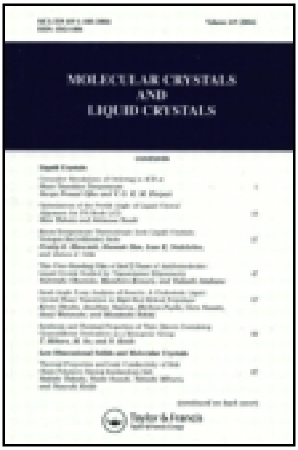

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Molecular Orbitals and Nonlinear Optical Properties for Terephthal-Bis-(4-N,N-Diethylamino Aniline) Defuvatives

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MOLECULAR ORBITALS AND NONLINEAR OPTICAL PROPERTIES FOR TEREPHTHAL-BIS-(4-N,N-DIETHYLAMINO ANILINE) DERIVATIVES

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Abstract Molecular orbitals and third-order susceptibility for terephthal-bis-(4-N,N-diethylamino aniline) are calculated. The electronic mechanism is explained approximately by a three level system. The effect of orbital shape upon the susceptibility is analyzed. It is found that molecular orbital distortion due to substituted nitrogen atoms, enhances the transition moment of 1Bu - 2Ag and contributes to the third-order susceptibility.

INTRODUCTION

Various works have been carried out to search for an organic molecule that has a large third-order susceptibility $\chi^{(3)}$. In general, the longer the conjugation length, the larger the $\chi^{(3)}$ becomes. This has been shown with theoretical models[1], and molecular orbital calculation of finite polyenes[2,3], and measurement of $\chi^{(3)}$ for various length molecules[4]. Flom et.al.[5], however, have measured $\chi^{(3)}$ for some polyacene quinones, and have found that some short-conjugated molecules have a larger $\chi^{(3)}$ than longer ones. He insists that third-order susceptibilities are not simply correlated with conjugation length. Substitution effects are dominant for some molecules even if they are centrosymmetric. To obtain centrosymmetric short-conjugated molecule which has large $\chi^{(3)}$, theoretical[6] and experimental[7,8] works have begun. We have reported symmetrical molecule SBA and SBAC as a new materials. Their $\chi^{(3)}$ value compares well with those of conjugated polymers even though they are short-conjugated molecules[8]. It is important to look into the electronic mechanism of these molecule in order to find out the substitution effects and to search for molecules with larger $\chi^{(3)}$.

In this work, molecular orbitals and third-order susceptibility for SBA and SBAC are calculated. These are terephthal-bis-(4-N,N-diethylamino aniline) and 2,5-dichloro-terephthal-bis-(4-N,N-diethylaminoaniline), and are shown in Fig. 1a. We have also calculated phenylene vinylenes, shown in Fig. 1b, i.e. p-bis-(styryl)benzene and p-bis-(p-vinyl styryl)benzene, which are PV1 and PV2 for short in this report. It is useful to study these molecules, to compare the effect of substituted nitrogen atoms or that of $N(Et)_2$ donors at each end of SBA and SBAC. The shape of molecular orbitals for these molecules are compared and the effect of the shape upon third-order nonlinearity is investigated.

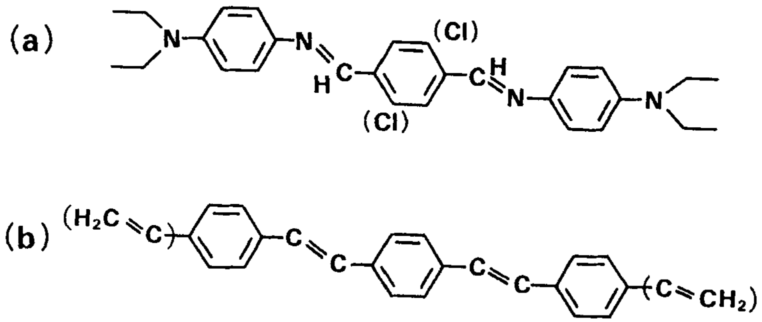

FIGURE 1 Calculated molecules: (a) SBA and SBAC, (b) PV1 and PV2.

CALCULATION

The geometry of these molecules has been optimized by a MNDO program to obtain bond lengths and angles. With the optimized structures, the excitation energies and the transition moments have been obtained by CNDO/S-SDCI. Using the obtained parameters, third-order susceptibilities have been calculated by the $\chi^{(3)}$ expression[9-11] which has been derived from time dependent perturbation. According to the $\chi^{(3)}$ expression, one sequence of four non-zero transition moments, which starts and ends at the ground state, contribute to the third-order susceptibility. As all the molecules mentioned above have C_{2h} symmetry, the process is $g - B_u - A_g - B_u - g$. The A_g and B_u excited states that contribute to the third susceptibility through the sequence of transition moments, are extracted.

