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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · JANUARY 1997

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### Theoretical Study of Hyperpolarizabilities of Spirolinked Push–Pull Polyenes

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*Received: July 8, 1996; In Final Form: October 28, 1996*<sup>®</sup>

The molecular hyperpolarizabilities,  $\beta$ , of spirolinked push–pull polyenes, where the several 1,4-cyclohexadiene rings linked through the tetrahedral  $sp^3$  carbon atoms and electron-donating and -withdrawing groups were introduced in the terminal 1,4-cyclohexadiene rings, were investigated through the *ab initio* and INDO/S molecular orbital calculations. It is concluded that the spiroconjugation path is applicable to an intervening backbone between the electron-donating and the electron-withdrawing groups, and spirolinked push–pull polyenes have a possibility to be excellent second-order nonlinear optical materials from the standpoint of transparency and relatively large  $\beta$  values.

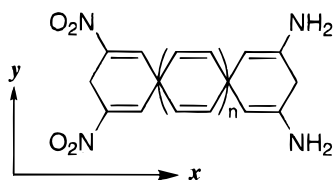
Up to now, almost all of the organic molecules investigated for the second-order nonlinear optical (NLO) materials contain electron-donating and withdrawing groups linked through an intervening  $\pi$  backbone. Though it is well established that the extension of the  $\pi$ -conjugation path between the electron-donating and -withdrawing groups strongly increases the molecular hyperpolarizabilities,  $\beta$ , the extension of the  $\pi$ -conjugation path also causes a bathochromic shift of the intramolecular charge-transfer absorption band, and thus the requirement of high transparency to visible light is missing. In principle, colored second-order NLO materials are undesirable for practical applications, since the NLO materials will be gradually destroyed by the nonlinear absorption. From a theoretical aspect, it is surely inevitable to induce a bathochromic shift of the  $\pi \rightarrow \pi^*$ -absorption band with  $\pi$ -conjugation length. We present

here one possibility to break through this dilemma based on the concept of spiroconjugation of polyene. We have investigated the molecular hyperpolarizabilities of spirolinked push–pull polyenes through the *ab initio* and semiempirical INDO/S molecular orbital (MO) calculations and found that the spiroconjugation path acts as an efficient intervening backbone between the electron-donating and -withdrawing groups. For the first time, we have shown that the spirolinked push–pull polyenes will be novel organic second-order NLO materials with both high transparency and relatively large  $\beta$  values.

The bonding concept of spiroconjugation was introduced some years ago by Hoffmann<sup>1</sup> and simultaneously by Simons and Fukunaga.<sup>2</sup> When four p orbitals are perpendicular in pairs to the intersecting planes, the overlap between p orbitals on atoms bound directly to the spirocarbon is considerable, and consequently exchange interactions may become significant. The four  $\pi$  systems generate various symmetry-adapted combinations of SS, SA, AS, and AA symmetry (S = symmetric, A =

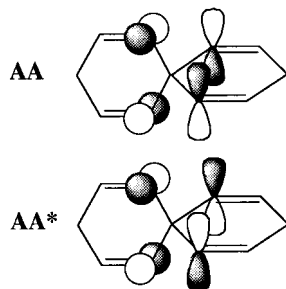
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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, December 1, 1996.



**Figure 1.** Molecular structure of spirolinked push-pull polyene and coordinate system.

antisymmetric, first with respect to one plane and then with respect to the other).<sup>3</sup> The AA type is unique among these combinations, and there are two types of AA combinations. As shown below, one is the bonding AA combination, AA, and the other is the antibonding AA combinations, AA\*.



Bucknum and Hoffmann suggest that the overlap across the spirocarbon is sufficient to produce a noticeable effect for the opening up of a gap between the bonding and the antibonding AA combinations but insufficient to reduce the excitation energy significantly.<sup>3</sup> That is, significant exchange interactions can be obtained without being accompanied by the reduction of excitation energy. The present study was motivated by these structural characteristics of the spiroconjugated compounds. Moreover, it is of great interest to clarify whether the charge transfer will occur through the spiroconjugation path.

