

Large Molecular Hyperpolarizabilities. Quantitative Analysis of Aromaticity and Auxiliary Donor–Acceptor Effects

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Abstract: The linear and nonlinear optical properties of donor–acceptor π -electron chromophores having conjugated bridges varying in aromaticity and electron excessivity are investigated using the INDO/1 semiempirical Hamiltonian. NLO response properties of such chromophores are more sensitive to the electron excessivity of the bridges than to bridge aromaticity. Electron-excessive/deficient heterocyclic bridges have lesser/greater tendency to deplete the electron density from the donor/acceptor groups and thus increase their donor/acceptor ability. Thus, electron-excessive heterocyclic bridges act as *auxiliary donors* while electron-deficient heterocyclic bridges act as *auxiliary acceptors*, significantly enhancing NLO response. Interposing charged five-membered auxiliary donor and acceptor fragments between strong donor or acceptor groups results in large computed second-order NLO response.

I. Introduction

Interaction of an intense laser field with materials produces a number of physical phenomena of interest in the field of nonlinear optics (NLO).¹ Such materials, capable of manipulating electromagnetic signals, are of potential importance in diverse technologies such as optical computing, telecommunications, information storage, etc.² Extensive research efforts have been directed toward modeling, synthesizing, and characterizing such photon-manipulating materials.^{3–5} Although to date, extended inorganic solids such as LiNbO₃, KH₂PO₄, and KTiOPO₄ have been the NLO materials of choice,^{1,6} recent studies have shown that organic molecules with extended conjugation exhibit NLO response and associated characteristics superior to the conventional inorganics.^{3–5} Important characteristics of molecular materials include ultrafast response times, low dielectric constants, better tailorability and processability, as well as large NLO responses. The bulk NLO response of such materials originates principally from the individual molecular building blocks, which considerably simplifies theoretical modeling and prediction of macroscopic NLO response.

One commonly used strategy to design π -electron chromophores for second-order NLO applications is to endcap a suitable conjugated bridge with strong electron donor and acceptor substituents.^{1e,f} Thus, an archetypical molecular chromophore used in NLO applications can be represented as D–B–A, with D the donor, B a conjugated bridge, and A an acceptor. There are then three obvious ways to optimize the NLO characteristics of such a chromophore. The first is to select a conjugated bridge and to increase the strength/number of the donor and acceptor groups.⁷ The second is to modify the nature of the conjugated bridge.⁸ Surprisingly, the types of conjugated bridges investigated experimentally to date fall mostly into relatively narrow categories, and include aromatic hydrocarbon structures such as benzene, naphthalene, thiophene, etc. and polyenes, polyynes, or some combination of these. The most widely used bridge is a combination of two phenyl fragments with an interposed polyene having two to eight carbon atoms. Such bridges, with strong donors such as an NMe₂ and acceptors such as NO₂, give rise to large second-order NLO responses.^{1d,f} The third approach is to increase the conjugation length of the bridge. A combination of these three strategies has proven successful, and most chromophores have been constructed following these strategies.

Another approach, proposed by Marder and co-workers,⁹ is to optimize the NLO response of a given molecular chromophore by distorting the nature of the conjugation itself. The question addressed in this approach is the following: given a particular donor, acceptor, and conjugated bridge, what is the best structural way to optimize the NLO response of the

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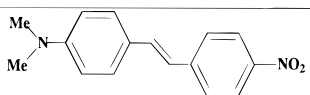
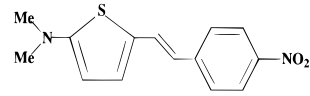
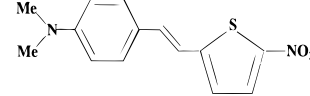
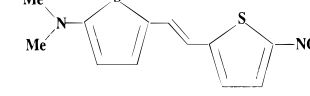
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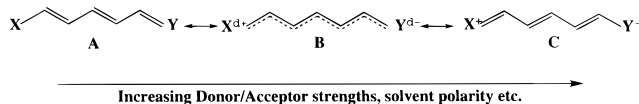
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Table 1. Experimental $\mu\beta$ Values^{11d} at an Excitation Energy of 0.65 eV for Benzenoid and Thiophene Compounds with Dialkylamino Donor and Nitro Acceptor Substituents

Chromophores		$\mu\beta$ 10^{-30} esu
Ia		580
Ib		600
Ic		660
Id		1040

chromophore? Theoretical and experimental studies have shown that large variations in NLO response result from distortion of a polyene bridge. Typical chromophores studied to substantiate this approach have been merocyanines. The conjugated bridge can be distorted from a polyenic-like structure (A) to a cyanine-like structure (B) to a polymethine-like structure (C) depending



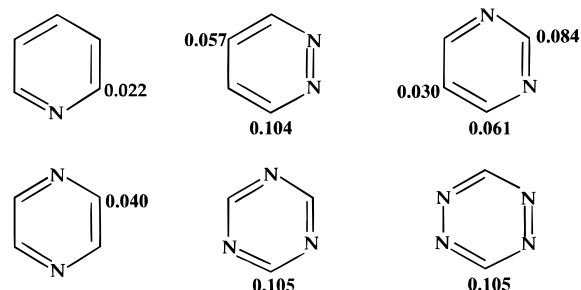
on the strength of the donor and acceptor substituents and the polarity of the solvent.^{9,10} This distortion has been indexed using the term bond-length alternation (BLA).^{9,10} It has been shown that distorting the BLA from a polyene-like structure to a polymethine-like structure tunes the NLO characteristics of the chromophore. Studies of several chromophores support this argument. However, it has also been recently shown that such large variations in NLO response properties can be observed *only* if there is a resultant stabilization, such as aromatic stabilization, of the distorted structure.¹⁰

