of the SHG tensor are calculated but the most appropriate quantity is the vector component, β,

theoretically defined as eqn. (1),[13] where β is aligned to lie along

$$\beta = \beta_{\mu\mu\mu} + 1/3 \sum_{i \neq \mu} (\beta_{\mu ii} + 2\beta_{ii\mu}) \qquad (1)$$

the direction of the molecular dipole moment and is therefore directly related to the non-linear coefficients derived from electric field induced second harmonic generation in solution. Generally around 50 excited states are included in the evaluation of the hyperpolarizability tensor.[14]

Molecular structures were calculated from empirical ones using both the AM1 method [15] of the MOPAC program [16] and the *ab initio* 3-21G basis set [17] from the GAMESS program.[18]

Results and discussion

Attempts to optimize the structures of the molecules considered here using the AM1 method were unsuccessful. While this method correctly predicts the expected planarity of 4'-dimethylamino-4-nitrostilbene (1a) and twisted structure of N-(4-dimethylaminobenzylidene)-4-nitroaniline (1d) in line with crystallographic data,[19] both N-(4-nitrobenzylidene)-4-dimethylaminoaniline (1c) and 4'-dimethylamino-4-nitroazobenzene (1b) are also predicted to be twisted in contradiction to the planar structures expected from crystallographic data on closely related structures.[19] For this reason, the structures were re-optimized using the 3-21G basis set and the results obtained in this case show a much better account of the geometry of all four molecules with the stilbene 1a, azobenzene 1b and benzylideneaniline 1c predicted to be essentially planar, while the acceptor ring of 1d is predicted to be twisted fully in accord with experimental data.[19] These structures were used directly for calculation with the CNDOVSB method.

The calculated dipole moments obtained using the semi-empirical method show the same trends and are of similar magnitude to the 3-21G results (Table 2) with 1d > b > a > c. Furthermore, the calculated transition energies (Table 2) show an excellent correlation with experimental data in both polar and non-polar solvents (Table 1). Here, both the bathochromic shift observed in moving from the stilbene 1a through to the benzylideneaniline 1c or the azobenzene 1b are well reproduced by the semi-empirical method. Furthermore, the large calculated hypsochromic shift of 34 nm found in moving from the stilbene 1a to the benzylideneaniline 1d (Table 2) also mirrors the experimental shift of 33 nm (Table 1) and is clearly a consequence of the lack of planarity in this system.

Table 2 Calculated dipole moments, transition energies, and hyperpolarizabilities of a donor–acceptor stilbene **1a**, azobenzene **1b** and the benzylideneanilines **1c** and **d**[a]

Molecule	$\mu_{3\text{-}21G}$	μ_g	μ_e	λ	f	N	β_0	$\beta_{0.914}$
1a	9.74	9.57	21.9	432	1.24	50	49.8	107.6
						200	50.3	109.6
1b	9.96	10.1	21.5	450	1.13	50	55.3	125.6
						200	55.5	128.2
1c	9.41	8.82	25.9	436	0.96	50	51.1	113.3
						200	50.6	113.6
1d	10.2	10.9	19.2	398	1.24	50	30.6	55.6
						200	31.1	57.4

[a] $\mu_{3\text{-}21G}$ is the ground state dipole moment at the 3-21G level (in D); μ_g and μ_e are the ground and excited state dipole moments at the CNDOVSB level (in D); λ and f are the corresponding transition energies (in nm) and oscillator strengths; N is the number of included excited states in the calculation of the hyperpolarizability tensor; β_0 and $\beta_{0.914}$ are the calculated hyperpolarizabilities at zero field and at 0.914 eV (1356 nm) respectively (in units of 10^{-30} cm^5 esu^{-1}).

