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Donor–Acceptor Diphenylacetylenes: Geometric Structure, Electronic Structure, and Second-Order Nonlinear Optical Properties

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Abstract: We present a theoretical study of the geometry and electronic structure in a series of donor–acceptor diphenylacetylene molecules containing one–four triple bonds in the conjugated segment. We investigate the second-order molecular polarizabilities β at the intermediate neglect of differential overlap/configuration interaction (INDO/CI) sum-over-states level; the theoretical results are compared to detailed experimental data which have been recently reported. We test the convergence of the sum-over-states approach and the validity of the two-state model. In compounds with one or two triple bonds in the conjugated segment, after examining a wide range of donors and acceptors, a linear dependence is obtained between β and, on the one hand, the inverse of the squared lowest transition energy $(1/\hbar\omega_{eg})^2$) and, on the other hand, the dipole moment change ($\Delta\mu$) in going from the ground state to the low-lying charge-transfer excited state. In these shorter compounds, we find the two-state model to provide excellent trends. However, the results indicate that increasing the conjugation length of the molecules beyond two triple bonds leads to a total breakdown of the two-state approximation; this is because of the appearance of several nearly isoenergetic excited states which significantly contribute to the molecular second-order polarizability β. This feature is fully consistent with the experimental data.

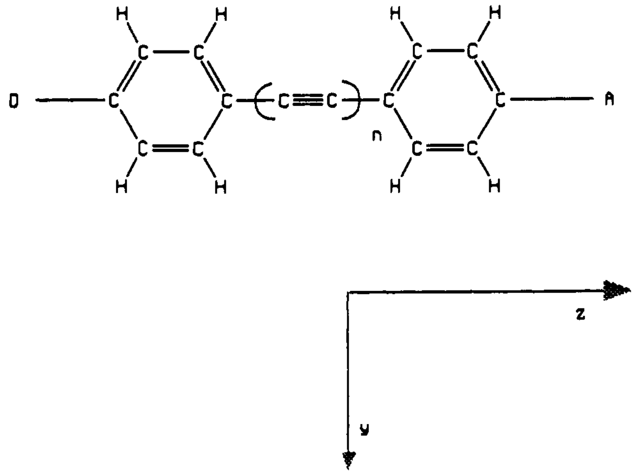
I. Introduction

Numerous experimental and theoretical studies have recently focused on the nonlinear optical (NLO) properties of organic materials.[1-3] These compounds are especially attractive for NLO applications because of (i) fast and high nonlinear optical responses; (ii) inherent synthetic flexibility; (iii) high damage thresholds; (iv) ease of processing into ultrathin films; and (v) the possibility of tailoring the material characteristics to suit a given nonlinear optical process. In this context, push–pull conjugated molecules, such as *p*-nitroaniline and its derivatives, *i.e.*, molecules which possess easily polarizable electron clouds and asymmetric charge distributions, display high second-order polarizability (β) values.

In this work, we theoretically study the relationships between the geometric and electronic structure and β in a series of donor–acceptor diphenylacetylene compounds containing one–four triple bonds in the conjugated segment (Figure 1). The reason for this choice of compounds is that extensive experimental data are available on a wide range of such molecules in terms of geometric structure,[4] electronic properties, and second-harmonic generation (SHG) response.[5] There is therefore room for detailed comparison between theory and experiment.

Our calculations are carried out at the semiempirical level including configuration interaction. Ab initio calculations are often considered to be more rigorous. However, for the whole series of molecules we want to examine in this work, they would prove to be computationally too expensive and would not allow for the inclusion of electron correlation effects. Furthermore, the availability of the corresponding experimental data affords the opportunity to probe in depth the reliability of the semiempirical approach.

Our methodology is presented in Section II. Section III is devoted to a discussion of the geometry and charge distributions in the ground state and lowest-lying charge-transfer excited state. The hyperpolarizability results are given and compared to experimental data in Section IV, where we also analyze the frequency dispersion of β in terms of second-harmonic generation.



D: NH_2, SCH_3, OCH_3, $NHCH_3$, $N(CH_3)_2$

A: NO_2, CN, $COCH_3$, CO_2CH_3, SO_2CH_3, CO(ϕ)

Figure 1. Molecular structure of the push–pull diphenylacetylenes studied in this work.

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II. Methodology

The geometries of all the molecules investigated in the present work are optimized at the semiempirical Hartree-Fock Austin Model One (AM1) level.[6] This method is known to afford accurate geometry estimates of organic molecules. The calculation of the molecular polarizabilities is based on the sum-over-states approach, *i.e.*, on the perturbation expansion of the Stark energy of the molecule.[7] Within the SOS approach, the *ijk* Cartesian component of the second-harmonic generation β is given by:[7]

$$\beta_{ijk}(-2\omega;\omega,\omega) = \frac{1}{4\hbar^2}\sum_{l\neq0}\sum_{m\neq0}\left(\frac{\langle0|\mu^i|m\rangle\langle m|\bar{\mu}^j|l\rangle\langle l|\mu^k|0\rangle + \langle0|\mu^i|m\rangle\langle m|\bar{\mu}^k|l\rangle\langle l|\mu^j|0\rangle}{(\omega_{m0}-2\omega)(\omega_{l0}-\omega)} + \frac{\langle0|\mu^j|m\rangle\langle m|\bar{\mu}^k|l\rangle\langle l|\mu^i|0\rangle + \langle0|\mu^k|m\rangle\langle m|\bar{\mu}^j|l\rangle\langle l|\mu^i|0\rangle}{(\omega_{m0}^*+\omega)(\omega_{l0}^*+2\omega)} + \frac{\langle0|\mu^j|m\rangle\langle m|\bar{\mu}^i|l\rangle\langle l|\mu^k|0\rangle + \langle0|\mu^k|m\rangle\langle m|\bar{\mu}^i|l\rangle\langle l|\mu^j|0\rangle}{(\omega_{m0}^*+\omega)(\omega_{l0}-\omega)}\right) \tag{1}$$

where $\langle0|\mu^i|m\rangle$ is the electronic transition moment between the ground state described by wave function $\langle0|$ and excited state $\langle m|$; $\langle m|\bar{\mu}^i|l\rangle$ denotes the dipole difference operator equal to $\langle m|\mu^i|l\rangle - \langle0|\mu^i|0\rangle\,\delta_{m1}$; $\hbar\omega_{l0}$ is the energy difference between state 1 and the ground state; ω is the frequency of incident light; and ω_{m0}^* is the complex conjugate to ω_{m0}.

The states are described via the Hartree-Fock semiempirical INDO/SCI[8] (intermediate neglect of differential overlap/single configuration interaction) method on the basis of the AM1 optimized geometries. The Coulomb repulsion integrals are expressed in terms of the Ohno-Klopman parameters.[9] Note that the Ohno-Klopman parameterization is usually used when both single and double excitations are taken into account while the Mataga-Nishimoto parameterization is generally taken in a single CI context since it introduces more electronic correlation.[10] In a recent paper,[11] we have shown that the choice of the parameters somewhat modifies the absolute values for the spectroscopic properties of interest but does not at all alter the trends found within the investigated series of molecules.

The calculations are carried out using a modified version of the ZINDO quantum-chemical package.[12] Previous studies have shown the suitability of semiempirical CI techniques[13-19] and especially the INDO/CI method[20-24] to evaluate the polarizabilities in organic molecules. To determine the singlet excited-state wave functions, we include those singly excited configurations (SCI) that are generated by the promotion of an electron from one of the highest 16 occupied molecular orbitals to one of the lowest 16 unoccupied levels, thus forming a basis of 257 configurations.