Recent synthetic studies have shown that replacing the homocyclic ring of a chromophore bridge with heteroaromatic rings also leads to enhanced second-order NLO response properties.^{7ab,11} For example, Jen et al. showed that replacing a homocyclic bridge, such as benzene, in 4-(*N,N*-dimethylamino)-4'-nitrostilbene (DANS, **Ia**) by a heterocyclic bridge, such as thiophene (**Ib–Id**), can lead to enhanced molecular hyperpolarizabilities (Table 1).^{11a,b} While several chromophores have been synthesized to demonstrate this aspect of NLO chromophore design, neither the theoretical basis nor the molecular origin of such an enhancement has yet been clearly and quantitatively defined. In most studies, it has been speculated that the thiophene acts as an additional donor in the bridge. It could also be possible that the reduced aromaticity of the thiophene compared to the benzene ring might result in enhanced molecular hyperpolarizability. A computational study

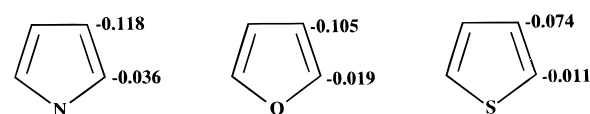
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π -Deficient Heterocycles



π -Excessive Heterocycles

**Figure 1.** Six- and five-membered heteroaromatic systems investigated in this paper. The classification of the systems is based on the ring carbon electron density. Hückel charge densities are also given.

by Jen et al.¹² shows that increased bridge electron density enhances the NLO coefficient. However, an in-depth understanding of the origin of the response variation with either the electron density or the aromaticity of five-membered ring bridge architectures is not yet available. Thus, a proper theoretical analysis of the two effects should be useful in designing new generations of chromophores with enhanced NLO responses.

In this paper, we investigate the effects of modifying both aromaticity and electron excessivity of chromophore bridges and study the effect of both on the linear and NLO properties of a number of linear, quasi-one-dimensional chromophore structures. In section II, we briefly introduce the concepts of electron excessivity and electron deficiency in heterocyclic systems and discuss how they can affect the molecular NLO response. We then define an aromaticity criterion and show how it affects NLO properties. Next, we briefly outline the computational methodology used to compute NLO response properties. NLO properties analyzed are the frequency-dependent polarizability and the second harmonic generation (SHG) coefficients. In section III, we present the results of our calculations and scrutinize the molecular origins of the enhanced NLO responses in these heterocyclic systems. This leads to the useful concepts that electron-excessive heterocycles act as auxiliary donors and electron-deficient ones act as auxiliary acceptors.

II. Issues and Computational Methodology

A. Electron Excessivity and Electron Deficiency. Heterocyclic five- and six-membered ring systems have generally been divided into two classes reflecting the electron density on the ring skeletal carbon atoms.¹³ A simple Hückel estimation¹⁴ of the electron density on the various atoms in five-membered aromatic heterocycles shows that there is an excess of electron density on the ring carbon atoms, and hence these molecules are called electron-excessive or electron-rich systems.¹³ Similarly, six-membered aromatic heterocyclic systems are termed electron-deficient because of the carbon atom electron deficiency.¹³ In Figure 1, Hückel-derived carbon atom electron densities and the

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Table 2. The C_{α} Atom π -Charge Density ($\rho(C_{\alpha})$) and Electron Excessivity/Deficiency ($\rho(C)$), Given by the Total Electron Density on the Carbon Atoms of the Heterocycle) and the Julg Aromatic Stability Index (A) in the Ground State of Various Five- and Six-Membered Ring Systems^a



X	$\rho(C_{\alpha})$	$\rho(C)$	A^b
CH ⁻	-0.200	-0.8	1.00 (1.00)
SiH ⁻	-0.107	-0.539	0.94 (0.93)
NH	-0.090	-0.331	0.97 (0.97)
S	-0.044	-0.135	0.92 (0.95)
O	-0.050	-0.179	0.88 (0.90)
PH	-0.105	-0.401	0.81 (0.79)
CH ₂	-0.019	-0.068	0.49 (0.68)
benzene	0.000	0.000	1.00
pyridazine	0.065	0.218	0.71
s-tetrazine	0.142	0.283	0.63

^a Results are from ZINDO computations. The *ab initio* Julg aromatic stability indices calculated by Schleyer et al.²⁴ are given in parentheses. ^b In eq 1, as given in ref 20 there is a dimensional inconsistency in the second term. Our actual calculations used Δq_i and d_i in atomic units.

corresponding classifications for some typical heterocyclic systems are presented. This simple calculation shows that the order in which the electron excessivity varies is pyrrole > furan > thiophene > benzene, the last of which is neither excessive nor deficient. The electron deficiency follows the order tetrazine \approx triazine > diazine > pyridine > benzene. Although this electron density order accords with speculation that increased bridge electron density, as might be achieved by introducing a heterocyclic fragment, could lead to enhanced chromophore NLO response properties, the exact mechanism by which this might occur is not obvious. To investigate the origin of the increased NLO response with increased bridge electron density, the electron densities of the π -frameworks of a series of unsubstituted five- and six-membered ring systems and of the corresponding NH₂- and NO₂-substituted systems are computed using the semiempirical INDO/1 Hamiltonian (as coded in the ZINDO package¹⁵) and analyzed. The geometries of all these molecules were optimized using the AM1 model Hamiltonian¹⁶ in the MOPAC quantum chemical package.¹⁷

ZINDO-derived electron densities (the difference between the computed charge density on the atoms and the number of π -electrons donated by the atom to the π -framework) on the carbon atoms of a series of five- and six-membered ring systems are presented in Table 2. The α -carbon atom electron density mirrors the electron richness of the five-membered ring systems and the electron deficiency of the six-membered ring systems. All the aromatic five-membered ring systems are electron excessive. Similarly, the six-membered rings are electron deficient, but only if the heteroatom is more electronegative than carbon. If a donor such as NH₂ is attached to the α -carbon, because of the intrinsic electron richness/deficiency of the ring carbon atoms to which the donor group is attached, the transfer of electron density from the N atom will be reduced/augmented. This will enhance/diminish the donor ability. Thus, appending a donor substituent to the α -position of an electron-deficient ring should reduce the donor ability of the donor substituent and hence decrease the NLO response property. Similarly, appending a donor to the α -position of an electron-rich ring should have the opposite effect.