We have carried out theoretical calculations on a series of spirolinked push-pull polyenes as shown in Figure 1. Molecular structures of all of the molecules were fully optimized at the *ab initio* RHF level of theory using a 6-31G basis set.<sup>4</sup> On the basis of these geometries, we have calculated the three crucial two-level properties (the oscillator strength  $f$ , the difference between the  $x$ -components of the dipole moments in the excited and the ground states  $\Delta\mu_x$ , and  $\lambda_{\max}$ ) of the lowest lying optical transition and the frequency-dependent  $\beta$  values. The  $\beta$  values for the second-harmonic generation were calculated by means of the sum-over-states (SOS) approach<sup>5-7</sup> in the framework of the time-dependent perturbation theory based on the semiempirical INDO/S Hamiltonian<sup>8-12</sup> with configuration interaction wave functions. In the SOS expression, all electronic states are included which are generated by singly exciting all electrons in the 30 highest occupied MOs to the 30 lowest unoccupied MOs with respect to the ground state. The calculated values of the  $x$ -components of the dipole moments in the ground state  $(\mu_x)_g$ , those in the lowest excited state  $(\mu_x)_e$ ,  $\Delta\mu_x$ ,  $f$ ,  $\lambda_{\max}$ , and  $\beta$  are shown in Table 1, along with those for widely adopted standard compounds 4-nitroaniline (*p*-NA).

It can be found that the  $\beta$  values are sufficiently large comparable to those of *p*-NA and increase with the number of 1,4-cyclohexadiene rings in the backbone. Surprisingly, blue-shift in  $\lambda_{\max}$  is obtained as additional conjugation units are added to the spiro backbone. Moreover,  $\Delta\mu_x$  has a maximum value for the  $n = 2$  backbone ( $\Delta\mu_x = 21.30$ ) and then gradually decreases. In the conventional  $\pi$ -conjugated push-pull polyenes, one anticipates an enhancement in the  $\beta$  value with an increase in  $\pi$ -conjugation length between the electron-donating

**TABLE 1: INDO/S and *ab Initio* Calculated Electronic Properties of Spirolinked Push-Pull Polyenes**

$n$	INDO/S <sup>a</sup>		<i>ab initio</i> $(\mu_x)_g$ (D)	INDO/S				$\lambda_{\max}$ (nm)
	$\beta(0)^b$	$\beta(1064)^c$		$(\mu_x)_g$ (D)	$(\mu_x)_e$ (D)	$\Delta\mu_x$ (D) <sup>d</sup>	$f$	
0	14.4	29.0	11.48	11.42	21.02	9.60	0.20	327
1	18.6	36.6	12.25	11.87	30.17	18.30	0.67	322
2	19.5	37.2	12.69	12.13	33.43	21.30	0.79	313
3	19.9	36.8	12.96	12.30	32.91	20.61	0.90	307
4	20.3	37.0	13.13	12.42	30.43	18.01	1.00	303
5	20.5	37.0	13.25	12.49	29.07	16.57	1.05	301
6	20.5	37.0	13.33	12.55	28.17	15.62	1.09	300
<i>p</i> -NA	12.0	25.1	8.21	8.49	18.86	10.37	0.50	345