We calculate the projection of the β vector components onto the μ dipole moment vector components in order to provide a meaningful comparison with the results of EFISH (electric field induced second-harmonic generation) measurements:[25]

$$\beta_\mu = \frac{\vec{\beta}\cdot\vec{\mu}}{\|\vec{\mu}\|} = \frac{\sum_i \beta_i\mu_i}{(\sum_i \mu_i^2)^{1/2}} \tag{2}$$

where component β_i is given by

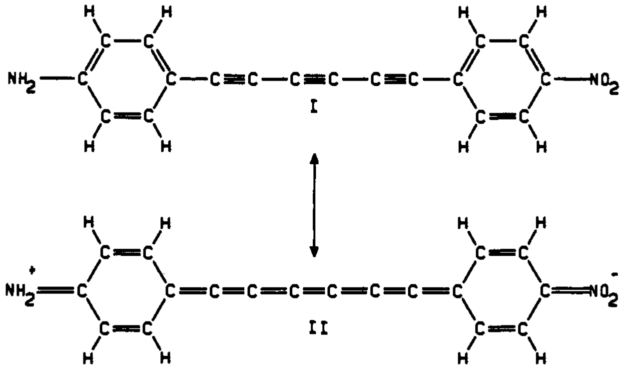
$$\beta_i = \beta_{iii} + (\beta_{ijj} + 2\beta_{jji} + \beta_{ikk} + 2\beta_{kki})/3$$

Since we also evaluate the frequency dependence of second-order polarizability β, we do not adopt Kleinman symmetry.

Note that in the rest of this paper, we will use the notation [D/A] $n = x$ for the push-pull diphenylacetylene compounds. D indicates the nature of the donor group, A the acceptor, and x corresponds to the number of triple bonds in the diphenylacetylene conjugated segment.

III. Geometric Structures and Charge Distributions

Graham *et al.*[4] have recently synthesized single crystals of diphenylacetylene molecules end-capped by an amino donor group and a nitro acceptor group (see Figure 1); they have determined the molecular structures by means of X-ray diffraction measurements.[4] In such compounds, one may envision two major resonance forms, as sketched below.



Resonance form I is referred to as acetylenic-like and is expected to dominate in the ground state. Resonance form II is quinoid/cumulenic-like and is expected to play a major role in the lowest-lying excited state which has been experimentally shown to possess charge-transfer character.[26] It is also of interest to examine whether resonance form II somehow contributes to the description of the ground state.

(a) Ground State. In our calculations, we forced planar conformations for all the molecules we studied, which is the situation found in the solid state due to crystal packing effects.[4] However, Barzoukas *et al.* have shown that in solution the $n = 1$ diphenylacetylene molecules exist as conformational mixtures.[27] EFISH results then correspond to an average polarizability β where the contributions from each conformation are weighted proportionally to the Boltzmann factors.[27] The conformational

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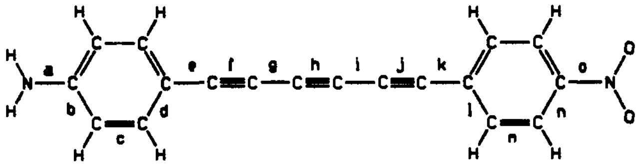
Table I. AM1 and Experimental (in italics) Geometries (in angstroms) of NH_2–NO_2 Diphenylacetylene Compounds



	n = 1	2	3
a	1.374/*1.379*	1.373/*1.384*	1.373/*1.381*
b	1.420/*1.391*	1.420/*1.384*	1.420/*1.395*
c	1.385/*1.370*	1.385/*1.369*	1.385/*1.365*
d	1.406/*1.398*	1.406/*1.402*	1.406/*1.388*
e	1.402/*1.436*	1.401/*1.422*	1.401/*1.425*
f	1.201/*1.183*	1.203/*1.203*	1.203/*1.203*
g	1.403/*1.435*	1.349/*1.388*	1.347/*1.368*
h		1.202/*1.183*	1.204/*1.208*
i		1.404/*1.437*	1.348/*1.369*
j			1.202/*1.194*
k			1.404/*1.431*
l	1.407/*1.398*	1.406/*1.381*	1.406/*1.386*
m	1.390/*1.377*	1.390/*1.369*	1.391/*1.373*
n	1.405/*1.378*	1.405/*1.384*	1.404/*1.384*
o	1.485/*1.462*	1.486/*1.460*	1.486/*1.466*
δr_1[a]	0.028/*0.025*	0.028/*0.024*	0.028/*0.027*
δr_2[a]	0.016/*0.011*	0.016/*0.014*	0.014/*0.014*

[a] δr_1 and δr_2 are the bond-length alternations in the phenyl rings attached to the NH_2 and NO_2 groups, respectively.

freedom in solution is related to the ease of rotation of the phenyl rings around the axis defined by the triple bonds.

Our choice of coplanar conformations is, however, not to affect the trends we obtain. For instance, in the [NH_2/NO_2] compounds, when the amino group is allowed to become pyramidal, the dipole moment value is hardly affected and the β_μ value is only decreased by about 1×10^{-30} esu. Furthermore, we note that the MNDO calculations of Barzoukas *et al.*[27] indicate that a rotation of 90° around the single C–C bond between one ring and the acetylenic bridge reduces the β component along the charge-transfer axis by a factor of 2 with respect to the coplanar situation.

In Table I, we present the AM1 optimized[28] and experimental solid-state geometries for the [NH_2/NO_2] $n = 1$–3 molecules. For all three compounds, there is absolutely no evidence for a quinoid/cumulenic contribution to the ground state from either X-ray diffraction data[4] or AM1 optimizations. Both experimental and theoretical results indicate that the weight of the quinoid/cumulenic resonance form is negligible in the ground state.

We also report in Table I the degree of bond-length alternation δr within the phenyl rings, *i.e.*, the difference in length between the phenyl carbon-carbon bonds inclined and parallel with respect to the molecular long axis (see labels on Table 1):

$$\delta r_1 = \frac{(b{-}c) + (d{-}c)}{2} \qquad \delta r_2 = \frac{(l{-}m) + (n{-}m)}{2}$$

These δr values are characteristic of the degree of quinoid character in each ring. In benzene, δr is equal to 0. A very slight quinoid character (*i.e.*, $\delta r \neq 0$) appears already in biphenyl. In a fully quinoid ring, δr would be on the order of 0.100–0.120 Å.

For $n = 1$, the experimental δr_1 and δr_2 values are 0.025 and 0.011 Å, respectively. The corresponding AM1 δr values are 0.028 and 0.016 Å, thus indicating a very good agreement with experiment. Since the AM1 δr value for biphenyl is 0.006 Å, we obtain that the donor and acceptor groups do slightly increase the quinoid character of the ring. From the δr values for $n = 2$ and $n = 3$, it is seen that the extension of the conjugated segment along the molecule does not affect these values, which remain small. In the $n = 1$–3 diphenylacetylene molecules, the triple bonds are calculated with AM1 to range between 1.201 and 1.204 Å; these values are very close to experiment. In this context, it is important to note that the AM1 geometry optimizations of 1,2-diphenylethyne, 1,3-butadiyne (HC≡C—C≡CH), and 1,3,5-hexatriyne (HC≡C—C≡C—C≡CH) (see Figure 2) lead to triple and single bonds within the acetylenic bridges which are almost identical to those in the push–pull diphenylacetylene compounds.[28] This result points out that the geometry of the acetylenic bridge is not altered by the presence of the donor/acceptor and/or phenyl groups. The presence of the amino and nitro substituents only slightly influences the geometry of the phenyl ring they are attached to. We stress that the same conclusion is valid for all the other substituents we have considered, see, *e.g.*, Table III for the [SCH_3/CN] compounds.

