Theoretical Investigation and Molecular Design of Some Azulene Derivatives with Large Hyperpolarizabilities

Peng Wang, Peiwang Zhu, and Cheng Ye*

Center for Molecular Science, Organic Solids Lab, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Alfred E. Asato and Robert S. H. Liu*

Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822

Received: March 15, 1999; In Final Form: June 28, 1999

The molecular hyperpolarizabilities and electronic properties of some azulene-containing chromophores have been investigated by employing AM1/FF and ZINDO/S-CI approaches. The calculation results show good agreement with the experimental values. It is found that the nonalternant azulene ring can be regarded as a more efficient conjugation bridge compared with benzene and thiophene because of its lower delocalization energy. Enhanced β values can be obtained by extending the conjugation length, altering substituted positions, or choosing appropriate substituents. The 1-donor-5-acceptor-azulenes are found to have large β values and small dipole moments (e.g., the 1-dithioylidenemethyl-5-[2,2-dicyanovinylbutadienyl]azulene has a high β_0 value of 181.7×10^{-30} esu, which is close to the highest reported values and a relatively small dipole μ of 5.3 D), and the latter properties may be helpful in reducing chromophore−chromophore electrostatic interactions and in optimizing the chromophore loading level and the order parameter while incorporated into the polymer matrix.

1. Introduction

Organic molecules with large hyperpolarizabilities (β) have drawn considerable attention over the past decade for their potential applications in optical data storage, telecommunications, and optical signal processing.[1,2] The focus of recent research has been on donor−acceptor-substituted π-conjugated molecules because the delocalized π-electrons of these molecules give rise to large electronic hyperpolarizabilities. Early investigations of the structure−property relationships of these molecules indicated that β increases with increasing donor and acceptor strengths and with extending π-conjugation length.[3,4] It has been realized that polyenes used as a π-conjugating bridge provide the most effective pathway for efficient charge transfer between the donor and acceptor groups.[5,6] Incorporation of benzene rings into push−pull polyenes is observed to limit or saturate molecular nonlinearity but to enhance thermal stability.[7] However, Marder and co-workers[8,9] have mentioned that the strength of the electron donor and acceptor must be optimized for the specific π-conjugating system, and the loss of aromaticity between the neutral aromatic form and the charge-separated zwitterionic form of the benzene ring is believed to be responsible for the reduced or saturated β values. Therefore, attempts have been made to design chromophores with less aromatic character in the ground state, such as replacing the benzene rings in stilbene derivatives by easily delocalizable five-membered heteroaromatic rings[10−12] or systems where loss of aromaticity in the neutral form is compensated by a gain of aromaticity in the charge-separated form.[9,13] Recent results show that the electron density of the π-conjugation plays a major role in determining second-order nonlinear optical (NLO) response properties.[12,14,15] The electron excessive/deficient heterocycles act as auxiliary donors/acceptors while connecting with electron donating/withdrawing groups, and the increasing donor/acceptor ability leads to a substantial increase in molecular β value.

The nonalternant azulene molecule has been of longstanding interest to theoretical chemists because of its unusual properties, such as a large permanent dipole moment (for a hydrocarbon),[16,17] $S_2 \rightarrow S_0$ fluorescence[18] and large hyperpolarizability.[19,20] The molecular dipole moment and π-electron densities of azulene have been ascertained by employing semiempirical quantum methods.[16,17,21,22] Morley[19,20] suggested that the dipole moments of the azulenes could be tuned by a careful selection of substituents or by the insertion of nitrogen atoms into either ring. Furthermore, the calculation results of various aromaticity theories[23−25] indicated that azulene possesses much lower aromatic delocalization energy (e.g., 4.2 kcal/mol from Dewar's result[23]) compared to benzene (20.0 kcal/mol), thiophene (16.1 kcal/mol), and naphthalene (30.5 kcal/mol). This strongly suggests azulene can be a potential candidate to be a conjugation path for chromophores with large β values. Recently, Asato et al.[26] reported several novel, thermally stable azulene-containing donor−acceptor chromophores with significant second-order NLO properties. In this paper, we reported the theoretical investigation of these azulene-containing chromophores by employing the semiempirical AM1/FF and ZINDO/S-CI approaches and the design of some novel chromophores with large β values.

2. Computational Approach

The geometric structures were fully optimized on the basis of the AM1[27] Hamiltonian in the MOPAC package[28] as well as the ab initio HF/6-31G level in the Gaussian 94 program package.[29] The PRECISE option was used as a convergence criterion for AM1 calculation of geometries. All the components

10.1021/jp990903i CCC: $18.00

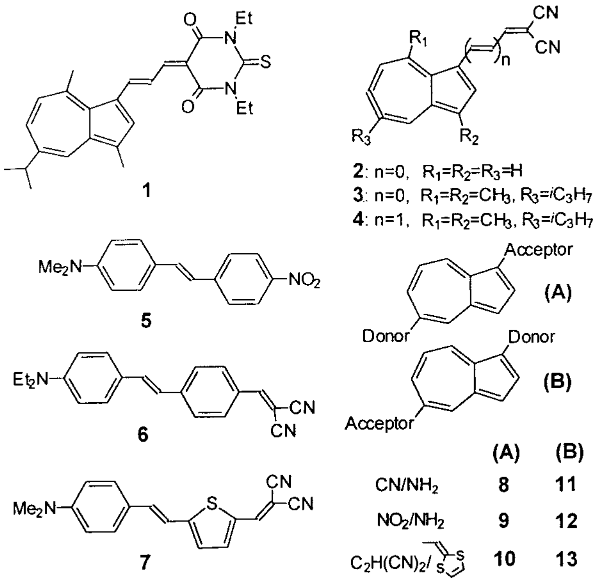


Figure 1. Chemical structures of the azulene derivatives studied in this work.

of β of the azulene derivatives were obtained by employing a finite field (FF) approach,[4] and then the β_μ, which is the vector component along the dipole moment direction, is given by

$$\beta_\mu = \frac{3}{5}\sum_i \beta_i \mu_i/|\mu| \qquad (1)$$

where $\beta_i = \sum_j \beta_{\mathrm{ijj}}$.

