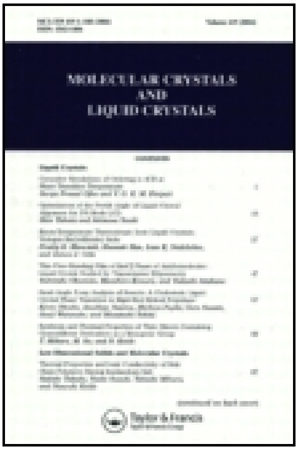

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CNDO/S—CI Calculations of Hyperpolarizabilities. III. Regular Polyenes, Charged Polyenes, Di-substituted Polyenes, Polydiacetylene and Related Species

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CNDO/S-CI Calculations of Hyperpolarizabilities. III. Regular Polyenes, Charged Polyenes, Disubstituted Polyenes, Polydiacetylene and Related Species

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The analytic formula for the third-order hyperpolarizability $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ is derived from time-dependent perturbation theory. An approximate formula for γ_{ijkl} in a static electric field is also presented. The γ_{zzzz} values (the chain axis components) for regular polyenes, charged polyenes, donor (D) – acceptor (A) disubstituted polyenes, polydiacetylene and related species are evaluated by the use of several quantities calculated for low-lying excited states by the CNDO/S-CI method. The signs and magnitudes of γ_{zzzz} and the effects of variations in chain length are investigated on the basis of the calculated results. For regular polyenes, the calculated γ_{zzzz} values are positive and a power law dependence on the chain length N is found with an exponent of 4.14. In contrast, the calculated values of γ_{zzzz} for charged polyenes (+) are negative, but possess a similar N-dependence with an exponent of 4.44. The signs, magnitudes and N-dependences of γ_{zzzz} for disubstituted polyenes with donor (D) and acceptor (A) groups and polydiacetylene are discussed in relation to the experimental data available.

Keywords: CNDO/S-CI, third-order hyperpolarizability, polyene, polydiacetylene

I. INTRODUCTION

The third-order hyperpolarizability $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ has been receiving intense interest recently. The analytic expression for $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ is derived here from time-dependent perturbation theory,[1] in a similar fashion to the derivation of the second-order hyperpolarizability $\beta_{ijk}(-2\omega;\omega,\omega)$ treated in previous papers.[2,3] However, the expression for $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ is considerably more complex and the higher excited states contribute to γ_{ijkl} significantly. Therefore, approximations of terms in the full formula of $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ are presented. The approximations clarify the virtual excitation processes[4,5] for the third-order nonlinear coefficients, and reduce the labors of calculation on the basis of the full formula. The approximate formula is applied to the evaluation of the γ_{zzzz} values (the chain axis components) for relatively short π-conjugated compounds. As previously,[2,3] the excitation energies, transition moments, and the differences of dipole moments between excited and ground states are calculated by the CNDO/S[6] single-excitation CI (SCI) procedure.

There are three objectives of this study: first, to examine the magnitudes and signs of the γ_{zzzz} values for regular polyenes and charged polyenes (+) and (−) and to clarify their dependences on the number N of carbon-atom sites;[7-9] second, to investigate the γ_{zzzz} values for disubstituted polyenes with donor (D)-acceptor (A), D-D, A-A groups and related species; and third, to calculate the γ_{zzzz} values for polydiacetylene and to examine the calculated results in relation to the experiments.[10,11]

II. THEORETICAL METHOD

A theoretical formulation for the third-order hyperpolarizability $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ is given by time-dependent perturbation theory.[1] However, the full expression for $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ is too complicated to provide a clear picture of the virtual excitation processes.[4,5] Thus, the processes have been separated into three different contributions[5] as shown in Figure 1. In order further to clarify the characteristics of the processes, the following approximations are introduced: (1) in compounds with π-conjugated linear chains, the chain axis component of $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ is assumed to be predominant, so that $\gamma_{iiii}(-3\omega;\omega,\omega,\omega)$, which corresponds to $\gamma_{zzzz}(-3\omega;\omega,\omega,\omega)$, is adopted as the characteristic quantity of the third-order hyperpolarizability; (2) for contributions of type (I) in Figure 1, all terms are considered; (3) for contributions of type (II) in Figure 1, the predominant term is considered to be the process (0*n*-*n*0-0*n*-*n*0). When *n* is set to *n*′, the term obtained is denoted type (II)′; (4) for contributions of type (III) in Figure 1, a reduction to the process (0*n*-*nm*-*mn*-*n*0) is made by eliminating the terms with $n \neq n'$ from the process (0*n*′-*n*′*m*-*mn*-*n*0). The reduced term is then denoted type (III)′.