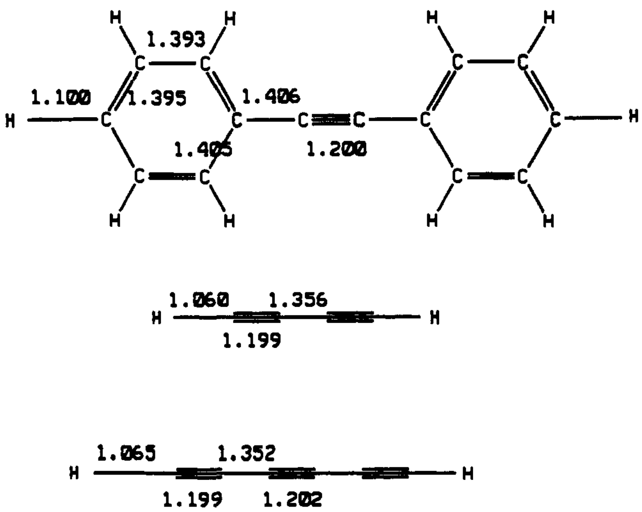


Figure 2. AM1 optimized bond lengths (in angstroms) for the molecules of diphenylethyne, 1,3-butadiyne, and 1,3,5-hexatriyne.

In order to quantify the ground-state charge transfer that could be triggered in the ground state by the presence of the donor and acceptor groups, we present in Table II the INDO total and π-charge distributions. As these are provided by means of a Mulliken population analysis, we are interested in trends rather than in absolute charge values. In the following, we discuss the distributions in terms of net charges per entity: the donor group, the acceptor group, each of the phenyl rings, and the whole acetylenic bridge.

From Table II, it is observed that the nature of the donor/acceptor groups and the length of the conjugated segment do not modify the total and π-charges within the acetylene bridges (these remain around $-0.140|e|$ for the total charge and close to 0 for the π-charge); however, they affect the charge distributions within the phenyl rings. In other words, the polarization due to the donor and acceptor groups ***does not extend past the phenyl rings***. All the donor groups act as π-donor and σ-acceptor entities. The phenyl rings directly attached to the donor groups act as π-acceptor and σ-donor entities. The phenyl rings attached to the acceptor groups are σ-donors and in the majority of cases also π-donors; the acceptor groups themselves are both π- and σ-acceptors.

The π-charge transfer going all the way from the donor to the acceptor is at most on the order of $0.15|e|$, the largest transfers being found when the donors are the (di)methylamino groups. It should be pointed out that a significant portion of the π-charge transferred by the donor is actually attracted by the phenyl ring it substitutes; this ring thus acts as a buffer against the π-charge transfer over the whole molecule.

The fact that both phenyl rings carry a total positive charge allows one to rationalize the very weak evolution of the ground-

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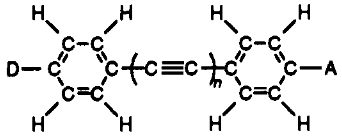
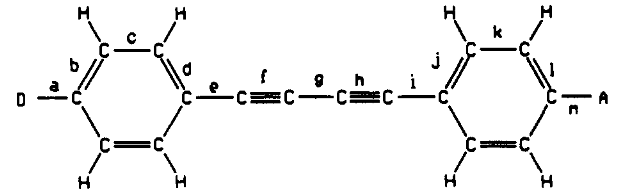
Table II. INDO Total Charge and π-Charge (in italics) Distributions per Entity in the Ground State (in charge unit |e|)



	substituent		charge				
n	D	A	D	ϕ_1	$-(C{\equiv}C)_n-$	ϕ_2	A
1	NH_2	NO_2	−0.021/*0.111*	0.127/*−0.078*	−0.130/*0.003*	0.230/*0.021*	−0.206/*−0.057*
2	NH_2	NO_2	−0.080/*0.110*	0.190/*−0.084*	−0.130/*0.007*	0.260/*0.022*	−0.240/*−0.055*
3	NH_2	NO_2	−0.080/*0.114*	0.180/*−0.090*	−0.140/*0.032*	0.280/*0.024*	−0.240/*−0.080*
1	SCH_3	NO_2	−0.034/*0.039*	0.135/*−0.016*	−0.133/*0.006*	0.236/*−0.033*	−0.204/*0.005*
2	SCH_3	NO_2	−0.033/*0.043*	0.130/*−0.023*	−0.132/*0.014*	0.237/*0.026*	−0.202/*−0.060*
1	SCH_3	CN	−0.035/*0.042*	0.126/*−0.023*	−0.140/*−0.001*	0.172/*−0.003*	−0.123/*−0.015*
2	SCH_3	CN	−0.039/*0.041*	0.125/*−0.020*	−0.145/*0.006*	0.181/*0.019*	−0.122/*−0.046*
1	OCH_3	NO_2	−0.148/*0.082*	0.250/*−0.038*	−0.134/*0.003*	0.233/*0.025*	−0.204/*−0.072*
1	NH_2	CN	−0.024/*0.113*	0.125/*−0.087*	−0.145/*−0.007*	0.168/*0.014*	−0.124/*−0.033*
1	$NHCH_3$	CN	−0.026/*0.254*	0.127/*−0.076*	−0.144/*−0.006*	0.168/*0.015*	−0.125/*−0.187*
1	$N(CH_3)_2$	CN	−0.018/*0.258*	0.119/*−0.087*	−0.145/*−0.006*	0.168/*0.015*	−0.124/*−0.180*
1	$NHCH_3$	NO_2	−0.019/*0.244*	0.134/*−0.072*	−0.137/*0.001*	0.228/*0.022*	−0.206/*−0.195*
1	$N(CH_3)_2$	NO_2	−0.090/*0.248*	0.204/*−0.084*	−0.137/*0.001*	0.229/*0.022*	−0.206/*−0.187*
1	NH_2	$COCH_3$	−0.035/*0.232*	0.136/*−0.068*	−0.144/*−0.003*	0.109/*0.047*	−0.066/*−0.208*
1	SCH_3	$COCH_3$	−0.184/*0.056*	0.273/*−0.033*	−0.141/*−0.001*	0.116/*0.050*	−0.064/*−0.072*
1	NH_2	CO_2CH_3	−0.024/*0.113*	0.143/*−0.086*	−0.144/*−0.004*	0.114/*0.046*	−0.089/*−0.069*
1	NH_2	SO_2CH_3	−0.024/*0.112*	0.127/*−0.087*	−0.146/*−0.007*	0.130/*−0.021*	−0.087/*0.003*
1	NH_2	$CO(\phi)$	−0.036/*0.233*	0.131/*−0.069*	−0.146/*−0.006*	0.104/*0.030*	−0.053/*−0.188*
1	SCH_3	CO_2CH_3	−0.184/*0.056*	0.274/*−0.032*	−0.140/*0.001*	0.135/*0.050*	−0.085/*−0.075*

Table III. AM1 Bond Lengths (in angstroms) and Bond-Length Alternations in the Phenyl Rings in the Ground State and the First Excited State for the $[SCH_3/CN]n = 1$ and 2 Molecules



	SCH_3/CN (*n* = 1)		SCH_3/CN (*n* = 2)	
	ground state	excited state	ground state	excited state
a	1.694	1.651	1.692	1.647
b	1.403	1.416	1.402	1.418
c	1.390	1.378	1.390	1.376
d	1.405	1.421	1.405	1.423
e	1.404	1.388	1.404	1.389
f	1.200	1.207	1.202	1.207
g	1.404	1.394	1.350	1.344
h			1.202	1.205
i			1.404	1.397
j	1.406	1.412	1.406	1.410
k	1.390	1.385	1.391	1.387
l	1.404	1.409	1.404	1.407
m	1.486	1.473	1.486	1.479
δr_1	0.014	0.041	0.014	0.045
δr_2	0.015	0.026	0.014	0.021

state dipole moment as a function of the number of triple bonds in the acetylenic bridge. This feature has been discussed previously.[28]