To illustrate this modulated donation, the total electron excessivity/deficiency ($\rho(C)$), presented in Table 2 for the various five- and six-membered ring systems, is plotted versus the donor and acceptor abilities of the NH₂ and NO₂ groups in the corresponding substituted chromophores (Figure 2). Here the donor ability is indicated by the π -electron density on the N atom and acceptor ability is indicated by

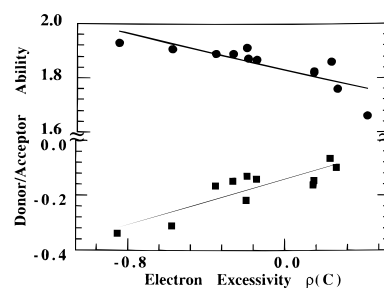
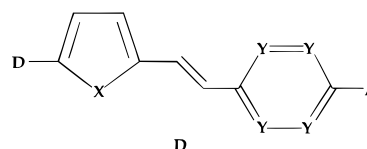


Figure 2. Variation of NH₂ donor (closed circles) and NO₂ acceptor (closed squares) substituent abilities as a function of the electron excessiveness/deficiency of the carbon atoms of appended five- and six-membered heterocyclic ring systems. The donor ability is indexed by the π -charge density on the N atom of the NH₂ group, and the acceptor ability is indexed by the π -charge density on the NO₂ group minus 4, the number of electrons donated by the NO₂ group to the π -framework of the chromophore. Some antiaromatic compounds (X = AlH, BH, CH⁺ in Table 2) are also included.

the total π -electron density on the NO₂ group minus 4.0, the number of electrons contributed by the NO₂ group to the π -framework. As the heterocycle electron excessivity decreases (negative values indicate more excessive heterocycles, and positive values indicate less excessive heterocycles), the substituent donor ability decreases since donation to the heterocyclic ring increases. Similarly, as the excessivity decreases, the acceptor ability of the NO₂ substituent increases. Thus, it indeed appears that the electron-excessive/deficient heterocycles weakly/strongly withdraw charges because of their electron excessivity/deficiency. The present picture is considerably different from the idea that electron-rich heterocycles potentially behave as additional donor substituents and that six-membered heterocycles behave as additional acceptors. The actual effect is that *electron-rich/poor ring systems weakly/strongly withdraw excessive electron density from the donor substituent through inductive effects, thereby increasing/decreasing the donor ability of the donor*. Thus, the nomenclature *auxiliary donor* for electron-excessive heterocycles and *auxiliary acceptors* for electron-deficient rings is suggested here.

Electron excessivity and deficiency ideas have been previously used in several contexts.^{18,19} Zhou et al. demonstrated¹⁸ that polymers with π -excessive thiophene and π -deficient pyridine or bipyridine exhibit fluorescence spectra that support intramolecular charge transfer in conducting polymers. Reinhardt et al. studied¹⁹ NLO chromophores where the electron-excessive aromatic heterocycles themselves act as donors and electron-deficient aromatic heterocycles act as acceptors. In this paper, we next examine archetypical chromophores with an arrangement such as **D**, where X = CH⁻, NH, O, S, SiH⁻, PH, or CH₂



and Y = CH, or N. Electron excessivity ideas have been used to construct chromophore bridges in which the heterocyclic moieties act as auxiliary donors and acceptors, thereby increasing the NLO response. Thus, according to the present idea, a bridge in which pyrrole is the auxiliary donor and tetrazine is the auxiliary acceptor should, a priori, afford the largest NLO response. The NLO properties of such structures will be analyzed in section III.

B. Aromaticity. There are a number of criteria to define the aromaticity of organic molecules,²⁰ with energetic, structural, and magnetic criteria most commonly used. Katritzky et al.²¹ postulated that the structural and energetic concepts are mutually orthogonal to

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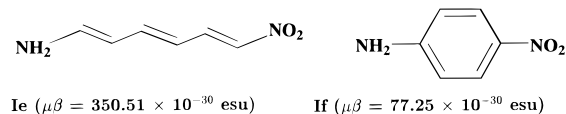
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the magnetic concepts, and that there are at least two types of aromaticity. However, strong proof for linear relationships among energetic, geometric, and magnetic criteria was recently provided by the *ab initio* calculations of Schleyer et al.²⁴ We have chosen a modified Julg aromaticity index (*A*),²⁰ which defines the aromaticity of organic molecules on the basis of bond-length deviations and charge gradients on the constituent atoms, given by^{20b}

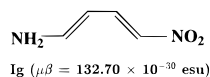
$$A = \left[1 - \frac{225}{N} \sum_i^N \left(\frac{d_i - d}{d} \right)^2 \right] \prod_i^N \left[1 - \left(\frac{\Delta q_i}{d_i} \right)^2 \right] \quad (1)$$

where *N* is the number of C–C bonds, *d_i* is the C–C bond length, *d* is the average C–C bond length, and Δq is the difference in charge density of adjacent carbon atoms. This index is particularly useful in heterocyclic molecules, since it includes the charge gradient in addition to the bond lengths. Note that eq 1 is somewhat different from the Julg aromaticity index expression used by Schleyer et al., which contains only heterocyclic bond lengths and neglects the second part of eq 1, which contains a charge gradient over the CC bond between atoms *i* and *j*.