The β values are often defined by using different conventions, which differ by constant multiplicative factors,[30] and additional numerical discrepancies may arise from improper treatment of degeneracy factors in different NLO processes.[30,31] The MOPAC−FF subroutine provides the computed values for the first hyperpolarizability as β and $^{\beta}/_{2}$. We use the larger value of β.

To compare with the observed β_ω value at different fundamental frequencies, the calculated zero-frequency value β_0 must be transformed by the two-level model[32] as follows:

$$\beta_0 = \beta_\omega[({\omega_0}^2 - 4\omega^2)({\omega_0}^2 - \omega^2)]/{\omega_0}^4 \qquad (2)$$

where β_0 and β_ω are the molecular first hyperpolarizability at the frequency of zero and ω, respectively. ω_0 is the transition frequency of the molecular charge-transfer state.

The spectroscopic properties were obtained by using the ZINDO/S singly excited configuration interaction (SCI) approach based on the AM1 geometries. The ZINDO/S[33] parameters were set as the $\sigma-\sigma$ overlap = 1.267 and the $\pi-\pi$ overlap = 0.585, and the SCI matrix included 20 occupied and 20 unoccupied states. The obtained values of ground and excited dipole moments μ_g and μ_e, oscillator strength f_{eg}, and the excited energy E_{eg} were conveniently used to evaluate the β values of the chromophores according to the two-level model.

3. Results and Discussions

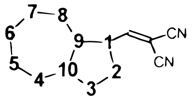
3.1. Structures. To verify the accuracy of using AM1 parametrization for optimizing geometric structures of azulene derivatives, we compared the AM1 structures (Figure 1) with the ab initio HF/6-31G results and the reported crystallographic data. Table 1 shows the results of 1-dicyanovinylazulene (**2**). It is well-known that azulene has two possible structures with C_{2v} and C_s symmetry with close calculated energies by theoretical and experimental results, and the most recent calculation showed that the bond-equalized C_{2v} structure is the minimum on the azulene hypersurface.[21] In our calculation, three different planar configurations were observed for each chromophore. Structures **I** and **II** with significant bond length alternation characteristics of both rings are obviously derived from isomeration of C_s symmetry of azulene. Structure **III**, where the bond lengths of the seven-membered ring show a tendency to be equal to each other (except for C9−C10), is similar to the ab initio HF/6-31G result with 1.5% error for bond lengths and 1% error for bond angles. The calculated heat of formation and β values based on the three AM1 structures show little difference, hence offering little ground for favoring one of the structure as the likely low-energy structure. Since results in the most recent calculation on azulene favors the bond-equalized structure (i.e., similar to the structure of **III**) and the AM1 parameters of **III** also show good agreement with the crystallographic data of 1-tricyanovinylazulene[19] with 3.4% error for bond lengths (although the latter has a stronger acceptor moiety), we shall proceed with the assumption that the calculation of azulene derivatives at the AM1 level can be considered to be reliable, and the AM1 structure of isomer **III** was used for further calculations.

It has been reported that in the substituted cyanovinyl aromatics, the malononitrile moiety will be twisted out of the aromatic ring[34,35] because of the steric interaction. In our calculations, we also found there exists a torsion angle between the azulene ring and the dicyanovinyl group. In chromophore **2**, the minimum energy is reached when the torsion angle is about 11.8°, and this angle can be reduced to less than 1° with extended conjugation length. However, stronger steric interaction between the 8-substituted methyl group and the malononitrile group can be observed in chromophore **3**. The torsion angle is about 36° and can be reduced to around 30° with extended conjugation length.

3.2. AM1 Hyperpolarizabilities. The calculated and experimental[26] results of four azulene-containing compounds (**1**−**4**) are summarized in Table 2 together with that of some reported NLO chromophores (**5**−**7**) for comparison. The AM1 $\mu\beta$ values of these azulene-containing chromophores show good agreement with the EFISH data, and there exists a linear correlation between the ZINDO/S $\lambda_{\max}$ values and the UV−vis spectrum data. The difference in the $\lambda_{\max}$ may be mainly due to solvent effects, since the experimental values were obtained in solvent and the calculated ones were for an isolated molecule in a vacuum. This can be proved by the large positive solvatochromism observed for **1** ($\lambda_{\max}$ = 567 in cyclohexane to λ = 639 nm in methanol).[26] It is also found that the calculated and experimental $\mu\beta$ values of **4** are larger than that of 4-*N*,*N*-dimethylamino-4′-nitrostilbene[36] (**5**) and close to that of 4-*N*,*N*-diethylamino-4′-dicyanovinyl-stilbene[37] (**6**) and 2-[4-dimethylaminophenylethylene]-5-[2,2-dicyanovinyl]thiophene[38] (**7**), although **6** and **7** possess stronger donors and longer conjugation lengths. This strongly suggests that azulene can be regarded as a more efficient conjugation bridge system compared with benzene and thiophene because of its lower delocalization energy, and chromophores with higher β values can be obtained by choosing more suitable donor−acceptor pairs.