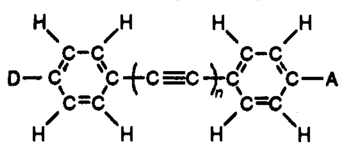
(b) Charge-Transfer Excited State. We have found it interesting to investigate with the AM1 method the relaxed geometry of the first singlet excited state S_1 (*i.e.*, the main charge-transfer excited state). At that level, the geometry optimization calculations simply incorporate the configuration resulting from the promotion of one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). We note that the INDO/SCI results indicate that the first excited state is essentially described by the HOMO–LUMO singly excited configuration, in particular in the case of the compounds where the donor is the methylthio group and the acceptor is the cyano group; this is the reason that, in Table III, we present the AM1 relaxed geometries in the S_1 state for these compounds. Clearly, there occurs an increased tendency toward the quinoid form in the S_1 excited state, as evidenced by the evolution of the δr_1 and δr_2 values when going from the ground state to the excited state. This effect is stronger in the case of the ring substituted by the $-SCH_3$ group (δr increases by 0.027 Å) than in the -CN substituted ring (δr increases by only about 0.010 Å). Overall, the geometry of the rings in the excited state can be quantified as being semiquinoid-like. Note that the triple bonds also slightly elongate, which indicates that they acquire a weak double-bond character.

We now turn to a discussion of the charge distribution in the S_1 excited state obtained at the INDO/SCI level, on the basis of the AM1 ground-state geometry. (We refer back to the ground-state geometry since processes taking place at optical frequencies are occurring on too fast a time scale to allow for the geometry relaxations.) The calculated total and π-charges are given in Table IV. The general characteristics for each entity are the same as in the ground state, except for (i) the acetylene linkages which show π-donor and σ-acceptor characters for molecules containing one or two triple bonds and (ii) the phenyl rings substituted by the acceptor which acquire a π-acceptor character. The latter feature indicates that the acceptor moiety can be considered to be formed by both the acceptor group and the ring to which it is attached.

If we examine the π-charge transfer, we generally observe that, in the excited state, the donor group acquires a larger positive π-charge and the ring it substitutes a smaller negative π-charge. This behavior, combined to the π-donor character of the acetylene bridge, leads to π-charge transfer to the phenyl–acceptor moiety. This transfer reaches at most 0.35|e|; this only corresponds to about a 0.2|e| charge-transfer increase with respect to the ground state. By and large, there does not occur any full electron charge transfer as would be implied by resonance form **II** sketched above.

It is also interesting to examine the π-charge transfer as a function of elongation of the acetylenic bridge. We have done so in the case of the $[NH_2/NO_2]$ compounds. In going from one to three triple bonds, the π-charge carried by the phenyl–NO_2 acceptor moiety *decreases* (going from −0.237|e| for *n* = 1 to −0.087|e| for *n* = 3). In the *n* = 3 molecule, it is actually the acetylenic bridge which plays the main acceptor role. Therefore, contrary to conventional wisdom, *increasing the conjugation*

Table IV. INDO Total Charge and π-Charge (in italics) Distributions per Entity in the First Excited State (in charge unit |e|)



	substituent		charge				
n	D	A	D	ϕ_1	$-(C{\equiv}C)_n-$	ϕ_2	A
1	NH_2	NO_2	−0.020/*0.161*	0.260/*0.003*	−0.060/*0.073*	0.100/*−0.104*	−0.280/*−0.133*
2	NH_2	NO_2	0.010/*0.144*	0.260/*−0.038*	−0.070/*−0.088*	0.070/*−0.085*	−0.270/*−0.109*
3	NH_2	NO_2	0.059/*0.194*	0.253/*0.032*	−0.290/*−0.139*	0.191/*−0.078*	−0.213/*−0.009*
1	SCH_3	NO_2	−0.008/*0.063*	0.198/*0.046*	−0.037/*0.102*	0.133/*−0.074*	−0.286/*−0.137*
2	SCH_3	NO_2	−0.019/*0.059*	0.157/*0.001*	−0.050/*0.105*	0.165/*−0.061*	−0.253/*−0.104*
1	SCH_3	CN	−0.008/*0.069*	0.128/*−0.019*	−0.074/*0.065*	0.082/*−0.072*	−0.128/*−0.043*
2	SCH_3	CN	−0.028/*0.052*	0.123/*−0.023*	−0.075/*0.077*	0.104/*−0.057*	−0.124/*−0.049*
1	OCH_3	NO_2	−0.129/*0.099*	0.332/*0.039*	−0.058/*0.082*	0.140/*−0.068*	−0.285/*−0.151*
1	NH_2	CN	0.020/*0.157*	0.151/*−0.062*	−0.109/*0.030*	0.069/*−0.085*	−0.131/*−0.040*
1	$NHCH_3$	CN	0.025/*0.301*	0.140/*−0.064*	−0.105/*0.033*	0.071/*−0.081*	−0.131/*−0.189*
1	$N(CH_3)_2$	CN	0.041/*0.322*	0.130/*−0.090*	−0.109/*0.029*	0.069/*−0.082*	−0.131/*−0.179*
1	$NHCH_3$	NO_2	0.030/*0.290*	0.206/*0.001*	−0.077/*0.062*	0.119/*−0.089*	−0.278/*−0.264*
1	$N(CH_3)_2$	NO_2	0.061/*0.310*	0.182/*−0.024*	−0.082/*0.057*	0.114/*−0.094*	−0.275/*−0.249*
1	NH_2	$COCH_3$	0.002/*0.265*	0.161/*−0.039*	−0.098/*0.043*	0.036/*−0.029*	−0.101/*−0.240*
1	SCH_3	$COCH_3$	−0.129/*0.111*	0.264/*−0.044*	−0.087/*0.053*	0.051/*−0.014*	−0.099/*−0.106*
1	NH_2	CO_2CH_3	0.022/*0.159*	0.161/*−0.051*	−0.102/*0.034*	0.035/*−0.050*	−0.116/*−0.097*
1	NH_2	SO_2CH_3	0.028/*0.165*	0.142/*−0.074*	−0.118/*0.023*	0.034/*−0.117*	−0.086/*0.003*
1	NH_2	$CO(\phi)$	0.001/*0.267*	0.147/*−0.054*	−0.088/*0.051*	0.027/*−0.045*	−0.087/*−0.219*
1	SCH_3	CO_2CH_3	−0.126/*0.114*	0.268/*−0.039*	−0.090/*0.051*	0.060/*−0.025*	−0.112/*−0.101*

length of the diphenylacetylene molecules does not give rise to a better charge separation along the molecule in the excited state.