Although most of the potential organic chromophores used in NLO applications contain an aromatic moiety such as benzene or a heterocyclic ring, a number of theoretical and experimental investigations suggest that nonaromatic bridges such as polyenes, cumulenes, and polyynes exhibit much larger NLO response properties than comparable aromatic analogues.^{7–9} For example, the INDO-derived second hyperpolarizability of 1-(dimethylamino)-6-nitro-*trans*-hexa-1,3,5-triene (**Ie**) is $\sim 5 \times$ larger than that of the aromatic counterpart *p*-nitroaniline (*p*-NA; **If**). The values in parentheses are the INDO-



derived $\mu\beta$ parameters at a fundamental excitation energy of 0.1 eV. The INDO-derived values are in good agreement with those obtained by other calculations.^{8e,12d} Although the larger NLO response of **Ie** has been attributed to the molecular length, it is not obvious whether length alone can account for such large NLO response properties. If length were the only criterion, it is difficult to rationalize the larger NLO response of 1-(dimethyl amino)-4-nitro-*cis*-buta-1,3-diene (**Ig**),



the molecular length of which is almost identical to that of *p*-NA. The smaller response of *p*-NA could be rationalized by the difficulty of polarizing an aromatic bridge, the electron delocalization of which is mainly restricted to the ring. This implies that when the bridge has greater aromatic character, polarization of the electrons by an external field becomes more difficult since the electrons tend to be localized in the rings: this would reduce NLO response. Thus, according to this

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criterion, a molecular architecture with less bridge aromatic stabilization should lead to greater NLO response.

The effect of aromaticity on the molecular hyperpolarizability can be understood in terms of the classical two-level model²² (eq 2). Here

$$\beta_{\text{two-state}} = \frac{3e^2}{2\hbar^3} \frac{\omega_{gfg} f_{ge} \Delta\mu_{ge}}{[\omega_{ge}^2 - \omega^2][\omega_{ge}^2 - 4\omega^2]} \quad (2)$$

ω_{ge} represents the optical transition energy to the lowest excited state, f_{ge} the associated oscillator strength, $\Delta\mu_{ge}$ the difference between the ground and excited state dipole moments, and ω the excitation energy of the light field. It can be seen that enhanced NLO response can be obtained by lowering the transition energy or increasing the transition moment or the change in dipole moment, $\Delta\mu$. It was proposed by Dirk et al.²³ that replacing a benzene ring with a heterocyclic ring such as thiazole reduces the resisting aromatic delocalization in the highly aromatic benzene ring and hence leads to an increase in the electron transmission between the donor and acceptor groups, increasing both the transition moment and change in dipole moment. Thus, a less aromatic bridge should lead to larger NLO response properties. Support for this aromaticity effect comes from the fact that the SHG coefficient of **Ia** is increased when either or both benzene rings are replaced by a less aromatic thiophene ring (**Ia** \rightarrow **Ib**, **Ic**, **Id**; Table 1).^{11b,c} While replacing an aromatic moiety such as benzene by a nonaromatic moiety such as a polyene, polyyne, or cyclopentadienyl cation could lead to substantially lower thermal/chemical stability, aromatic heterocyclic rings have the advantage that, while there is a reduction in the energy cost to break the aromatic stabilization, substantial thermodynamic stabilization remains.

For preliminary analysis, the molecular Julg aromaticity indices, calculated for optimized geometries, and the charge densities are presented in Table 2. There is a good agreement with the aromaticity indices (values in parentheses) recently computed by Schleyer et al.²⁴ This mirrors the good agreement of geometries obtained from the present AM1-level calculations and *ab initio*-derived geometries.²⁴ The discrepancies in the Julg parameters for several of the heterocycles arises from the difference in the formulas used to compute the Julg parameters (second term in eq 1). The first observation apparent in Table 2 is that *variation in the aromaticity of the five-membered ring systems in general parallels variation in electron richness*. Even though a linear relationship between the aromaticity index and electron excessivity is not observed, the aromaticity index generally decreases with a decrease in electron excessivity. This is reasonable because the aromaticity index defined in eq 1 depends on the heterocyclic ring carbon atom electron densities. However, some discrepancies are observed. For five-membered rings, for example, although the PH heterocycle is more electron-rich than furan, pyrrole, or thiophene, the latter are more aromatic. For six-membered heterocycles, the electron deficiency increases with a decrease in aromaticity. Thus, for six-membered heterocycles, both aromaticity and electron density effects appear to track, but this is not so in the case of aromatic five-membered heterocycles. Thus, quantitatively analyzing the effects on NLO response of attaching donor/acceptor groups to a five-membered ring in a typical chromophore of type **D** should elucidate differences or similarities between aromaticity and electron density effects and hyperpolarizability.

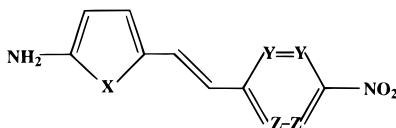
C. Computational Details. The NLO properties are computed via the computationally efficient correction vector method, using the INDO/1 Hamiltonian. This method is more efficient than the commonly used sum-over-states (SOS; uncoupled Hartree–Fock) scheme, but the results are identical, if the summation is carried over all the states obtained from the configuration interaction matrix. The correction vector method and the small matrix algorithm used to solve the linear equations are given elsewhere.^{10,25,26}