The influence of the extended conjugation length on the NLO properties was investigated on dicyanovinyl-substituted guaiazulene chromophores (**3**, **4**, and their homologues). It is found that the energy gaps between the HOMO and LUMO ($\Delta E_{\mathrm{HOMO-LUMO}}$) decrease while β_0 values increase with the

TABLE 1: Comparison of the AM1 Optimized Molecular Structure (Bond Length (Å) and Bond Angle (deg)) of 1-Dicyanovinylazulene (2) with the HF/6-31G Calculation and the Crystallographic Data of 1-Tricyanovinylazulene[19]



	AM1			ab initio	crystallographic data
	I	II	III	HF/6-31G	1-tricyanovinylazulene
C1−C2	1.442	1.401	1.433	1.420	1.434
C1−C9	1.419	1.460	1.432	1.424	1.437
C2−C3	1.384	1.426	1.395	1.375	1.349
C3−C10	1.447	1.410	1.433	1.411	1.407
C4−C5	1.403	1.368	1.391	1.387	1.368
C4−C10	1.369	1.406	1.382	1.386	1.392
C5−C6	1.371	1.418	1.381	1.386	1.381
C6−C7	1.404	1.361	1.397	1.389	1.384
C7−C8	1.370	1.420	1.401	1.386	1.383
C8−C9	1.401	1.373	1.387	1.389	1.384
C9−C10	1.476	1.481	1.478	1.470	1.464
C1−C2−C3	109.6	109.5	109.5	110.1	
C1−C9−C10	107.4	105.6	107.3	106.6	
C2−C3−C10	108.8	108.5	109.2	108.9	
C2−C1−C9	107.8	108.4	107.5	107.3	
C3−C10−C9	106.5	108.0	106.4	107.0	
C4−C5−C6	128.4	125.6	127.7	128.3	
C4−C10−C9	129.2	129.3	128.5	128.3	
C5−C6−C7	129.4	130.7	128.7	129.3	
C5−C4−C10	128.5	129.7	129.6	129.3	
C6−C7−C8	129.6	131.5	129.7	129.2	
C7−C8−C9	128.7	126.0	129.6	129.4	
C8−C9−C10	126.1	126.8	126.1	126.3	

TABLE 2: Comparison of the AM1/FF Results with the Experimental Data[26,36−38] (Units of μ, β, and $\mu\beta$ Are Debye, $\times 10^{-30}$ esu, and $\times 10^{-48}$ esu, Respectively)

	experimental		calculation				
chromophores	λ_{max} (nm)[a]	$\mu\beta$[b]	λ_{max} (nm)	μ	β_o	$\mu\beta_o$	$\mu\beta_\omega$[d]
1	582	1323	504.0	9.0	82.0	733.9	1297
2	425	153	411.8	6.3	8.3	52.7	69.3
3	470	216	440.8	7.8	20.6	160.7	227
4	513	911	459.3	9.9	54.2	536.6	817
5	427[c]	482	377.2	8.6	43.3	372.4	491
6	468	1100	440.8	7.7	64.4	495.9	697
7		1208[c]	443.3	7.4	59.3	438.8	

[a] In *p*-dioxane. [b] At 1900 nm. [c] In chloroform. [d] Transform by experimental λ_{max}.

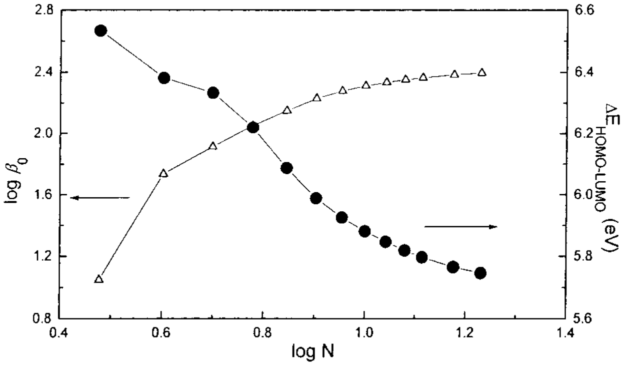


Figure 2. Dependence of the log β_0 and $\Delta E_{HOMO-LUMO}$ values on log *N* values. *N* refers to the number of ethylene units; for the aromatic azulene ring, $N = 3$. ● refers to $\Delta E_{HOMO-LUMO}$ and △ refers to log β_0 values.

increasing *N* values (*N* refers to the number of ethylene units (Figure 2); for the aromatic azulene ring, $N = 3$). The molecular hyperpolarizabilities can be described as $\beta_0 = AN^{2.86}$ when *N* is smaller than 8. However, both $\Delta E_{HOMO-LUMO}$ and β_0 tend to reach a limiting value as the chain length is increased. Assuming that the HOMO reflects the nature of the ground state and the LUMO reflects that of the excited state, the saturation of the β_0 value at large chain length can be well explained by the saturation in $\Delta E_{HOMO-LUMO}$ (which reflects the transition energy E_{eg}) within the two-level model.[32] It should be mentioned that a torsion angle about 30° was observed between the guaiazulene moiety and the "ene" plane even when $n > 5$, which is mainly caused by the steric exclusion effect of the 8-methyl group and will reduce the molecular β values.