IV. Hyperpolarizability Results

A number of authors have already theoretically investigated the second-order polarizability of push–pull diphenylacetylene compounds. Matsuzawa and Dixon[29] and Barzoukas *et al.*[27] have reported β results from finite-field semiempirical calculations based on MNDO or PM3 Hamiltonians and the AM1 Hamiltonian, respectively. We also note that Morley has used a CNDO-CI/SOS approach to compare the efficiency of polyyne bridges to that of polyene bridges between donors and acceptors.[30] Here, our interest is to provide a much more detailed discussion than previously done of theoretical (INDO-CI/SOS) results of push–pull diphenylacetylenes in comparison to the experimental data of Stiegman *et al.*[5]

(a) Convergence of the SOS Approach. Following Oudar[31] and assuming that the optical response of a push–pull molecule is primarily governed by the ground state $|0\rangle$ and a low-lying intramolecular charge-transfer (ICT) state $|e\rangle$, a simple expression for β_{zzz} can be derived from eq 1 (where z corresponds to the charge-transfer dipole moment axis, see Figure 1):

$$\beta_{zzz}(-2\omega;\omega,\omega) = {}^{3}/_{2}\underbrace{\frac{\Delta\mu_z M_{ge}^{\,2}}{(\hbar\omega_{eg})^2}}_{\text{static}}\ \underbrace{\frac{\omega^4_{eg}}{(\omega^2_{eg}-4\omega^2)(\omega^2_{eg}-\omega^2)}}_{\text{dispersion factor}} \qquad (3)$$

This forms the basis of the two-state model, which has been shown to give reasonable estimates of β in a number of organic molecules.[31,32]

In principle, eq 1 requires that the summation be carried over a complete state basis set (SBS). Here, as is usually done, we take into account a finite SBS size of 50 states for each molecule and calculate the β components. In all the systems studied in this work, we find that the β_{zzz} component along the charge-transfer axis determines the value of β.

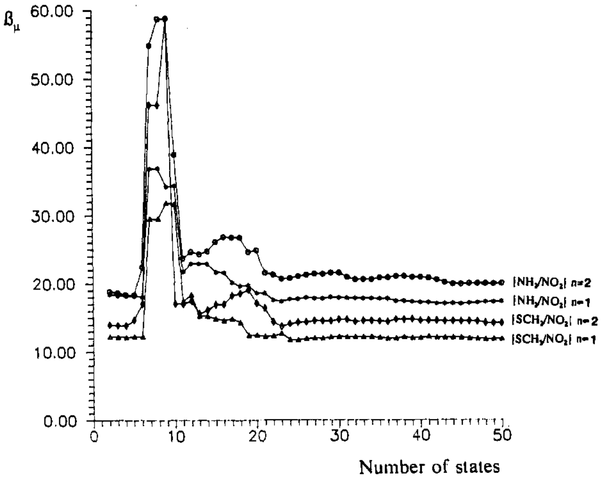


Figure 3. Plot of β_μ (in 10^{-30} esu) as a function of the number of states in the case of $[NH_2/NO_2]$ $n = 1,2$ and $[SCH_3/CN]$ $n = 1,2$.

In Figure 3, we present the convergence of the SOS approach as a function of the number of states taken into account (up to 50) for two sets of push–pull compounds: (i) $[NH_2/NO_2]$ with $n = 1$ and 2 and (ii) $[SCH_3/NO_2]$ with $n = 1$ and 2. The results demonstrate that for these push–pull diphenylacetylene molecules, a SBS of 30 states is sufficient to obtain a converged β_μ value (a similar convergence is obtained for the other molecules we studied).

In Table V, we make the comparison, for the $n = 1$ and $n = 2$ compounds, between the static β_μ values obtained on one hand, using 50 states in the SOS approach and, on the other hand, only two states (the ground state and the first excited state), *i.e.*, applying the two-state model. (It should be borne in mind though that the first excited state, as we describe it here, is based on a set of 257 configurations.) We find that the trends in the two-state model results are fully consistent with the trends in the converged β_μ values; actually even the absolute differences are small: at most 2×10^{-30} esu and in most cases around 1×10^{-30} esu. This, however, does not mean that the first excited state provides the only significant contribution to the second-order polarizability in these compounds. When examining Figure 3, we observe that two or three other states have large individual

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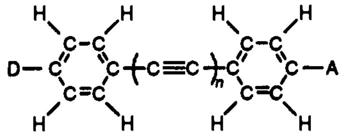
(29) Matsuzawa, N.; Dixon, D. A. *J. Phys. Chem.* **1992**, *96*, 6232.
(30) Morley, J. O., submitted for publication.
(31) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.
(32) Zyss, J.; Oudar, J. L. *Phys. Rev. A* **1982**, *26*, 2016.

Table V. Measured (ref 5) and INDO/SCI Calculated Electronic Properties of the Diphenylacetylene Compounds[a]



	substituent		$\hbar\omega_{eg}$		M_{ge}		$\Delta\mu$		β_μ		
n	D	A	exptl	INDO	exptl	INDO	exptl	INDO	exptl	INDO	β_μ two-state
1	NH_2	NO_2	3.27	3.69	6.16	8.62	9.5	5.79	24	17.3	18.5
2	NH_2	NO_2	3.23	3.60	5.48	9.08	8.5	5.07	28	20.0	18.8
1	SCH_3	NO_2	3.46	3.85	6.16	8.22	5.4	4.82	20	11.9	12.3
2	SCH_3	NO_2	3.34	3.69	5.57	8.50	3.5	3.97	17	14.2	14.0
1	SCH_3	CN	3.80	3.98	6.00	8.18	8.0	2.06	15	5.7	4.6
2	SCH_3	CN	3.37	3.90		8.78	2.8	1.78	17	6.0	4.8
1	OCH_3	NO_2	3.57	3.84	5.57	8.13	6.2	5.04	14	12.2	13.1
1	NH_2	CN	3.62	3.80	6.00	8.47	4.3	2.92	20	9.5	8.4
1	$NHCH_3$	CN	3.43	3.83	5.57	8.55	3.5	2.88	27	9.2	8.3
1	$N(CH_3)_2$	CN	3.32	3.81	4.69	8.69	3.1	3.21	29	10.3	9.7
1	$NHCH_3$	NO_2	3.10	3.72	6.58	8.62	7.7	5.88	46	17.1	18.3
1	$N(CH_3)_2$	NO_2	2.98	3.70	5.75	8.77	5.7	6.19	46	18.3	20.3
1	NH_2	$COCH_3$	3.69	3.83	5.48	8.25	12.6	2.86	12	8.7	7.3
1	SCH_3	$COCH_3$	3.73	3.90	5.75	8.19	4.6	2.78	9.8 ± 2	7.1	6.7
1	SCH_3	CO_2CH_3	3.78	3.92	6.71	8.20	4.4	3.09	8	7.9	7.6
1	NH_2	CO_2CH_3	3.68	3.81	5.39	8.43	10.6	3.46	15	10.6	9.7
1	NH_2	SO_2CH_3	3.67	3.90	6.16	7.81	6.6	2.59	13	6.4	6.0
1	NH_2	$CO(\phi)$	3.52	3.92	4.47	8.48	9.9	2.68	19	7.5	6.7

[a] The M_{ge} and $\Delta\mu$ values are in D, the $\hbar\omega_{eg}$ values in eV, and the β_μ values are in 10^{-30} esu (the β_μ's are measured at 1.91 μm; the calculated values are static).

contributions but these nearly cancel each other. We have been unable to assess in detail the reason for this cancellation.[33] However, we note that positive contributions to the SOS β_μ from these other states are mainly due to configurations involving charge transfer from the donor side to the acceptor side of the molecules. Negative contributions mostly come from configurations corresponding to localized excitations, for instance excitations within the phenyl rings or excitations within the acetylenic segment involving the perpendicular π-system (negative contributions to β from the latter excitations have already been pointed out by Morley[30]).

(b) Relationship Between Electronic Properties and Second-Order Polarizability. Within the two-state model, the second-order polarizability can be conveniently described as a function of spectroscopic and excited-state properties of the molecule. The parameters in eq 3, *i.e.*, $\Delta\mu$, $(M_{ge})^2$, and $\hbar\omega_{eg}$, can be evaluated experimentally from solvatochromic effects[34] for $\Delta\mu$ and M_{ge} and from UV–visible spectra for $\hbar\omega_{eg}$.