III. Results and Discussion

A. Electron Density Criterion. The linear and NLO response properties of a chromophore series sequentially varied

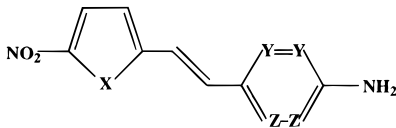
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Table 3. Linear and NLO Response Properties of AM1-Optimized Chromophore set **II**^a

chromophore	X	Y	Z	λ_{\max} (nm)	$\Delta\mu$ (D)	α_{ex} (10^{-23} esu)	β_{vec} (10^{-30} esu)	$\mu\beta$ (10^{-48} esu)
IIa	CH=CH	CH	CH	363.2 (402) ^b	15.03	49.95 (3.2) ^b	31.72 (40.0) ^b	281.63
IIb	CH=CH	N	CH	339.0	5.07	29.58	12.66	138.83
IIc	CH=CH	N	N	340.2	4.41	29.05	10.72	117.27
IId	S	CH	CH	402.1 (460) ^c	14.04	51.88	43.89	429.17 (480) ^d
IIe	S	N	CH	422.6	12.99	54.17	53.81	524.65
IIf	S	N	N	449.3	11.86	60.59	72.22	877.61
IIg	O	CH	CH	409.9	13.65	50.79	46.60	421.67
IIh	O	CH	N	425.0	13.16	51.21	53.17	487.26
IIi	O	N	N	451.8	11.97	59.41	69.78	821.16
IIj	NH	CH	CH	418.0	15.57	53.68	55.67	500.21
IIk	NH	N	CH	429.9	11.17	54.57	62.49	570.71
III	NH	N	N	461.4	12.66	62.39	83.42	979.95

^a The NLO coefficients are calculated at a nonresonant excitation energy of 0.1 eV. ^b Experimental values for CHCl₃ solutions in parentheses are from ref 7a. The experimental excitation energy is 0.65 eV. ^c The experimental value for dioxane solutions in parentheses is from ref 11e. ^d The experimental $\mu\beta_0$ for dioxane solutions in parentheses is from ref 11e.

Table 4. Linear and NLO Response Properties of AM1-Optimized Chromophore set **III** Calculated at a Nonresonant Excitation Energy of 0.1eV

chromophore	X	Y	Z	λ_{\max} (nm)	$\Delta\mu$ (D)	α_{ex} (10^{-23} esu)	β_x (10^{-30} esu)	$\mu\beta$ (10^{-48} esu)
IIIa	CH=CH	CH	CH	363.2	15.03	49.95	31.72	281.63
IIIb	CH=CH	N	CH	356.0	10.65	47.13	25.36	227.75
IIIc	CH=CH	N	N	355.3	9.93	48.59	20.80	182.08
IIId	S	CH	CH	424.2 (498) ^a	10.67	57.25	45.02 (98) ^a	459.49
IIIe	S	N	CH	418.5	9.65	54.25	36.14	411.43
IIIf	S	N	N	416.6	8.56	56.53	31.08	314.36
IIIg	O	CH	CH	423.7 (478) ^a	10.66	52.40	37.47 (83) ^a	373.93
IIIh	O	N	CH	414.2	9.75	48.44	27.74	341.17
IIIi	O	N	N	410.8	9.65	50.46	23.23	233.62
IIIj	NH	CH	CH	416.5	10.46	53.60	33.48	340.39
IIIk	NH	N	CH	409.3	9.52	49.93	24.40	307.33
III	NH	N	N	408.1	6.67	39.42	14.20	128.16

^a Experimental values for CHCl₃ solutions in parentheses are from ref 7a. The experimental excitation energy is 0.65 eV.

in electron excessivity and deficiency are presented in Tables 3 and 4. In these chromophores, the bridges are comprised of two aromatic rings separated by an ethylenic moiety. In one ring, the electron excessivity, increasing from benzene to pyrrole, is varied, and in the other ring, the electron deficiency, increasing from benzene to tetrazine, is varied. In set **II**, a donor substituent is appended to the electron-excessive ring and an acceptor group to an electron-deficient ring. This pattern is reversed in set **III**.

The calculated properties of chromophore set **II** are compiled in Table 3. The table shows that an increase in both the electron deficiency and electron excessivity leads to bathochromic shifts in the absorption spectra, with the maximum shifting from 363 nm for **IIa** to 461 nm for **III**. The NLO response also increases with an increase in electron excessivity on the donor terminus and electron deficiency on the acceptor terminus. For example, keeping the electron-deficient center fixed and increasing the electron excessivity of the electron-rich rings from benzene to pyrrole effects an SHG coefficient increase ranging from 90% when the electron-deficient center is benzene to $\geq 700\%$ when the electron-deficient center is tetrazine. A similar but smaller increase in the SHG coefficient is observed when the electron-excessive ring is held constant and the electron-deficient center

is varied from benzene to tetrazine. This effect is pronounced when the electron-rich center is weaker and is not significant when the electron-rich center is benzene. A combination of the two effects results in an almost 3-fold increase in the SHG coefficient, as observed on proceeding from **IIa** to **III**. Where available, the experimental data for these chromophores support this conjecture.⁷

The variation in the NLO response properties of chromophore set **II** does not parallel the variation in $\Delta\mu$. For example, in all the chromophores, $\Delta\mu$ decreases when a benzene ring is replaced by an electron-deficient diazine or tetrazine ring. However, a small increase in $\Delta\mu$ is observed when a benzene ring is replaced by an electron-rich pyrrole, but not when the electron-rich center is a furan or thiophene. From the two-level model (eq 2) it would be expected that, in general, a decrease in $\Delta\mu$ should result in a decrease in the SHG coefficient. However, in the present case the decrease in $\Delta\mu$ is also accompanied by a large decrease in the optical gap which in turn effects an increase in the SHG coefficient. The lowering of $\Delta\mu$ as more N atoms are added to the benzene ring is expected as the charge transfer from the donor group is quenched by an electronegative N atom at the *ortho* position.