Table 3 Calculated atomic charge distributions at key positions of a donor–acceptor stilbene **1a**, azobenzene **1b** and the benzylideneanilines **1c** and **d**

Structure	State[a]	Atomic charge				
		N[b]	X	Y	N[c]	O
1a	G	−0.942	−0.154	−0.214	0.172	−0.392
	g	−0.131	−0.009	−0.061	0.821	−0.512
	e	0.027	−0.120	−0.028	0.787	−0.539
1b	G	−0.948	−0.384	−0.412	0.179	−0.388
	g	−0.141	−0.093	−0.151	0.815	−0.516
	e	0.031	−0.316	−0.239	0.795	−0.530
1c	G	−0.952	−0.716	0.230	0.178	−0.389
	g	−0.153	−0.279	0.140	0.815	−0.516
	e	0.031	−0.380	0.064	0.776	−0.546
1d	G	−0.944	0.267	−0.739	0.175	−0.392
	g	−0.144	0.181	−0.316	0.815	−0.522
	e	0.007	0.000	−0.297	0.783	−0.540

[a] G is the ground state value at the 3-21G level; g and e are the ground and first excited state values at the CNDOVSB level. [b] Nitrogen of the NMe$_2$ group. [c] Nitrogen of the NO$_2$ group.

An analysis of the key ground state atomic charge distributions at the nitrogen atom of the NMe$_2$ group, the nitrogen and oxygen atoms of the NO$_2$ group and the bridging carbons or nitrogen atoms (X and Y) between the donor and acceptor rings, show that the 3-21G and CNDOVSB methods produce similar trends though the former gives a much larger charge polarization than the latter (Table 3). In both the stilbene **1a** and azobenzene **1b**, the bridging atoms (X and Y) are both negative though the latter shows the greatest magnitude at these positions as expected. In the benzylideneanilines **1c** and **d**, however, the bridging bond is polarized with the nitrogen atom negative and the carbon positive.

On excitation to the first dominant charge transfer excited state, there is a substantial change in charge distribution with the nitrogen atom of the NMe$_2$ group now positive, with the displaced electrons transferred mainly to the first bridging atom (X) and also to the second bridging atom (Y) when nitrogen is present, with a concomitant increase in the dipole moment in all cases (Tables 2 and 3). However, there is no increase in the charge at the nitrogen atom (Y) of the twisted benzylideneaniline **1d** on excitation presumably because of the reduced conjugation with the acceptor ring.

The calculated hyperpolarizabilities predict that the azobenzene **1b** has a slightly larger static field value than the stilbene **1a** or the benzylideneaniline **1c**, but the isomeric benzylideneaniline **1d** is predicted to have the smallest value mainly because of the reduced conjugation in this molecule (Table 2). Furthermore, the calculated value for the stilbene **1a** at 49.8 is very close to the experimental value of 52 (see Table 1 for units) though that for the benzylideneaniline **1c** is some-

what overestimated by comparison with the experimental data. Because the order of hyperpolarizabilities obtained here might be an artifact of the number of excited states included in the calculation of the tensor, the effect of increasing the number of included states from 50 to 200 was also explored but found to have very little effect on the final values obtained (Table 2). The hyperpolarizability is therefore dominated by a relatively small number of excited states with the maximum effect exerted by the lowest energy charge transfer state.

The frequency dependent hyperpolarizabilities are much larger because the denominator of the expression used for calculation [13] contains reciprocal terms such as $(\Omega_{ng} - 2\Omega_{ng})$ where Ω_{ng} is the transition energy and Ω is the frequency of the applied field. At a field of 0.914 eV or 1356 nm, the frequency doubled term, 2Ω, at 678 nm is quite close to the transition energy of each molecule, resulting in a small value for the energy denominator and a substantial increase in the hyperpolarizability. The azobenzene **1b** shows the largest resonance enhancement factor of around 2.3 because its absorption at 450 nm is closest to the frequency doubled value of 678 nm whereas the non-planar benzylideneaniline **1d** with a predicted absorption at 398 nm shows a smaller enhancement of 1.82.

It is concluded that the CNDOVSB method gives an excellent account of the transition energies of the molecules considered here using structures derived from 3-21G optimizations. The azobenzene **1b** is predicted to have the largest hyperpolarizability of this series, followed by the stilbene **1a** and nitrobenzylideneaniline **1c** which are predicted to have comparable values, with the benzylidenenitroaniline **1d** showing the smallest value.

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