Approximations (3) and (4) are illustrated in Figure 2. These are considered to be reliable unless many higher excited states contribute to the third-order nonlinear excitation processes. Approximations (3) and (4) are expected to be applicable to

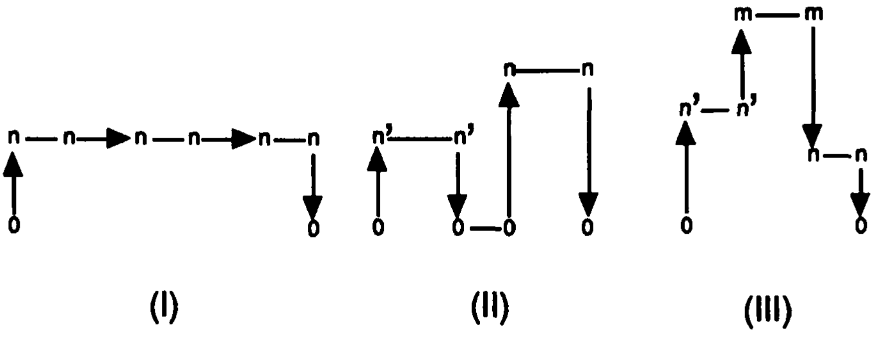

FIGURE 1 Three types of contributing terms to $|\gamma_{zzzz}|$

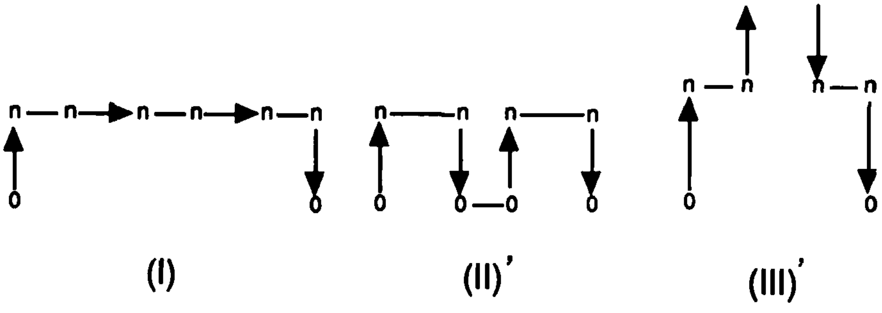

FIGURE 2 Approximation of terms illustrated by types (II) and (III) contributions in Figure 1.

small molecules and/or relatively short conjugated chains. The approximate analytic formula for $\gamma_{iiii}(-3\omega;\omega,\omega,\omega)$ is given, using the above approximations, as

$$
\begin{aligned}
&\gamma_{iiii}(-3\omega;\omega,\omega,\omega) = \\
&\sum_{n=1} (\mu^{i}_{n0})^2(\Delta\mu^{i})^2 \frac{E_{n0}(E_{n0}^2 + (\hbar\omega)^2)}{(E_{n0}^2 - (3\hbar\omega)^2)(E_{n0}^2 - (2\hbar\omega)^2)(E_{n0}^2 - (\hbar\omega)^2)} \\
&- \sum_{n=1} (\mu^{i}_{n0})^4 \frac{E_{n0}}{(E_{n0}^2 - (3\hbar\omega)^2)(E_{n0}^2 - (\hbar\omega)^2)} \\
&+ \sum_{\substack{m,n=1 \\ m\neq n}} (\mu^{i}_{n0})^2(\mu^{i}_{mn})^2 \frac{E_{n0}^2E_{m0} + 4\,E_{n0}(\hbar\omega)^2 - 3E_{m0}(\hbar\omega)^2}{(E_{n0}^2 - (3\hbar\omega)^2)(E_{n0}^2 - (\hbar\omega)^2)(E_{m0}^2 - (2\hbar\omega)^2)} \qquad (1)
\end{aligned}
$$

In the case of a static electric field, Equation (1) is reduced to Equation 2.

$$
\gamma_{iiii}(0;0,0,0) = \sum_{n=1} \frac{(\mu^{i}_{n0})^2(\Delta\mu^{i})^2}{E_{n0}^3} - \sum_{n=1} \frac{(\mu^{i}_{n0})^4}{E_{n0}^3} + \sum_{\substack{m,n=1 \\ m\neq n}} \frac{(\mu^{i}_{n0})^2(\mu^{i}_{mn})^2}{E_{n0}^2\,E_{m0}}, \qquad (2)
$$

where the first, second and third terms correspond to the type (I), type (II)' and type (III)' contributions of Figure 1, respectively. From Equation (2), the terms expressed by type (I) and type (III)' contributions are positive in sign, while the type (II)' contribution is a negative. Therefore, the overall sign of γ_{iiii} is determined by the detailed balance between the (I+III')- and (II')-terms.