In Table V, we compare the results obtained on the $n = 1$ and $n = 2$ compounds by the INDO/SCI technique to the experimental data reported by Stiegman *et al.*[5] From their investigations, these authors concluded that (i) the value of β is dominated by the energy of the intramolecular charge transfer (ICT) transition ($\hbar\omega_{eg}$); (ii) the effect on the β value of modifications in (square) transition dipole moments $(M_{ge})^2$ and state dipole moment differences ($\Delta\mu$) is weak; (iii) as the conjugation length (*i.e.*, the number of triple bonds) increases, the state dipole moment difference ($\Delta\mu$) decreases. We now analyze in detail the relationships between the converged β_μ values and M_{ge}, $\hbar\omega_{eg}$, and $\Delta\mu$ for molecules containing one triple bond in the conjugated path and compare our results to the experimental data in the context of the two-state model.

Relationship between β_μ and M_{ge}. The experimental and theoretical M_{ge} values are rather large and evolve little as a function of substitution. Experimentally, the M_{ge} values are measured to range between 4.47 and 6.71 D and are calculated theoretically between 7.81 and 9.08 D. These results indicate that the transition dipole moment between the ground state and the first excited state does not play a major role in the evolution of β as a function of the nature of the donor–acceptor groups. Indeed, Figures 4a and 4b show very poor linear correlations between the β values and the squared electronic transition dipole moments.

Relationship between β_μ and $\hbar\omega_{eg}$. In Figure 5, we present plots of β_μ as a function of the inverse of the squared transition energy corresponding to the ICT band $(1/(\hbar\omega_{eg})^2)$. There occurs here clearly, both for the experimental (Figure 5a) and theoretical (Figure 5b) results, a significant degree of linear relationship (correlation coefficient values of 0.95 and 0.93, respectively). Note that the theoretical values for the ICT transition energy are consistently larger than the corresponding experimental estimates. This can be explained by the fact that the experimental data are collected in solution while the INDO/SCI results are obtained on isolated molecules (gas phase). Another source of discrepancy between experiment and theory can be related to the choice of the Coulomb repulsion (γ) parameters used in the INDO method[11].

The experimental and theoretical results on push–pull diphenylacetylenes having one triple bond in the acetylene bridge confirm the well-established feature that there usually exists a strong correlation between the ICT transition energy and β.

Relationship between β_μ and $\Delta\mu$. When the dependence of β_μ on the state dipole difference $\Delta\mu$ is investigated, discrepancies surface between theory and experiment. Experimentally, it appears (see Figure 6a) that there is hardly any correlation between $\Delta\mu$ and the magnitude of β. On the contrary, a high linear correlation is obtained theoretically ($r = 0.96$) (see Figure 6b). A detailed comparison between the experimental and theoretical $\Delta\mu$ values, presented in Table V, indicates disagreement in the following cases. (i) The experimental $\Delta\mu$ values appear to be rather inaccurate when NH_2 is the donor according to Stiegman *et al.*[5] This is due to specific interactions of the amino group with the solvent used in the experiments (chloroform). (ii) Experimentally, $\Delta\mu$ for the $[SCH_3/CN]$ $n = 1$ molecule is obtained to be larger (8.0 D) than that for the $[SCH_3/NO_2]$ $n = 1$ molecule (5.4 D), even though NO_2 is usually considered to be a better acceptor group than CN. Our INDO/SCI results go in the direction opposite to experiment and are in agreement with the

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[33] We point out that when we use the Mataga–Nishimoto Coulomb repulsion parameters for the $n = 1$ and 2 compounds (ref 11), this cancellation does not occur; the two-state model β_μ values are generally larger than the converged values. Even so, however, the two-state model also provides excellent *trends* as is the case when using the Ohno–Klopman parameters.

[34] Reference 3, p 114.

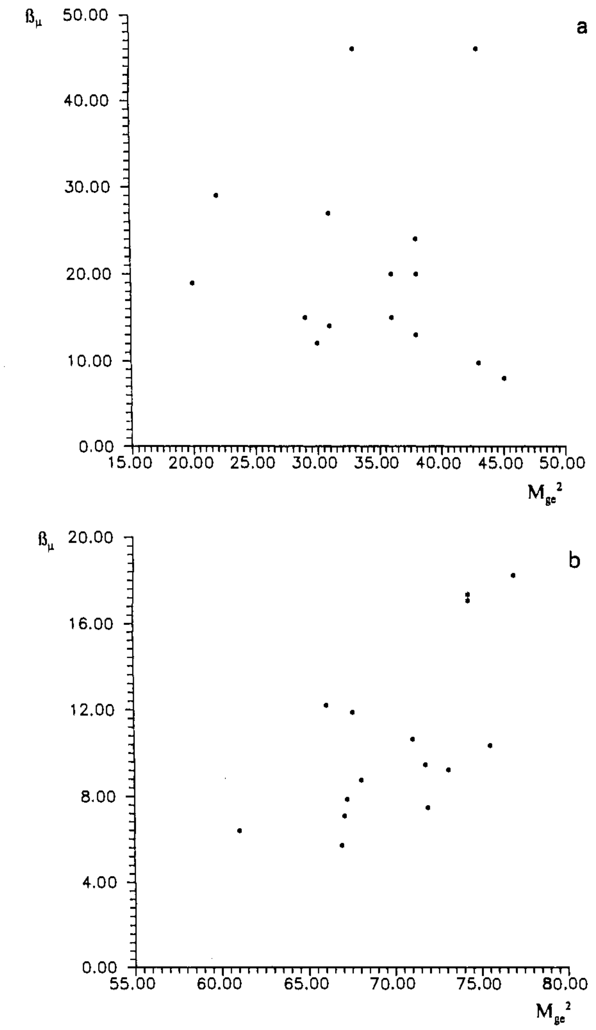


Figure 4. Plot of β_μ (in 10^{-30} esu) as a function of the square of the transition moment between the ground state and the first excited state M_{ge}^2 (in D^2): (a) experimental results and (b) INDO/SCI results.

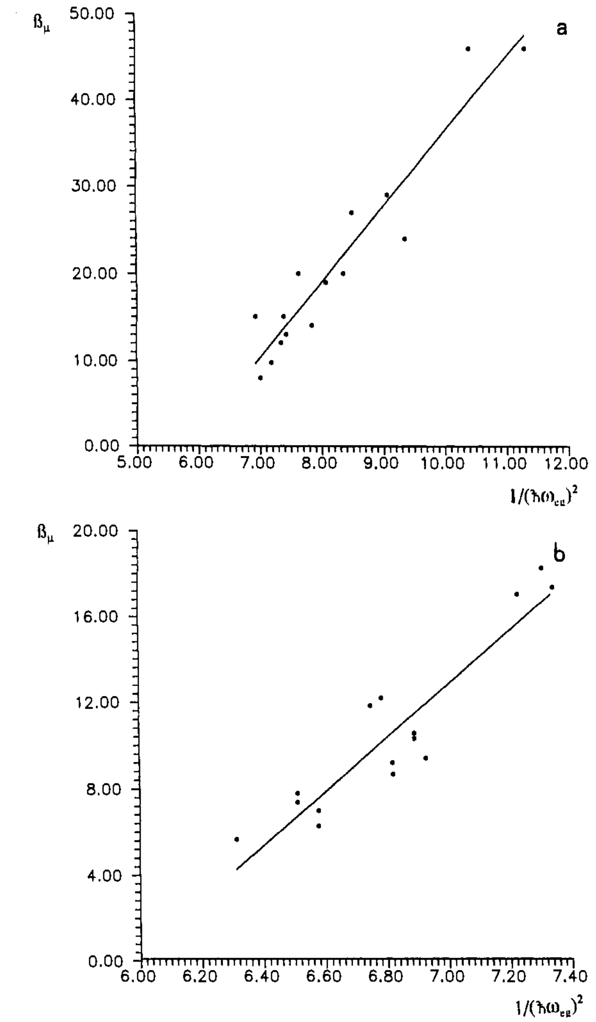


Figure 5. Plot of β_μ (in 10^{-30} esu) as a function of the inverse of the square of the first transition energy $1/(\hbar\omega_{eg})^2$ (in $eV^{-2} \times 10^2$): (a) experimental results and (b) INDO/SCI results.

larger β_μ measured and calculated for the [SCH_3/NO_2] compound. (iii) The experimental $\Delta\mu$ for the [$NH_2/COCH_3$] $n = 1$ compound is larger than that for [NH_2/NO_2] although the $COCH_3$ group is weaker an acceptor than the NO_2 group. Theoretical results give $\Delta\mu$ values of 2.86 D for the [$NH_2/COCH_3$] compound and 5.79 D for the [NH_2/NO_2] compound.