To design new chromophores containing azulene with larger hyperpolarizabilities, we also investigated the substitution effects of the azulenes by alternating donor−acceptor pairs and substituted positions. As is well-known, the major contribution to the hyperpolarizability in the 1,5-donor−acceptor substituted azulenes comes from the charge transfer from the donor group directing to the acceptor group, and the position of charge-transfer band can be predicted by the Hammett substituent constant. Figure 3 shows the correlation between the β_0 values with the substituent constant σ^+/σ^-.[39,40] The β_0 values of 5-acceptor-1-methoxy-azulenes increase with the increasing σ^- values and can give an order of increasing acceptor strength as $-CF_3$, $-CN$, $-CHO$, $-NO_2$, $-C_2H(CN)_2$, $-C_2(CN)_3$. The β_0 values of 1-donor-5-cyanoazulenes decrease with the increasing σ^+ values and can give an order of increasing donor strength as $-Cl$, $-Me$, $-OMe$, $-NH_2$, $-N(Me)_2$. These results coincide with their donor−acceptor abilities. Accordingly, substantial efforts should be devoted to searching for stronger donors and acceptors to reach a larger NLO response. 1-Dithioylidene-methyl-5-dicyanovinyl-azulene (**13**) was found to possess a large β_0 value as 93.2×10^{-30} esu and a relatively low dipole moment of 4.8 D. It is also found that 1,5- and 2,6- are the best positions for disubstitution and that the β values are sensitive to different connecting methods. The seven-membered/five-membered ring of azulene is electron excessive/deficient and they can act as auxiliary donor/acceptor while connecting with electron donat-

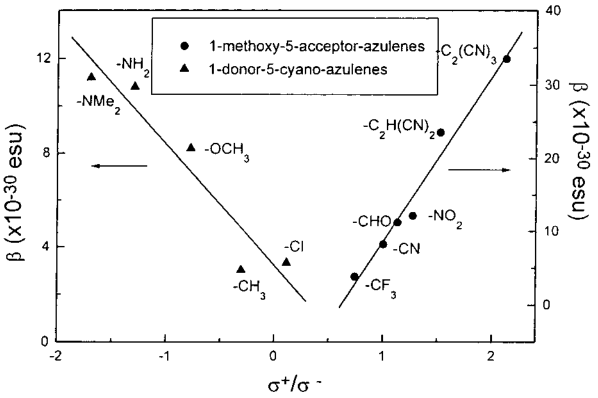


Figure 3. Correlation between the β values with the Hammett substituent constants.

TABLE 3: Comparison of the AM1 Calculation for the Nonlinearity of 1-Acceptor-5-donor-azulenes and 1-Donor-5-acceptor-azulene

	1-acceptor-5-donor-azulenes		1-donor-5-acceptor-azulenes	
donor/acceptor	μ (D)	β_0 ($\times10^{-30}$ esu)	μ (D)	β_0 ($\times10^{-30}$ esu)
CN/OCH$_3$	5.1	7.8	3.8	8.2
CN/NH$_2$	6.3	9.2	4.7	10.8
CN/NMe$_2$	6.2	3.4	3.8	11.2
CN/ 	6.3	19.9	3.5	42.0
NO$_2$/OCH$_3$	8.5	2.8	6.5	12.1
NO$_2$/NH$_2$	9.8	5.2	7.4	18.0
NO$_2$/ 	9.4	29.5	6.4	69.3
C$_2$H(CN)$_2$/NMe$_2$	9.4	18.1	4.9	31.9
C$_2$H(CN)$_2$/ 	9.8	55.8	4.2	94.8

ing/withdrawing groups. Hence, the 1-acceptor-5-donor-azulenes were expected to have enhanced β values. However, it is found that 1-donor-5-acceptor-azulenes are more efficient to give larger β values together with lower dipole moments (Table 3). Similar results were reported by Morley[19] for 2,6-nitro/amino disubstituted azulenes, and some SCF and Hückel predictions[41] on the substitution effects also suggested that the acceptor should go to the seven-membered ring while the donor should go to the five-membered ring. To understand this phenomenon, the ZINDO/S electronic properties and AM1 molecular frontier orbital properties have been investigated.

3.3. ZINDO/S Electronic Properties and Two-Level Model Analysis. According to the two-level model,[4,32] the linkage between molecular β and the details of a low-lying charge-transfer transition can be described as

$$\beta \propto \Delta\mu_{eg} f_{eg}/E_{eg}^{3} \tag{3}$$

TABLE 4: ZINDO/S Electronic Properties of Some Azulene-Containing Chromophores and Their AM1/FF β_0 Results

	μ_g[a]	μ_e[a]	$\Delta\mu_{eg}$[a]	f_{eg}	λ_{max}[b]	E_{eg}[c]	$\Delta\mu f/E_{eg}^3$	β_0[d]
1	13.3	19.6	6.3	1.4937	504.0	2.46	0.63	82
2	11.6	11.9	0.24	0.7528	411.8	3.01	0.01	8.3
3	12.0	15.1	3.0	0.7509	440.8	2.81	0.10	20.6
4	13.0	20.3	7.4	1.1963	459.3	2.70	0.45	54.2
8	8.7	6.9	−1.8	0.2597	375.4	3.30	−0.01	9.18
9	11.3	16.1	4.9	0.5568	429.6	2.89	0.11	5.15
10	14.5	15.2	0.7	1.1693	439.6	2.82	0.04	55.8
11	6.5	11.5	5.0	0.3160	416.7	2.98	0.06	10.84
12	8.1	18.6	10.5	0.4616	488.6	2.54	0.30	17.98
13	8.2	19.8	11.6	0.7721	467.9	2.65	0.48	94.8

[a] In units of debye. [b] In units of nanometers. [c] In units of electronvolts. [d] AM1/FF results.