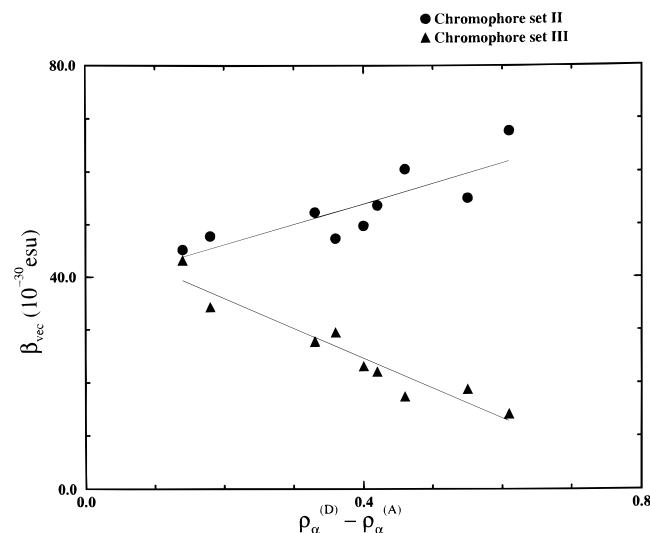


Figure 3. Variation of the NLO response properties of chromophore sets **II** and **III** as a function of the difference in electron excessivity of the donor-end and acceptor-end heterocycles. Here $\rho^{(D)}$ and $\rho^{(A)}$ represent the electron excessivity/deficiency of the auxiliary donor/acceptor substituents, respectively.

The response properties of chromophore set **III** presented in Table 4, clearly show a trend in NLO coefficients opposite that observed for set **II** in Table 3. There is a general decrease in the NLO response with an increase in the electron deficiency and electron excessivity. This result is intuitively reasonable since both electron deficiency and electron richness act against the charge transfer in these chromophores. In such an arrangement, the electron-rich center reduces the acceptor ability of the acceptor substituent and the electron-deficient center reduces the donor power of the donor substituent. A combination of the two effects results in an almost 2-fold reduction in the SHG coefficient. Thus, a comparison of the NLO coefficients of chromophore sets **II** and **III** clearly supports the arguments presented in section II.A: the most efficacious bridge is one in which the donor group is attached to the electron-rich center and the acceptor group is attached to the electron-deficient center. Additionally, it can be seen that *the effect of the electron-rich ring (auxiliary donor) is far stronger than that of the electron-deficient ring (auxiliary acceptor)*. Of the three electron-rich five-membered heterocycles examined, pyrrole, which is most electron-rich, clearly has the strongest effect on the NLO response properties.

In Figure 3, the variation of NLO response properties of chromophore sets **II** and **III** is plotted as a function of the difference in electron excessivities of the donor-end and acceptor-end heterocycles. In this figure, $\rho^{(D)}$ and $\rho^{(A)}$ are the electron densities of the bridge auxiliary donor and acceptor, respectively. It can be seen from the figure that while NLO response properties of chromophore set **II** increase with an increase in electron excessivity, those of chromophore set **III** decrease. This increase in electron density on the heterocyclic ring acts as an auxiliary donor and hence leads to an increase in NLO response properties.

B. Aromaticity. While the electron density criterion explains the NLO properties of the majority of the chromophores in Table 3, significant discrepancies are observed in Table 4. For example, replacing the benzene ring at the acceptor end of the chromophore with an electron-rich thiophene, furan, or pyrrole fragment also leads to an increase in the NLO response. While this is difficult to explain exclusively on the basis of electron density arguments, it can be easily understood on the basis of aromaticity arguments: the NLO response increases

Table 5. NLO Response Properties of Donor–Acceptor Five-Membered Ring Systems (Chromophore Set **IV**) Calculated at an Excitation Energy of 0.1 eV^a

chromophore	X	β_x (10^{-30} esu)		
		D = NH ₂ , A = NO ₂	D = NH ₂ , A = H	D = H, A = NO ₂
IVa	CH ⁻	7.32	0.61	8.94
IVb	NH	5.59	1.07	7.08
IVc	S	5.49	1.39	6.04
IVd	O	5.42	1.01	5.54
IVe	SiH ⁻	7.71	0.76	12.04
IVf	PH	6.17	0.63	5.66
IVg	CH ₂	6.04	1.39	5.85
If	CH=CH	10.2	1.59	4.03
Ig		14.04	2.23	4.92

^a See the text for details on the geometries.

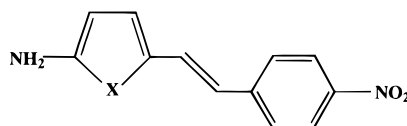
with decreasing optical gap (decreasing aromaticity). The decrease in the optical gap can also be associated with the decrease in aromaticity as discussed in section II.B. Such variation in the NLO response is also found in the case of six-membered heterocyclic systems when the donor group is attached to the phenyl fragment.

To obtain a better understanding of the interplay of these effects, the linear and NLO properties of a series of donor–acceptor systems having a five-membered heterocyclic bridge, varying both in electron richness and aromaticity, were computed (chromophore set **IV**).²⁷ The aromatic stability index presented in Table 2 was used as a guideline to vary the aromaticity. The results are presented in Table 5. We first focus on the nonaromatic polyene **Ig** and on *p*-NA (**If**), the archetypical chromophore having the most aromatic ring. It is difficult to explain the large NLO response properties of these chromophores on the basis of electron density arguments. Neither **Ig** nor *p*-NA are electron-excessive; however, they exhibit far larger NLO coefficients than the most electron-excessive bridges. However, the aromaticity criterion explains the large NLO response of **Ig** compared to *p*-NA, as well as the response of chromophores with cyclopentadienide, pyrrole, thiophene, and furan bridges.