The theoretical $\Delta\mu$ values appear thus to be very reasonable and provide the expected correlation with the β values. In our opinion, the statement in ref 5 that, in push–pull diphenylacetylenes, "the dipole moment change does not correlate well with the donor–acceptor strength or with the magnitude of β" should thus be taken with caution.

To summarize the theoretical results, we obtain that both $\Delta\mu$ and the energy of the ICT transition dominate the magnitude of β. This is confirmed by plotting β as a function of $\Delta\mu/(\hbar\omega_{eg})^2$ (see Figure 7). The linear correlation is obvious and provides the highest correlation coefficient found in the present studies (0.98). Note, however, that in all cases, the value of $\Delta\mu$ remains relatively small, well below 10 D. This is consistent with our analysis of the total charge distributions in going from the ground state to the lowest, intense charge-transfer excited state.

(c) Conjugation Length Effects. Passing from $n = 1$ to $n = 2$. The theoretical results in Table V show that increasing the conjugation length from one to two triple bonds in the acetylene bridge for the [NH_2/NO_2], [SCH_3/NO_2], and [SCH_3/CN] compounds leads to a decrease in the state dipole moment difference, $\Delta\mu$. The transition energy between the ground state and the first excited state also decreases. As $(M_{ge})^2$ is little affected, the decreases in both $\Delta\mu$ and $(\hbar\omega_{eg})^2$ result in the fact that the β_μ values remain almost constant. This is in good agreement with the experimental trends reported by Stiegman *et al.*[5] When β_μ is plotted as a function of $\Delta\mu/(\hbar\omega_{eg})^2$ for the three $n = 2$ compounds, Figure 8, the linear correlation is very good, indicating the same dependence as that observed for the $n = 1$ compounds.

Passing from $n = 2$ to $n = 3$ and 4. We have also analyzed the conjugation length effect for the [NH_2/NO_2] molecules upon increasing the number of triple bonds in the acetylenic bridge to 4. So far, we have reported INDO/SCI results using the Ohno–Klopman parameterization for the evaluation of the two-electron integrals in the INDO Hamiltonian; however, in a previous work,[11] we have shown that the use of the Mataga–Nishimoto parameterization allows a better agreement with experiment in terms of the evolution of the first transition energy as a function of conjugation length. In this part of the work, we therefore make use of the Mataga–Nishimoto parameters, see Table VI.

The theoretical results in Table VI show that increasing the conjugated bridge from one to four triple bonds leads to a decrease in the transition energy between the ground state and the first excited state in excellent agreement with the experimental trends reported by Stiegman *et al.*[5] The INDO/SCI β_μ value sharply increases in going from two to three triple bonds, a feature which is also in agreement with the experimental data. On the contrary, a decrease would have been predicted when applying the two-state model. It is important to note that the same feature holds true when we use the Ohno–Klopman parameters.

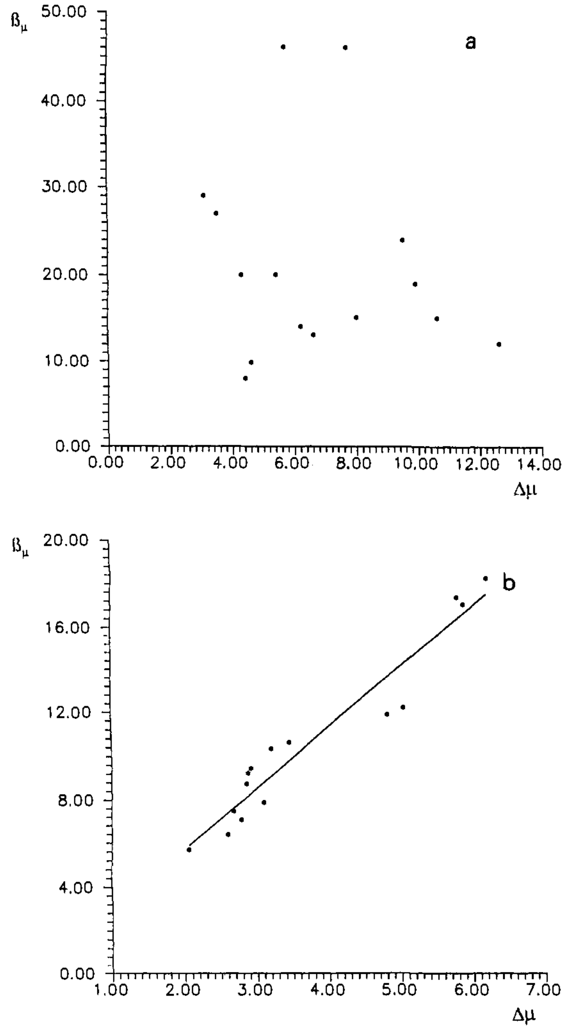


Figure 6. Plot of β_μ (in 10^{-30} esu) as a function of $\Delta\mu$ (in D): (a) experimental results and (b) INDO/SCI results.

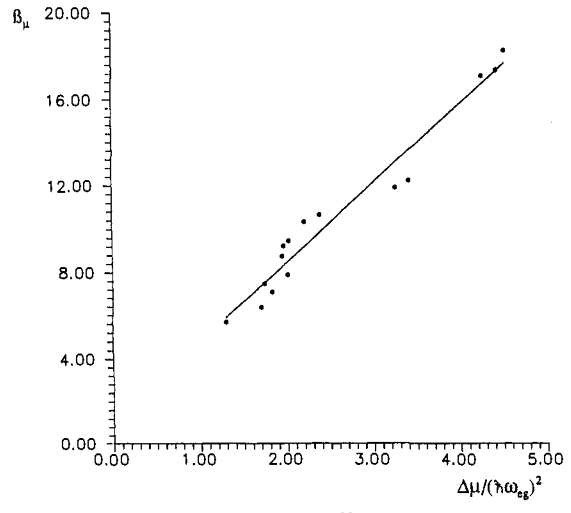


Figure 7. INDO/SCI plot of β_μ (in 10^{-30} esu) as a function of $\Delta\mu/(\hbar\omega_{eg})^2$ (in D eV^{-2} × 10) for molecules containing one triple bond in the acetylene bridge.