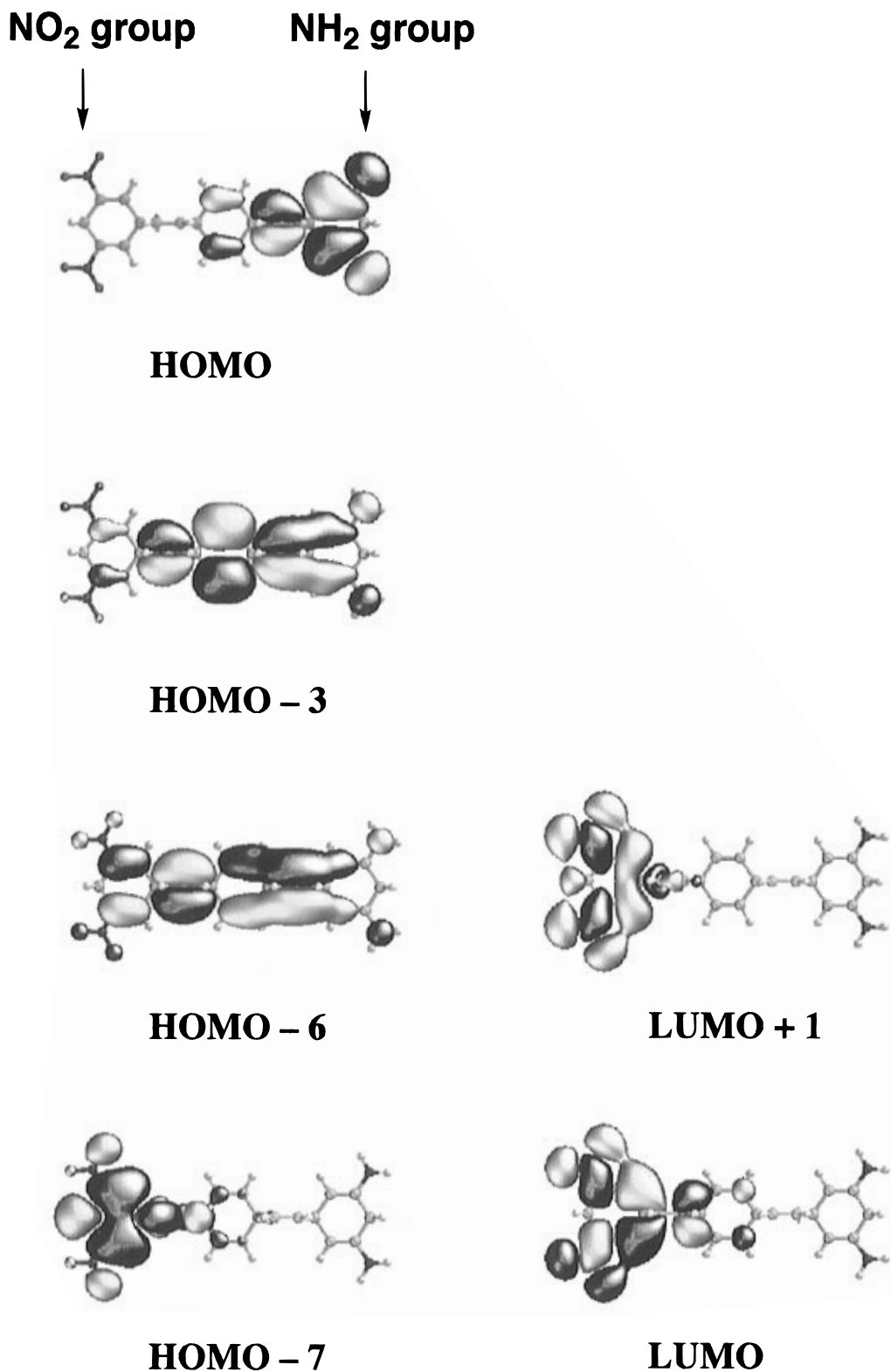
<sup>a</sup> All  $\beta$  are in units of  $10^{-30}$  cm<sup>5</sup> esu<sup>-1</sup> and calculated using the following equation:  $\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$ ,  $\beta_i = (1/3)\sum_k(\beta_{ikk} + \beta_{kik} + \beta_{kki})$ ,  $k = x, y, z$ . <sup>b</sup> Static  $\beta$  values. <sup>c</sup> Frequency-dependent  $\beta$  values at 1064 nm. <sup>d</sup>  $\Delta\mu_x = (\mu_x)_e - (\mu_x)_g$ .

and electron-withdrawing groups.<sup>13</sup> However, the NLO response in spirolinked polyene architecture does indeed saturate at very short conjugation lengths ( $n = 4$ ). This early saturation of  $\beta$  was also observed in push-pull polyynes, and Jain and Chandrasekhar concluded that this phenomenon was ascribable to configuration mixing of  $\pi \rightarrow \pi^*$  transitions.<sup>14</sup> Brédas and co-workers attribute the saturation to a breakdown in the two-level approximation as the conjugation length is increased.<sup>15</sup> Also, another possible explanation for the unexpected saturation is that a partial breaking of the charge-transfer plane is occurring as proposed by Barzoukas and co-workers.<sup>16</sup>

To consider these anomalous behavior in  $\beta$ ,  $\lambda_{\max}$ , and  $\Delta\mu_x$ , we have calculated the lowest excited states for the  $n = 3$  backbone through the *ab initio* CIS/6-31G method.<sup>17</sup> The wave function of the lowest excited state,  $|\Phi_e\rangle$ , was found to be given as

$$|\Phi_e\rangle = 0.34|\Psi_{\text{HOMO}-3 \rightarrow \text{LUMO}}\rangle - 0.32|\Psi_{\text{HOMO}-7 \rightarrow \text{LUMO}+1}\rangle - 0.28|\Psi_{\text{HOMO}-6 \rightarrow \text{LUMO}}\rangle + 0.22|\Psi_{\text{HOMO} \rightarrow \text{LUMO}}\rangle$$