RESULTS AND DISCUSSION

It is found that following two terms contribute to the third-order susceptibilities most effectively in this calculation for SBA and SBAC.

$g - 1B_u - g - 1B_u - g$ (term 1)

$g - 1B_u - 2A_g - 1B_u - g$ (term 2)

where $1B_u$ and $2A_g$ are the lowest excited states within each respective symmetrical representaiton. The contribution of the term 2 has positive sign, while the term 1 has negative sign, in a long-wavelength off-resonant region. Several other sequences of transition moments, where higher Ag excited states are used, also contribute to the third-order susceptibility. These contributions have positive signs. To have large third susceptibility, either the positive summation value due to several Ag excite states or the nagative value due to term 1 must be much larger than the other. In this calculation, the positive contribution is greater for all the molecules mentioned above. The calculated values of third susceptibility at 0.656 eV are γ(SBAC) = 7.7 x 10^{-35} esu, γ(SBA)=6.4 x 10^{-35} esu, γ(PV1) = 3.8 x10^{-35} esu and γ(PV2) = 6.8 x10^{-35} esu. The γ values per unit length of SBA and SBAC are greater than those of PV1 and PV2, as the conjugation length of PV2 is longer than that of SBA. This reason is studied with respect to the transition moment between excited states. In the result of SBA and SBAC, the term 2 is most effective. So, the contribution from the transition moment of $1B_u - 2A_g$ is important, because this moment causes the difference between term 1 and term 2.

In the sequence of term 2, the transition $g - 1B_u$ is mainly composed of a HOMO-LUMO transition. As for the intermediate transition $1B_u - 2A_g$, three kinds of orbital transitions are used, for the 2Ag state is expressed mainly as linear combination of three configurations according to the result of CI. The three orbital transitions are HOMO-1 to HOMO, HOMO to LUMO and LUMO to LUMO+1. Here, HOMO-1 represents the orbital level just under the HOMO, and LUMO+1 represents the level over the LUMO. The $B_u - A_g$ transition moment is expressed by the moments between molecular orbitals which exchange in the Slater matrix when the transition occurs. We can estimate the transition moment by looking into these orbitals. The LCAO coefficients of the orbitals for SBA and PV2 are shown in Fig. 2, where horizontal axis represents the position of the carbon atoms. In this figure, the signs of the first and second coefficients of every four coefficients are reversed so as to visualize the shapes easily. Comparing the orbitals between LUMO and LUMO+1 for SBA, most of the respective LCAO coefficients of the atoms on the left side of the molecule have the opposite signs, while most of those on the right side have same signs. This also