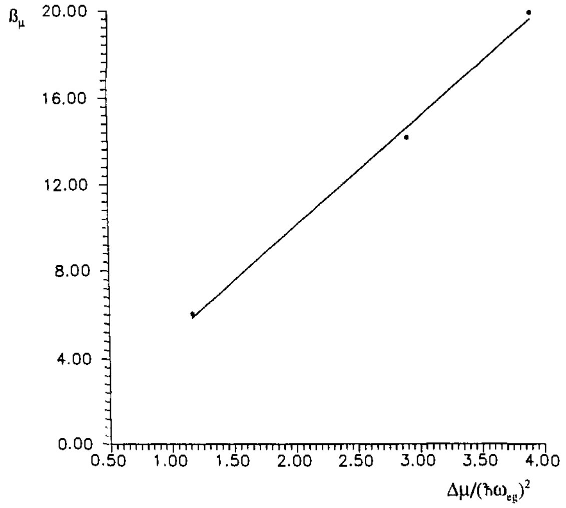
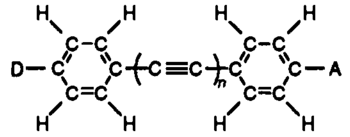


Figure 8. INDO/SCI plot of β_μ (in 10^{-30} esu) as a function of $\Delta\mu/(\hbar\omega_{eg})^2$ (in D eV^{-2} × 10) for molecules containing two triple bonds in the acetylene bridge.

Table VI. Effect of the Conjugation Length on the Calculated $\hbar\omega_{eg}$ (eV), μ_g (D), $\Delta\mu$(D), M_{eg} (D), and β_μ (10^{-30} esu) Values for the [NH_2/NO_2] Compounds Using the Mataga–Nishimoto Parameterization in the INDO Formalism[a]



n	D	A	$\hbar\omega_{eg}$	$\Delta\mu$	M_{ge}	β_μ two-state	β_μ
1	NH_2	NO_2	3.36	13.54	9.05	57.1	33.4
2	NH_2	NO_2	3.21	9.50	8.57	39.5	40.0
3	NH_2	NO_2	3.01	5.28	6.73	15.4	46.2
4	NH_2	NO_2	2.86	3.50	5.35	7.1	54.4

[a] The converged sum-over-states β_μ values are given together with those obtained when applying the two-state model.

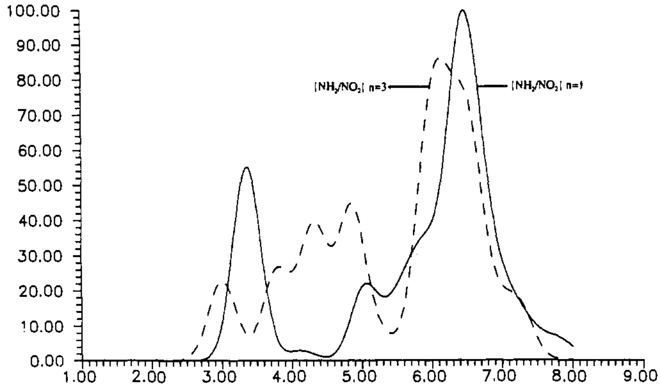


Figure 9. INDO/SCI simulation of the UV-visible spectra of the [NH_2/NO_2] $n = 1, 3$ molecules, using the Mataga–Nishimoto parameterization.

The explanation of the β_μ increase with conjugation length and the corresponding failure of the two-state model can be found in the following. We present in Figure 9 the theoretical electronic absorption spectra of the [NH_2/NO_2] $n = 1$ and $n = 3$ compounds. The spectrum simulations have been performed by convoluting the electronic transitions by Gaussians whose full width at half-maximum have been set at 0.2 eV, in order to obtain a resolution in good agreement with the experimental spectra.[5] In the $n = 1$ case, there are two main distinct peaks at 3.4 and 6.4 eV; the ICT transition at 3.4 eV dominates the β response. The situation is similar in the $n = 2$ case. If we increase the length of the conjugated segment to three triple bonds, there occurs a clustering of multiple transitions within a 4-eV span from the lowest peak whose intensity decreases; these features are in excellent qualitative agreement with the experimental data.[5] As a result of this clustering, *several states need to be taken into account to describe the β response of the molecule; the two-state model is then no longer adequate.*

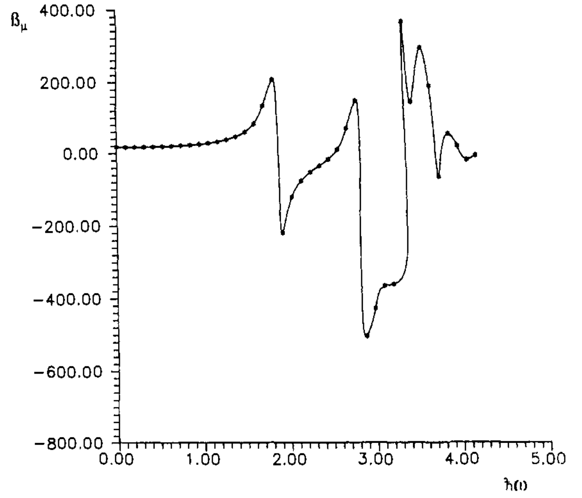


Figure 10. Frequency dependence of the INDO/SCI calculated SHG spectrum in the case of the $[NH_2/NO_2]$ $n = 2$ molecule (β_μ in 10^{-30} esu, $\hbar\omega$ in eV).

(d) Dynamic Second-Harmonic Generation Response. It is also of interest to investigate the dynamic response of the second-order molecular polarizability. This allows us to evaluate how much the static values we have discussed so far on the theoretical site evolve with optical frequency. Figure 10 illustrates the SHG response of the $[NH_2/NO_2]$ $n = 2$ molecule obtained from the INDO-SCI/SOS formalism (using the Ohno–Klopman parameters). We calculate the two-photon resonance to occur at $\hbar\omega_{eg}/2 = 1.8$ eV; experimentally, it would occur at ca. 1.6 eV. This resonance is far from the frequency used in the EFISH measurements ($\hbar\omega = 0.65$ eV) reported by Stiegman *et al.*[5] As a result, the theoretical SHG β_μ value at 0.65 eV (20.6×10^{-30} esu) is hardly different from the β_μ static value (17.3×10^{-30} esu). All the other molecules studied in this work present equivalent characteristics.

A final point to mention is that it is usually the case that "experimental" β static values are estimated on the basis of extrapolations from the measured dynamic values according to the dispersion factor in the two-state model (eq 3). Above, we have shown instances where the two-state model fails to describe the β response, *e.g.*, the $[NH_2/NO_2]$ $n = 3$ and $n = 4$ compounds. However, even in these cases, we find that the use of the dispersion factor coming from the two-state model still provides a reasonable "experimental" β_μ static value from the dynamic value.

V. Synopsis

The results of the present work show the suitability of a combined AM1 and INDO-CI/SOS approach to reproduce the geometric structure and the evolution of the second-order polarizability in donor–acceptor diphenylacetylene molecules. We obtain an excellent agreement with the data reported by Stiegman and co-workers.[4,5]

The main conclusions are as follows. (i) The geometric structure of the push–pull diphenylacetylene molecules is such that the acetylenic bridge is hardly affected by substitution and retains a strong single-bond/triple-bond alternation. (ii) The π-charge transfer all the way from the donor to the acceptor is extremely modest in the ground state and never exceeds some $0.35|e|$ in the lowest lying excited state. (iii) The transition moment to the main charge-transfer excited state is little dependent on the nature of the donor and the acceptor. However, M_{ge} decreases when the length of the molecule is increased. (iv) There is a high degree of linear correlation between β_μ and, on one hand, the inverse of the (squared) transition energy between the ground state and the first excited state and, on the other hand, the value of $\Delta\mu$. The latter feature is in contrast to the experimental data which, rather unexpectedly, indicate no correlation between β and $\Delta\mu$. Moreover, we also find that the calculated $\Delta\mu$ values correlate well with the generally accepted donor–acceptor strengths. (v) As the conjugated segment length increases from one to four triple bonds in the acetylene bridge, both the first transition energy and the state dipole moment difference $\Delta\mu$ decrease. The two-state model is shown to break down in terms of estimating the β evolution with chain length. This is due to the appearance in the larger compounds of several low-lying nearly isoenergetic excited states which all contribute significantly to the β response.

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