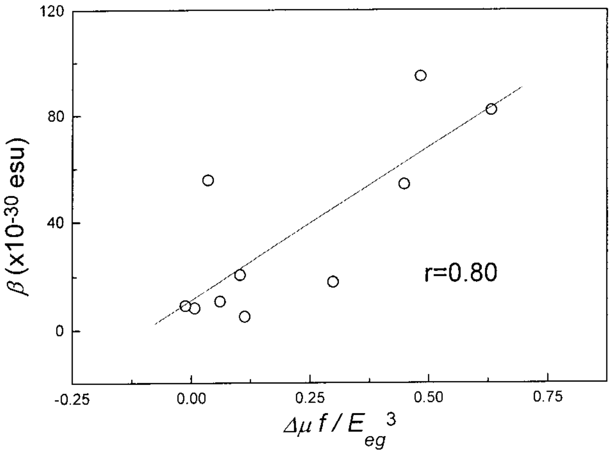


Figure 4. Correlation between the ZINDO/S $\Delta\mu_{eg}f_{eg}/E_{eg}^{3}$ and the AM1/FF β_0 values.

where $\Delta\mu_{eg} = \mu_e - \mu_g$ is the difference of dipole moments between excited (charge transfer) and ground states, E_{eg} is the transition energy, and f_{eg} is the oscillator strength. The influence of different substitution effects on β values can be analyzed separately from the variances of the three electronic properties. The electronic properties of these azulene-containing chromophores were investigated by employing the ZINDO/S-CI approach based on their AM1 geometry structures. The calculated values of μ_g, μ_e, $\Delta\mu_{eg}$, f_{eg}, and E_{eg} are shown in Table 4 together with the AM1/FF β_0 values. The calculated transition energies for chromophores **1**−**4** reproduce the experimental data well. However, discrepancies for the ground-state dipole moment μ_g are found between the ZINDO/S and AM1 results. This is due to the different parameters they used. Figure 4 shows the correlation between the $\Delta\mu_{eg}f_{eg}/E_{eg}^{3}$ from ZINDO/S and the AM1/FF β_0 values. It is found that there exists good linear correlation between these two calculations. However, the large derivations of β_0 values for chromophore **10** and **13** may be caused by the limitation of the two-level frame to very strong donor−acceptor pairs. The enhancement of β values with increasing donor−acceptor abilities and extending conjugation length can be attributed to the increasing $\Delta\mu_{eg}$, f_{eg}, and decreasing E_{eg} values. However, when 1-acceptor-5-donor-azulenes (**8**−**10**) are compared with 1-donor-5-acceptor-azulenes (**11**−**13**), it is found that the latter compounds possess smaller f_{eg} and E_{eg} values, and the main reason for their larger β values comes from the contributions of $\Delta\mu_{eg}$. Morley[19] has pointed out that the difference between two 2,6-nitro/amino disubstituted azulenes can be attributed to the special electronic properties of the azulene ring. As is sketched in Figure 5, which is based on his CNDO results, analysis of the charge distribution in azulene shows dramatic changes between the ground and the third excited state (the major contributor to the β value of azulene), which lead to a reversal in the sign of μ_g and μ_e. The direction of the μ_g vector is from the seven-membered ring to the five-membered ring. while that of μ_e is from the five to the seven.[16,19] In traditional D−π−A chromophores, both μ_g and μ_e are in the direction from the donor to the acceptor and μ_g is usually smaller than μ_e. Thus, by a simple vector additivity model, introduction of an electronic acceptor into the large ring and a donor into the small ring may result in a decrease and increase in the ground- and excited-state dipole moments, respectively. The reversed connection method may lead to an

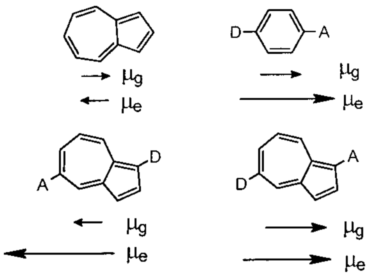


Figure 5. Schemes for explanation of the difference of $\Delta\mu_{eg}$ of 1-acceptor-5-donor-azulenes and 1-donor-5-acceptor-azulenes by vector additivity model.

TABLE 5: Calculated (ZINDO) Data for the Excited States That May Contribute to the β Tensor of 1-Nitro-5-aminozzulene (9)

singlet state[a]	$\Delta\mu_{eg}$ (D)	f_{eg}	λ_{max} (nm)	E_{eg} (eV)	major transition	$\Delta\mu f/E_{eg}^3$
S_{11}	4.9	0.5568	429.6	2.89	HOMO → LUMO	0.1135
S_{18}	2.7	0.1910	310.2	4.00	HOMO-1 → LUMO	0.0081
S_{21}	−1.6	0.8138	270.7	4.58	HOMO → LUMO + 2 HOMO-1 → LUMO + 1	−0.0136
S_{27}	2.5	0.2061	234.8	5.28	HOMO → LUMO + 3 HOMO-4 → LUMO + 1	0.0035
S_{30}	0.54	0.1190	225.5	5.50	HOMO → LUMO + 4 HOMO-4 → LUMO	0.0004
S_{32}	0.55	0.1220	225.1	5.51	HOMO → LUMO + 4 HOMO-4 → LUMO	0.0004
S_{34}	−5.7	0.5456	220.9	5.61	HOMO-3 → LUMO	−0.0176
S_{36}	0.20	0.1232	213.9	5.80	HOMO → LUMO + 3	0.0001
S_{39}	−2.0	0.4122	208.5	5.95	HOMO → LUMO + 5 HOMO → LUMO + 7	−0.0039
S_{61}	4.9	0.1358	185.0	6.70	HOMO-6 → LUMO + 1	0.0022
S_{62}	1.5	0.1382	183.0	6.78	HOMO-6 → LUMO	0.0007
S_{66}	3.2	0.1772	178.6	6.94	HOMO-1 → LUMO + 3 HOMO-6 → LUMO	0.0017