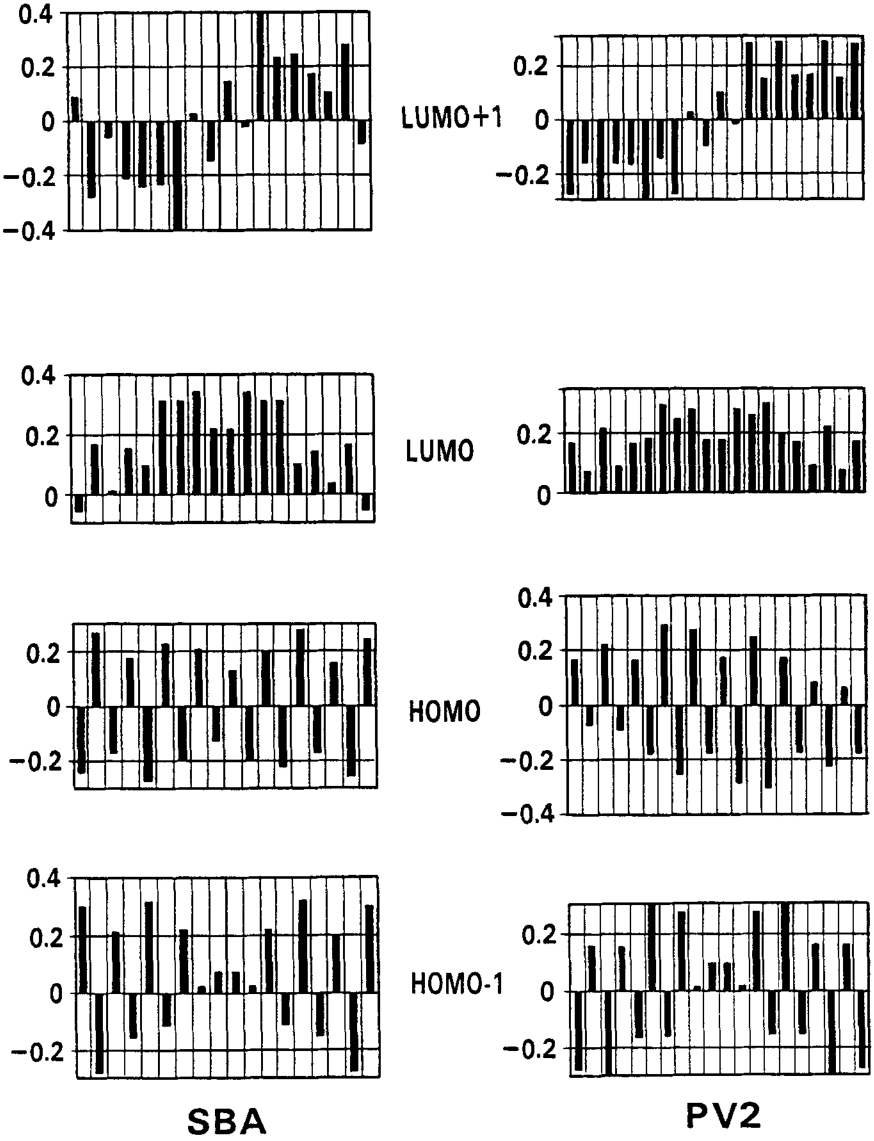

FIGURE 2 Molecular orbital LCAO coefficients of SBA and PV2. The signs of the first and second coefficients of every four atoms are reversed.

applies to the relationship between HOMO-1 and HOMO for SBA. These are significant reasons for large transition moments between B_u and Ag states. The relationships described here are also applicable to SBAC, PV1 and PV2(Fig. 2). And also applicable to polyene and its derivatives[12].

Next, let us regard the difference between SBAs and phenylene vinylenes. For the pai-conjugation like phenylene vinylene where only carbon atoms make up pai-conjugation, electron hole symmetry appears, in which the coefficients of the i-th highest occupied orbital are equal to those of the i-th lowest unoccupied one on reversing the sign of the coefficients of alternate carbon atoms. This kind of symmetry was found in polyacetylene[13-15]. This symmetry is also obviously observed between HOMO and LUMO for phenylene vinylenes, and also observed between HOMO-1 and LUMO+1 as is shown in Fig. 2. So, the electron distributions are approximately the same between an occupied orbital and the corresponding unoccupied one. But in the case of SBA and SBAC, where the pai-conjugation does not consist only of carbon atoms but also of nitrogen atoms, the electron-hole symmetry does not hold. On comparing occupied orbitals with unoccupied ones, around HOMO and LUMO, the distribution for the occupied ones somewhat moves towards the extremities while that for the unoccupied ones somewhat moves towards the center.

The important thing is how this orbital distortion has an effect upon Bu - Ag transition moment. To understand it, we have to consider the molecular orbital distortion and electron correlation effect simultaneously. In the case of PV1 and PV2, the energy of transition from HOMO-1 to HOMO is close to that from LUMO to LUMO+1, and the transition dipole moments for these transitions are almost equal because of the electron-hole symmetry. If we take into account the perturbation due to electron correlation, these two transitions mix and the higher one borrows the intensity of transition moment from the lower one. In other words, the lowest transition $1B_u$-$2A_g$ loses the quantity of transition moment among the several $1B_u$-nA_g transitions. As for SBA and SBAC, however, the electron-hole symmetry does not hold and the energy of the transition from HOMO-1 to HOMO is smaller than that from LUMO to LUMO+1. In this case, the lowest $1B_u$ - $2A_g$ transition does not lose so much of the quantity of the transition moment because the difference of the transition energies decreases the effect of the perturbation due to electron correlation. Therefore the $1B_u$ - $2A_g$ transition moment for SBA and SBAC is larger than that of phenylene vinylenes. The calculated transition moment of $1B_u$ - $2A_g$ for SBA is 2.83 (eÅ) while that for PV2 is 1.67. This contributes the $\chi^{(3)}$ value positively. This effect helps to enhance the non-resonant $\chi^{(3)}$. And we can presume that this effect will appear clearly over and around the two-photon resonant point with the $2A_g$ state.

SUMMARY AND CONCLUSION

Molecular orbitals and third-order suseptibilities for SBA and SBAC are calculated. The effect of orbital shape on the susceptibility is analysed. The following two reasons are found to be responsible for the third susceptibility.

(1) The large moments of orbital transitions from HOMO-1 to HOMO and from LUMO to LUMO+1 contribute to the transition moment between B_u and A_g excited states, and contribute to the third susceptibility. This explanation also applies to phenylene vinylenes and finite polyenes.

(2) The orbital distortion occurs for SBA and SBAC. This type of distortion breaks electron-hole symmetry, supresses the effect of electron correlation and enhances the third susceptibility.

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