In order to calculate γ_{iiii} by the use of Equation (2), the excitation energies (E_{n0}), transition moments (μ_{0n}, μ_{nm}) and the differences of dipole moments (μ_{nn}) between excited and ground states need to be known. Here, the CNDO/S approximation including the single-excitation configuration interaction (SCI) is employed to calculate these quantities. In these SCI calculations[2,3], only the π electron orbitals are included, because π-π^* excitations contribute predominantly to low-lying excited states and because the π-electron contribution to γ_{ijkl} is known to be more dominant than the σ-electron contribution.[4,5]

III. RESULTS

Organic systems studied here are schematically shown in structural formula (A)-(I) of Figure 3. The compounds are placed on the z-x plane, and the coordinate *z* axis is chosen along the chain axis. Under this assumption, a dominant component of γ_{ijkl} is given by γ_{zzzz}. Bond lengths and bond angles for these systems are assumed on the basis of experimental data and the bond alternation has been taken into account. For regular polyenes, lengths of 1.35 and 1.45 Å are assumed for the double and single bonds, respectively. For the charged polyenes, it is assumed that the alternation between single and double bonds is inverted at the center of the chain.

Table I summarizes the γ_{zzzz} values in a static electric field and the values of the three types of contribution for the varying number N of carbon-atom sites in systems (A)-(I). Figures 4-12 show the lg-lg plots of the absolute value of γ_{zzzz}, *i.e.*, $|\gamma_{zzzz}|$, and each part of $|\gamma_{zzzz}|$ versus the number N of carbon-atom sites. Table II shows virtual excitation process which makes the most dominant contribution to each part, together with the γ_{zzzz} values at N = 9 for (B), (C), (G) and at N = 8 for the remaining systems.

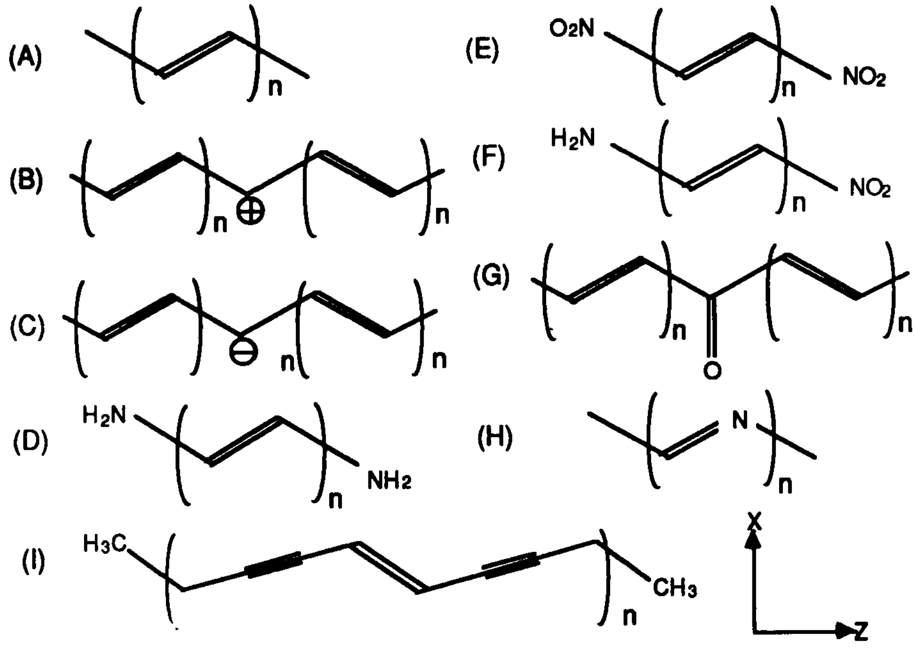

FIGURE 3 Schematic diagrams of systems studied.

TABLE I

Calculated values of the three types of contribution and the total $\gamma_{zzzz} \times 10^{36}$ [esu] for system (A)-(I).