[a] The ground states are regarded as S_1. All singlet states with oscillator strength larger than 0.1 are listed.

increase and decrease in the ground- and excited-state dipole moments, respectively. It is found that our ZINDO/S-CI results are in good agreement with this deduction, and the larger difference between the excited and ground dipole moments of 1-donor-5-acceptor-azulenes can be well understood on the basis of this vector additivity scheme. As will be discussed below, these novel chromophores with large β and relatively small μ_g values may be helpful in getting optimum macroscopic optical nonlinearities[42] while incorporated into a macroscopic environment such as the poled polymeric materials.

3.4. Molecular Orbital Analysis. The ZINDO/S results for the excited states that may contribute to the molecular hyperpolarizabilities of 5-amino-1-nitro-azulene (**9**) and 1-amino-5-nitro-azulene (**12**) are listed in Tables 5 and 6, respectively. It is found that a single, low-excited state, which can be described as HOMO → LUMO excitation, makes the dominant contribution to the intrinsic β values for these two chromophores. The contributions from other electronic configurations are less than 20% and can be approximately neglected. To clarify the origin of the different NLO response between the two chromophores, we investigated the frontier orbital properties of chromophores **9** and **12**. Figure 6 shows the AM1 molecular orbital diagram of the HOMO and LUMO of **9** and **12**, and the open circle and solid circle reflect the sign of the orbital coefficients. The changes of the square of the orbital coefficients for HOMO → LUMO excited configurations are also presented, and the solid circle and the open circle reflect the loss and gain of electron density, respectively. The area of these symbols reflects the magnitude of the coefficients. The HOMOs are mainly centered on the five-membered ring and the amino group, while the LUMOs are mainly on the seven-membered ring and the nitro group. Thus, the five-membered ring of azulene shows some electron-donating properties, while the seven-membered ring is electron-withdrawing, and chromophore **12** shows more efficient charge transfer compared with **9**. It is also found that the change in electron density of the HOMO → LUMO excited configuration of **9** is more significant than that of **12**, which is in accordance with its larger oscillator strength f_{eg}. In chromophore **9**, the five-membered ring and the amino group lose electron density and act as donors while the seven-membered ring acts as acceptor, and there exist two competitive charge transfers that reduce the molecular β value. However, in chromophore **12**, there exists only one charge transfer from the electron-donating amino group direct to the electron-withdrawing nitro group. Thus, **12** possesses a longer conjugation length and more efficient charge transfer compared with **9** and has larger β value.

3.5. Benefits to Reduce Electrostatic Interaction. The most popular method to obtain macroscopic noncentrosymmetric materials was electronic field poling of the NLO chromophore containing polymers near the glass-transition temperature (T_g) of the polymer matrix.[1,43] It has generally been assumed that the macroscopic optical nonlinearity will scale as $\mu\beta$/MW (MW: molecular weight of the used chromophore), and the relationship between the macroscopic second-order susceptibility $\chi^{(2)}$ of the poled polymer and molecular hyperpolarizability β of the chromophore can be approximately defined as

$$\chi^{(2)} = NF\beta\langle\cos^3\theta\rangle \tag{4}$$

where N is the chromophore number density, F contains all local field effects, and $\langle\cos^3\theta\rangle$ reflects the polar order parameter. Synthesis of chromophores with $\mu\beta$ values on the order of 10^{-44} esu has led to expectations of electrooptic coefficients for organic materials that substantially exceed that of lithium niobate. However, most of these chromophores possess relatively large ground-state dipole moments, and the electrostatic repulsion between these high-μ chromophores opposes the optimization of the chromophore loading level (N) and the order parameters. Dalton[42,43] et al. has suggested the order parameter should be defined as

$$\langle\cos^3\theta\rangle = \frac{\mu E_p F}{5kT}\left[1 - L^2\left(\frac{W}{kT}\right)\right] \tag{5}$$

where E_p and T are the poling electric field and temperature, respectively, and $L[W/(kT)] = \coth[W/(kT)] - kT/W$ is the Langevin function. The statistically average electrostatic interaction energy W between chromophores can be expressed as the sum of three terms, namely, the orientation force, the induction force, and the dispersion force:

$$W = \frac{1}{R^6}\left(\frac{2\mu^4}{3kT} + 2\mu^2\alpha + \frac{3I\alpha^2}{4}\right) \tag{6}$$

where R is the average distance between chromophores, α is the polarizability, and I is the ionization potential.