where  $|\Psi\rangle$  is the Slater determinant obtained for the ground electronic state and  $|\Psi_{\text{HOMO} \rightarrow \text{LUMO}}\rangle$  is the monoexcited configuration state function, in which an electron is excited from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO). Figure 2 shows the MOs which are concerned with the above expression. The charge density around the nitro groups is enhanced in both the LUMO and LUMO + 1. On the other hand, the HOMO exhibits enhanced charge density around the amino groups. Moreover, we have calculated the difference electron density between the ground and the lowest excited states as shown in Figure 3.<sup>18</sup> The yellow-colored region indicates the region in which electron density decreases upon transition to the excited state, and the black-colored region indicates the region in which electron density increases upon the transition. From both Figures 2 and 3, it has become apparent that the nitro groups act as electron-withdrawing groups and the amino groups act as electron-donating groups and that a charge transfer across the spiroconjugated bridge takes place. This finding is significant for development a new class of second-order NLO materials in which an intervening backbone between the electron-donating and the electron-withdrawing groups is not constructed by the conventional  $\pi$ -conjugation path but constructed by the spiroconjugation path. Considering the definition of a dipole moment, the anomalous behavior of  $\Delta\mu_x$  can be attributable to the decrease in the charge-transfer amount with the increase in spiroconjugation length. However, it is not easy to account for the anomalous behavior in  $\lambda_{\max}$ . Moreover, in spite of the blue-shift in  $\lambda_{\max}$  with conjugation length, the oscillator strength continues to increase. These

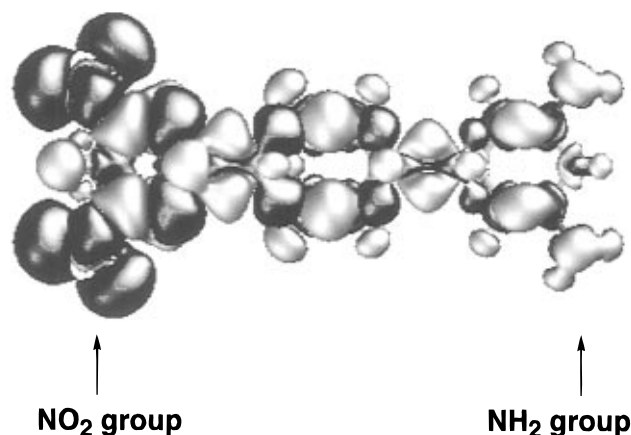


**Figure 2.** Molecular orbitals for the  $n = 3$  backbone calculated by the *ab initio* RHF/6-31G method.

results suggest one of the characteristic features of spirolinked polyenes, since this kind of phenomenon cannot be observed in the  $\pi$ -conjugated compounds. Thus, the early saturation of  $\beta$  would be attributable to the decrease in the charge-transfer amount and the increase in the transition energy with the increase in spiroconjugation length. It has been considered that the charge transfer occurs through a complex mechanism which involves the exchange interaction between the orthogonal  $\pi$  orbitals and by the substantial overlap of the  $\pi$  orbitals. However, more detailed work is needed to clarify the charge

transfer mechanism in spiroconjugated systems. These topics are currently investigation.

In conclusion, we have shown one possibility for constructing a novel highly transparent second-order NLO material with large  $\beta$  value based on the concept of spiroconjugation. It is noteworthy that the spiroconjugation path is applicable to a novel backbone between electron-donating and electron-withdrawing groups without inducing a bathochromic shift observed in the case for the conventional push-pull polyenes or polyynes. Though the detailed mechanism for these phenomena has not



**Figure 3.** Difference electron density between the ground and the lowest excited states for the  $n = 3$  backbone calculated by the *ab initio* CIS/6-31G method. The yellow-colored region indicates the region in which electron density decreases upon transition to the excited state, and the black-colored region indicates the region in which electron density increases upon the transition.

become apparent at the present stage, the interaction between the  $\pi$  orbitals by a through-space overlap shown above would be considered to play an important role. We have considered that even though the NLO responses of these chromophores are nowhere close to the large NLO responses found in  $\pi$ -conjugated bridges of similar molecular dimensions, these chromophores present new directions to be explored. The very fact that one can obtain a charge transfer across a spiroconjugated bridge is quite important and interesting. That is, spiroconjugated NLO materials can be classified as a completely new kind of material in the second-order NLO materials.

**Acknowledgment.** The idea of this study arose from some stimulating conversations with Prof. Tomokazu Iyoda at Tokyo

Metropolitan University. J.A. is deeply grateful to Dr. T. Iyoda for extensive discussions. We thank Makoto Ogura and Atsuya Takahashi of Fujitsu, Ltd., for the use of the latest version of the MOS-F package and the ANCHOR II system. We also thank Azuma Matsuura and Tomoaki Hayano of Fujitsu Laboratories, Ltd., for the helpful discussions of the semi-empirical MO method and the  $\beta$  calculation.

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