If we focus only on five-membered rings, the results clearly demonstrate the dominance of electron excessivity over aromaticity. For example, Table 5 shows that substituting an electron-excessive heterocyclic with a donor substituent results in a diminution of NLO response, while substituting an electron-deficient heterocycle by a donor results in enhancement. Similarly, attaching an acceptor to an electron-excessive ring results in an enhancement, while a reversed substitution pattern results in a smaller NLO response. It is also found that both phenyl and butadiene bridges exhibit a small response when functionalized with a single donor or acceptor substituent. Although the NLO response of donor-substituted heterocycles increases with a decrease in aromaticity, this is not the case when the substituent is an acceptor. This observation lends strong support to the importance of electron excessivity effects. The NLO response properties of single donor- or single acceptor-substituted chromophores presented in Table 5 appear to contradict the donor/acceptor ability variation presented in Figure 2. From Figure 2 it would be expected that substituting an electron-excessive ring with a donor should lead to an

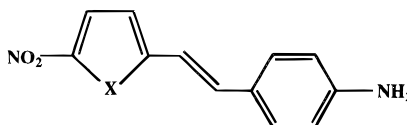
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Table 6. Linear and Nonlinear Optical Properties of AM1-Optimized Chromophores (Chromophore Set V)^a

chromophore	X	λ_{\max} (nm)	$\Delta\mu$ (D)	α_{xx} (10^{-23} esu)	β_x (10^{-30} esu)		$\mu\beta$ (10^{-48} esu)
					optimized	planar	
Va	CH ⁻	587.7	12.16	137.66	237.80	632.15	<i>b</i>
Vb	NH	418.0	15.57	53.68	55.67	58.74	500.21
Vc	S	402.1	14.04	51.88	43.89	48.29	429.17
Vd	O	409.9	13.65	50.79	46.60	45.19	421.67
Ve	SiH ⁻	604.2	12.65	136.41	263.74	452.64	<i>b</i>
Vf	PH	401.8	15.02	50.38	45.90	94.59	459.20
Vg	CH ₂	414.4	14.24	51.98	51.45	54.17	473.50

^a The NLO coefficients are computed at a nonresonant excitation energy of 0.1 eV. ^b Since the dipole moment for a charged species is gauge-dependent, $\mu\beta$ is not defined.

Table 7. Linear and Nonlinear Optical Response Properties of AM1-Optimized Chromophore Set VI^a

chromophore	X	λ_{\max} (nm)	$\Delta\mu$ (D)	α_{xx} (10^{-23} esu)	β_x (10^{-30} esu)		$\mu\beta$ (10^{-48} esu)
					optimized	planar	
VIa	CH ⁻	440.3	3.75	64.71	14.66	6.63	<i>b</i>
VIb	NH	416.5	10.46	53.60	33.48	29.78	340.39
VIc	S	424.2	10.67	57.25	45.02	41.55	459.49
VI d	O	423.7	10.66	52.40	37.47	32.46	373.93
VIe	SiH ⁻	427.4	1.59	74.80	11.56	3.40	<i>b</i>
VI f	PH	434.0	8.39	68.05	39.24	34.94	392.74
VI g	CH ₂	426.1	11.08	52.04	37.41	40.27	337.91

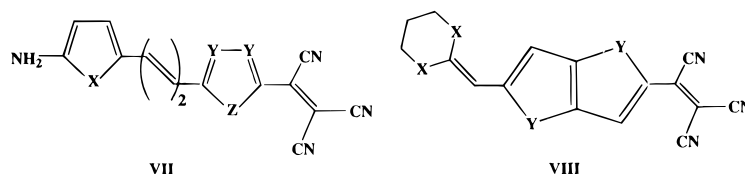
^a The NLO coefficients are calculated at a nonresonant excitation energy of 0.1 eV. ^b Since the dipole moment for a charged species is gauge dependent, $\mu\beta$ is not defined.

increase in the NLO response as the donor strength increases. However, when single donor or acceptor groups are appended to the heterocycles, the rings themselves become the acceptor or donor. For example, when the cyclopentadienide anion fragment is functionalized with an NH₂ group, the cyclopentadienide anion is the acceptor, and since it is a poor acceptor, a very small NLO response is obtained. On the other hand, when cyclopentadienide acts as a donor, which is the case when NO₂ is the substituent, a large NLO response is obtained. Comparing directly chromophores from Tables 3 and 4 permits a focus on charge effects isolated from aromaticity, since the same intervening bridges (same aromaticity) are found for pairs such as **IIIa** and **IIa** or **IIIk** and **IIk**. We see, by direct comparison, that, in most cases, and for all cases with large variation in substituent characteristics, the $\mu\beta$ parameters for chromophores in Table 3 (electron-excessive ring on the donor end) are greater than those for the corresponding chromophores in Table 4 (electron-excessive ring on the acceptor end).

To further distinguish aromaticity from electron density effects on the NLO coefficients, additional chromophores having stilbene-like bridges and in which one phenyl ring is replaced by a five-membered heterocyclic ring were studied. An acceptor group is substituted at the phenyl ring and a donor group at the five-membered heterocyclic ring (chromophore set V, Table 6). This substitution pattern is reversed in chromophore set VI (Table 7). In these chromophores, unlike sets **II** and **III**, both the electron excessivity and the aromaticity of the five-membered rings are varied. If the electron density of the five-membered ring plays an important role, chromophores in which the electron-rich rings are functionalized by an acceptor should

have small NLO responses and those in which the electron-rich rings are functionalized with an electron donor should have enhanced NLO responses, irrespective of the aromaticity of the five-membered ring system. The linear and NLO response properties of the AM1 and idealized planar geometries of chromophore sets V and VI are presented in Tables 6 and 7, respectively. In Table 6, it is seen that the NLO coefficients of these chromophores are influenced more by the bridge electron density than by aromaticity. For example, the X = CH⁻ and SiH⁻ chromophores, which have the highest electron excessivity (Table 2), exhibit the largest NLO coefficients, and thiophene, which is the least electron-excessive of the aromatic heterocycles, exhibits the smallest NLO coefficient. (Related calculations show that the NLO coefficients of the anti-aromatic rings also follow the electron density criterion.) Similarly, in chromophore set V, the most electron excessive X = CH⁻ and SiH⁻ systems exhibit extremely small NLO coefficients, and the least electron-excessive thiophene system exhibits the largest NLO coefficients in the aromatic systems.