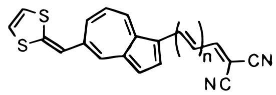
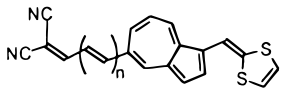
Because 1-donor-5-acceptor-azulenes possess large β values together with relatively small μ values, it may be helpful in reducing the chromophore−chromophore electrostatic interaction to obtain optimum macroscopic optical nonlinearities. We have extended the conjugation lengths of **10** and **13** to get more efficient chromophores for use in poled polymers. The calculated results are shown in Table 7. It is found that high β_0 values that are close to the highest reported value of some thiobarbituric

TABLE 6: Calculated (ZINDO) Data for the Excited States That May Contribute to the β Tensor of 1-Amino-5-nitro-azulene (12)

singlet state[a]	$\Delta\mu_{eg}$ (D)	f_{eg}	λ_{max} (nm)	E_{eg} (eV)	major transitions	$\Delta\mu f/E_{eg}^3$
S_9	10.5	0.4616	488.6	2.54	HOMO → LUMO	0.2966
S_{18}	7.7	0.1918	323.2	3.84	HOMO → LUMO + 2 HOMO-1 → LUMO	0.0262
S_{22}	3.6	1.167	269.8	4.60	HOMO-1 → LUMO+1	0.0433
S_{36}	−0.2	0.160	216.3	5.73	HOMO → LUMO+7 HOMO-3 → LUMO	−0.0002
S_{37}	6.7	0.1439	212.6	5.83	HOMO → LUMO + 5	0.0049
S_{44}	0.1	0.9413	198.8	6.24	HOMO-4 → LUMO + 1	0.0004
S_{72}	4.6	0.165	175.1	7.08	HOMO-4 → LUMO + 2 HOMO-6 → LUMO + 1	0.0021

[a] The ground states are regarded as S_1. All singlet states with oscillator strength larger than 0.1 are listed.

TABLE 7: Comparison of the AM1 Results of 10, 13, and Their Homologues with Extended Conjugation Length

		μ (D)	β_0 ($\times 10^{-30}$ esu)	α ($\times 10^{-23}$ esu)	I (eV)	$1 - L^2[W/(kT)]$ [a]		
						$R = 10$ Å	$R = 12$ Å	$R = 15$ Å
	$n = 0$	9.8	55.8	9.01	7.888	0.463	0.857	0.9883
	$n = 1$	10.2	108.4	10.8	7.757	0.377	0.791	0.9812
	$n = 2$	10.3	176.5	12.8	7.609	0.322	0.731	0.9734
	$n = 0$	4.2	94.8	9.02	7.339	0.823	0.976	0.9983
	$n = 1$	4.5	135.9	10.6	7.271	0.722	0.955	0.9968
	$n = 2$	5.3	181.7	12.2	7.298	0.598	0.920	0.9940

[a] The poling temperature T is taken as 400 K for popular guest−host systems.

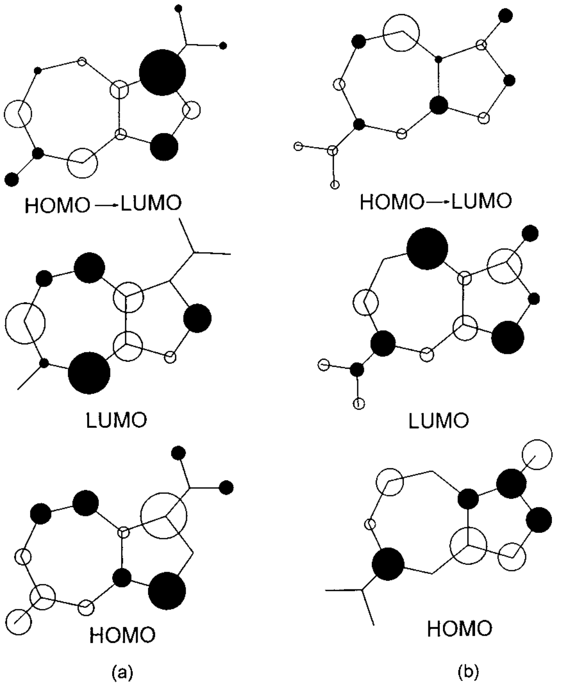


Figure 6. AM1 molecular diagram and change of electron density of the HOMO → LUMO excited configuration: (a) 5-amino-1-nitro-azulene, **9**; (b) 1-amino-5-nitro-azulene, **12**.

acid derivatives (i.e., $\mu\beta = 1.2 \times 10^{-44}$ esu reported by Ikeda et al.[44] and its relative AM1 results of $\beta_0 = 206.8\times 10^{-30}$ esu) can be achieved for both series of chromophores at $n = 2$. The 1-donor-5-acceptor-azulenes show similar polarizabilities, lower ionization potentials, and dipole moments, and the factor $1 - L^2[W/(kT)]$ can be close to 1 at smaller average chromophore separation distances (i.e., at larger chromophore number density) compared with the 1-acceptor-5-donor-azulenes. Thus, this series of azulene-containing chromophores is helpful in optimizing the chromophore loading level and the order parameter while incorporated into a polymer matrix and may be potential candidates for high-performance electrooptical devices.

4. Conclusion

In this paper, the molecular hyperpolarizabilities and electronic properties of some azulene-containing chromophores have been investigated by employing AM1/FF and ZINDO/S-CI approaches. It is found that the calculation results are in good agreement with the experimental values. The nonalternant azulene ring can be regarded as a more efficient conjugation bridge compared with benzene and thiophene because of its lower delocalization energy. It is also found that enhanced β values can be obtained by extending the conjugation length, altering substituted positions, or choosing appropriate substituent pairs. Molecular orbital analysis indicates that the five-membered ring acts as electron-donating, while the seven-membered ring acts as electron-withdrawing groups. Hence, the 1-donor-5-acceptor-azulenes are preferred because they possess more efficient charge transfer. The AM1/FF results also show that such chromophores possess large β values and small dipole moments that can be well explained by their large difference between the ground- and excited-state dipole moments based on the two-level model. The 1-dithioylidenemethyl-5-[2,2-dicyanovinylbutadienyl]azulene is found to have a high β_0 value of 181.7×10^{-30}esu, which is close to the highest reported values, and a relatively small μ of 5.3 D. The latter property is helpful in reducing chromophore−chromophore electrostatic interactions and in optimizing the chromophore loading level and the order parameter while incorporated into a polymer matrix.