(A)

N	0n-nn-nn-n0	0n-n0-0n-n0	0n-nm-mn-n0	Total
4	0.0	-2.09	2.98	0.887
6	0.0	-12.0	17.5	5.60
8	0.0	-39.3	58.1	18.8
10	0.0	-94.0	138	43.9
12	0.0	-184	266	81.9

(B)

N	0n-nn-nn-n0	0n-n0-0n-n0	0n-nm-mn-n0	Total
5	0.0	-9.18	6.86	-2.33
9	0.0	-145	111	-33.8
13	0.0	-712	551	-160

(C)

N	0n-nn-nn-n0	0n-n0-0n-n0	0n-nm-mn-n0	Total
5	0.0	-14.2	11.6	-2.59
9	0.0	-184	150	-33.8
13	0.0	-822	673	-149

(D)

N	0n-nn-nn-n0	0n-n0-0n-n0	0n-nm-mn-n0	Total
4	0.0	-6.27	8.22	1.86
6	0.0	-25.6	35.1	9.47
8	0.0	-68.9	96.3	27.4
10	0.0	-145	203	57.9
12	0.0	-261	361	99.3

(E)

N	0n-nn-nn-n0	0n-n0-0n-n0	0n-nm-mn-n0	Total
4	0.0	-7.61	19.8	12.2
6	0.0	-33.2	67.1	33.9
8	0.0	-91.7	157	65.0
10	0.0	-194	305	111
12	0.0	-347	514	166

(F)

N	0n-nn-nn-n0	0n-n0-0n-n0	0n-nm-mn-n0	Total
4	14.8	-7.46	9.58	17.0
6	42.7	-30.6	38.0	50.1
8	90.4	-82.4	102	110
10	157	-172	216	202
12	237	-304	394	327

TABLE I

(*Continued*)

(G)

N	0n-nn-nn-n0	0n-n0-0n-n0	0n-nm-mn-n0	Total
5	0.0	-1.01	4.29	3.28
9	0.0	-18.8	45.8	27.1
13	0.0	-96.1	170	73.4

(H)

N	0n-nn-nn-n0	0n-n0-0n-n0	0n-nm-mn-n0	Total
4	1.05	-1.04	1.55	1.57
6	6.83	-5.29	9.59	11.1
8	23.2	-15.1	32.0	40.1
10	52.5	-32.0	77.2	97.7

(I)

N	0n-nn-nn-n0	0n-n0-0n-n0	0n-nm-mn-n0	Total
4	0.0	-26.9	11.8	-15.1
8	0.0	-1210	557	-659
12	0.0	-16000	5040	-11000

From the calculated results, it is seen: (a) that the first excited state is predominant in type (I) and type (II)′ contributions; (b) that both the first and second excited states contribute to type (III)′ contributions in centrosymmetric systems such as a regular polyene; and (c) that a plurality of excited states, including a few higher states, contribute to type (III)′ contributions in noncentrosymmetric systems such as a D-A disubstituted polyene.

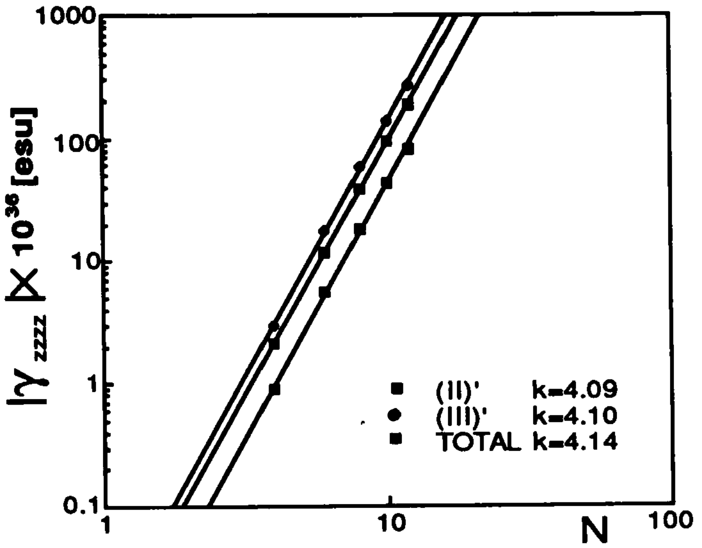

FIGURE 4 log-log Plot of $|\gamma_{zzzz}|$ versus the number of carbon atoms N for (A). k; slope.