On the basis of the above patterns, we computed the linear and NLO properties of a series of chromophores known to exhibit large NLO responses (**VII** and **VIII**; Table 8).^{11,12,28} These chromophores were modified on the basis of the auxiliary donor and acceptor principles presented in the earlier paragraphs to yield chromophores exhibiting larger NLO response properties. From Table 8, it can be seen that NLO responses of chromophores constructed incorporating the present electron excessivity and deficiency principles are far larger than the NLO responses those that do not. For example, replacing a benzene ring in chromophore **VIIa** by a pyrrole ring on the donor end

Table 8. Linear and NLO Response Properties of AM1-Optimized and Planar Geometries of Chromophore Sets **VII** and **VIII** at an Excitation Energy of 0.1eV

chromophore	X	Y	Z	λ_{\max}		$\Delta\mu$ (D)		β_x (10^{-30} esu)		$\mu\beta$ (10^{-48} esu)	
				optimized	planar	optimized	planar	optimized	planar	optimized	planar
VIIa	CH=CH	CH	CH=CH	387.3	408.7	16.62	16.18	39.37	61.32	339.1	563.7
VIIb	CH=CH	CH	S	471.5	482.9 (662) ^a	12.30	11.18	71.59	87.53	670.8	877.4 (4146) ^b
VIIc	CH=CH	CH	N	468.8	469.3	10.90	10.29	64.94	67.15	703.4	749.7
VIIId	S	CH	CH=CH	427.9	444.4	15.09	16.57	62.00	85.62	625.0	891.7
VIIe	NH	CH	CH=CH	428.2	446.8	17.50	18.70	68.53	94.35	555.2	891.0
VIIIf	NH	N	N=N	482.1	482.1	17.40	17.40	132.89	132.89	1505.0	1505.0
VIIIa	S	S		483.0	482.1 (570) ^c	8.45	8.46	55.84	55.88	607.4	607.3 (2200) ^d
VIIIb	S	N		489.9	491.5	9.66	8.71	61.57	62.96	734.3	789.8
VIIIc	NH	N		526.9	523.4	9.24	8.50	86.67	83.21	1122.1	1126.22

^a The experimental value for dioxane solutions at an excitation energy of 0.65 eV in parentheses is from ref 12. ^b The extrapolated experimental $\mu\beta_0$ value for dioxane solutions in parentheses is from ref 12. The laser excitation energy is 0.65 eV. ^c The experimental value for dioxane solutions at an excitation energy of 0.65 eV in parentheses is from ref 12. ^d The experimental $\mu\beta$ for dioxane solutions in parentheses is from ref 12. The laser excitation energy is 0.65 eV.

and replacing the benzene ring by a tetrazine ring on the acceptor end (**VIIIf**) result in a 200% increase in NLO response. Similarly, replacing a fused thiophene bridge (**VIIIa**) by a fused pyrrole bridge (**VIIIc**) results in a 2-fold increase in $\mu\beta$. Direct experimental comparison is difficult. Both $\mu\beta$ and λ_{\max} are computed here for the vapor phase whereas the experimental data for **VIIb** and **VIIIa** were measured in dioxane; solvent effects are expected to red shift the optical absorption maximum and to enhance the β response for aromatic chromophores.²⁹ Furthermore, dispersion considerations argue that the experimental β for **VIIIa** measured at 0.65 eV should be substantially larger than the β at 0.1eV calculated here. Finally, these INDO-based studies are not expected to afford extremely accurate predictions, but rather to illustrate reliable trends. Thus, the experimental discrepancies appearing in Table 8 are explicable, and do not detract from the key conclusions.

These results demonstrate that the electron density criterion is useful in designing new, high-performance chromophores for second-order NLO applications. We have shown for a wide variety of chromophore architectures that the arrangement most favorable for NLO applications in neutral molecules is one in which a strong donor is appended to an electron-rich center (auxiliary donor) and a strong acceptor is appended to an electron-deficient center (auxiliary acceptor) with the two fragments connected by a suitable conjugated bridge. This yields, among the chromophores considered here, a maximal $\mu\beta$ for chromophore **VIIIf**, the $\mu\beta$ of which is roughly 5 times that of **DANS (Ia)** (the computed $\mu\beta$ of which is 281.63×10^{-48} esu at this wavelength).

Conclusions

From the linear and NLO response properties of π -electron chromophores, the bridges of which differ both in aromaticity

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and in electron excessivity or electron deficiency, we conclude that electron density plays the major role in determining second-order NLO response properties. *The electron-excessive heterocycles act as auxiliary donors; they exhibit a lesser tendency to deplete charge from donor substituents and hence increase the donor ability. Similarly, electron-deficient heterocycles act as auxiliary acceptors, withdrawing electron density from acceptor substituents and hence increasing the acceptor ability. This increased donor/acceptor ability leads to a substantial increase in NLO response.* Appending a strong donor to an electron-excessive system such as pyrrole, furan, or thiophene and a strong electron acceptor to an electron-deficient system such as pyridazine or tetrazine yields chromophores with substantially larger NLO responses than chromophores which do not have the auxiliary donors or acceptors in the bridge. We find that the cyclopentadienide anion is the most electron-rich five-membered heterocyclic ring and cyclopentadienyl cation is the most electron-deficient of the five-membered ring systems, while tetrazine is the most electron deficient six-membered heterocycle. It is also found that *charged five-membered ring systems, such as the cyclopentadienyl cation or anion, act as additional acceptor/donor groups and exhibit extremely large NLO response properties (an order of magnitude larger than DANS) when functionalized by strong donor/acceptor groups.*

These computations suggest that choice of bridges as well as donor and acceptor structures based on the overall criterion of electron deficiency or excessivity, coupled with previous design principles (polarity of donors, acceptor groups, bond length alternation, aromaticity), can result in significantly enhanced molecular second-order NLO response properties.

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