Acknowledgment. This project was supported by NSFC (Nos. 59790050 and 29704009) and NAMCC (No. 863-715-002-0120) and partially by U.S. Army Research Office (No. DAAH04-96-1-0031).

References and Notes

(1) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers*; Wiley: New York, 1991.

(2) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987.

(3) Marder, S. R., Sohn, J. E., Stucky, G. D., Eds. *Materials for Nonlinear Opticals: Chemical Perspectives*; ACS Symposium Series 455; American Chemical Society, Washington, DC, 1991.

(4) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.

(5) Blanchard-Desce, M.; Ledoux, I.; Lehn, J. M.; Malthete, J.; Zyss, J. *J. Chem. Soc., Chem. Commun.* **1988**, 736.

(6) Marder, S. R.; Perry, J. W.; Bourhill, G.; Gorman, C.; Thiemann, B.; Mansour, K. *Science* **1993**, *261*, 186.

(7) Singer, K. D.; Sohn, J. F.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. W. *J. Opt. Soc. Am. B* **1989**, *6*, 1339.

(8) Marder, S. R.; Gorman, C. B.; Tiemann, B. G.; Cheng, L.-T. *J. Am. Chem. Soc.* **1993**, *115*, 2524.

(9) Marder, S. R.; Beratan, D. N.; Cheng, L.-T. *Science* **1991**, *252*, 103.

(10) Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Drost, K. J. *Tetrahedron Lett.* **1993**, *34*, 1747.

(11) Wong, K. Y.; Jen, A. K.-Y.; Rao, V. P.; Drost, K. J. *J. Chem. Phys.* **1994**, *100*, 6818.

(12) Rao, V. P.; Jen, A. K.-Y.; Chandrasekhar, J.; Namboothiri, I. N. N.; Rathna, A. *J. Am. Chem. Soc.* **1996**, *118*, 12443.

(13) Marder, S. R.; Cheng, L.-T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhoy, J. *Science* **1996**, *271*, 335.

(14) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 6575.

(15) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *Chem. Mater.* **1998**, *10*, 753.

(16) Bunker, R. J.; Peyerimhoff, S. D. *Chem. Phys. Lett.* **1969**, *3*, 37.

(17) Anderson, A. G.; Steckler, B. M. *J. Am. Chem. Soc.* **1959**, *81*, 4941.

(18) Beer, M. B.; Longuer-Higgins, H. C. *J. Chem. Phys.* **1955**, *23*, 1390.

(19) Morley, J. O. *J. Am. Chem. Soc.* **1988**, *110*, 7660.

(20) Morley, J. O. *J. Chem. Soc., Perkin Trans. 2* **1989**, 103.

(21) Grimme, S. *Chem. Phys. Lett.* **1993**, *201*, 67.

(22) Elblidi, K.; Boucetta, A.; Benali, B.; Kadiri, A.; Cazeau-Dubroca, C.; Nouchi, G.; Pesquer, M. *J. Mol. Struct.: THEOCHEM* **1995**, *343*, 57.

(23) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969.

(24) Kollmar, H. *J. Am. Chem. Soc.* **1979**, *101*, 4832.

(25) Ichikawa, H.; Ebisawa, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1161.

(26) Asato, A. E.; Liu, R. S. H.; Rao, V. P.; Cai, Y. M. *Tetrahedron Lett.* **1996**, *37*, 419.

(27) Dewar, M. J. S.; Zoebisch, E. G.; Healy, F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(28) Stewart, J. J. P. QCPE Program 455, 1983, version 6.0, 1990.

(29) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 94*, revision E.4; Guassian, Inc.: Pittsburgh, PA, 1994.

(30) Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, *97*, 7590.

(31) Orr, B. J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513.

(32) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

(33) Ridly, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1976**, *42*, 223.

(34) Zhao, C. Y.; Zhang, Y.; Fang, W. H.; You, X. Z. *J. Mol. Struct.: THEOCHEM* **1996**, *367*, 73.

(35) Wang, P.; Zhu, P. W.; Wang, C. G.; Ye, C. *J. Mol. Struct.: THEOCHEM* **1999**, *459*, 155.

(36) Cheng, L.-T.; Tam, W.; Stevenson, S.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631.

(37) Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commum.* **1993**, 90.

(38) Cheng, L.-T.; Tam, W. U.S. Patent 5272218, 1993.

(39) Katz, H. E.; Singer, K. D.; Sohn, J. E.; Dirk, C. W.; King, L. A.; Gordon, H. M. *J. Am. Chem. Soc.* **1987**, *87*, 6561.

(40) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.

(41) Grayson, M. *Int. J. Quantum Chem.* **1997**, *61*, 919.

(42) Harper, A. W.; Dalton, L. R.; Garner, S. M.; Chen, A.; Kalluri, S.; Steier, W. H.; Robinson, B. H. *J. Opt. Soc. Am. B* **1998**, *15*, 329.

(43) Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jen, A. K.-Y.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060.

(44) Ikeda, H.; Sakai, T.; Kawasaki, K. *Chem. Phys. Lett.* **1991**, *179*, 551.