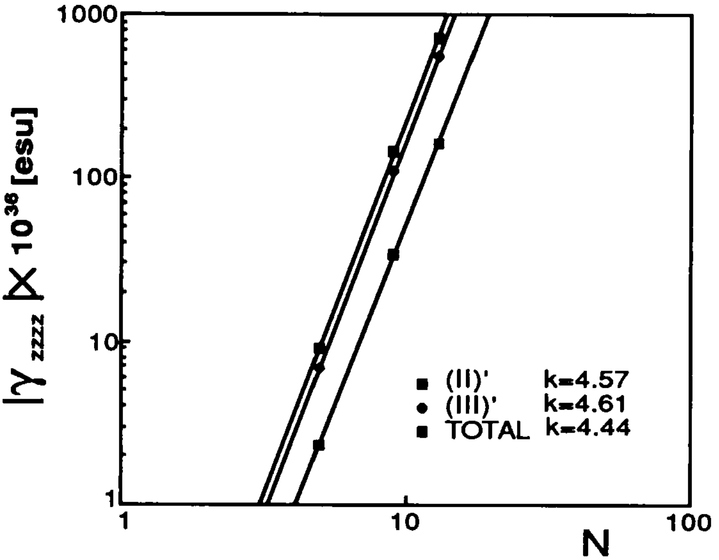

FIGURE 5 log-log Plot of $|\gamma_{zzzz}|$ versus the number of carbon atoms N for (B). k; slope.

The contributions of type (I) for the regular polyene (A) are found to be zero since $\Delta\mu$ disappears because of the centrosymmetric structure. In type (II)' and type (III)' contributions for the regular polyene (A), the absolute values of the type (III)' contribution are larger than those of the type (II)' contribution, so that the net γ_{zzzz} values are positive in sign. In this system, the process (01-10-01-10) is dominant in the type (II)' contribution while the process (01-12-21-10) is dominant

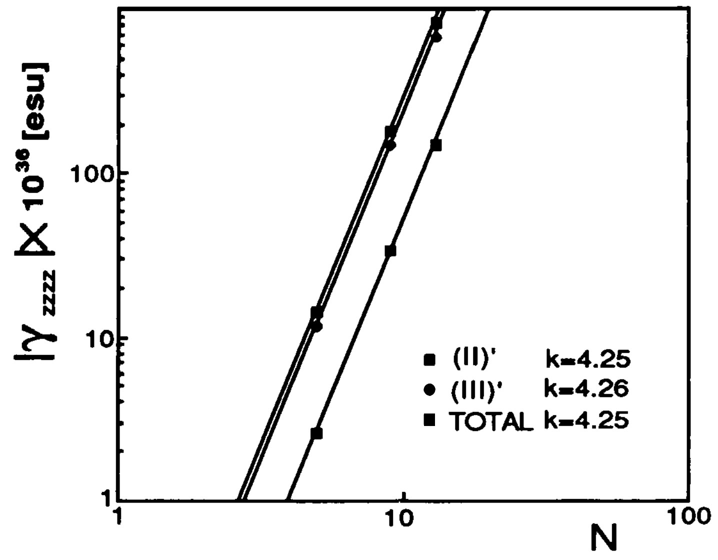

FIGURE 6 log-log Plot of $|\gamma_{zzzz}|$ versus the number of carbon atoms N for (C). k; slope.

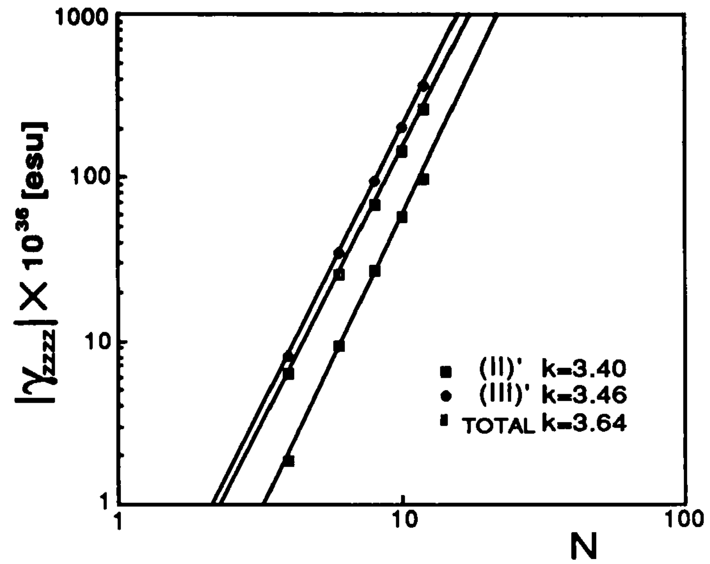

FIGURE 7 log-log Plot of $|\gamma_{zzzz}|$ versus the number of carbon atoms N for (D). k; slope.

in the type (III)′ contribution throughout all the numbers N of carbon-atom sites. Figure 4 shows that the calculated values of type (II)′, type (III)′ and γ_{zzzz} all fit well expressions of the form:

$$\gamma_{zzzz} = aN^k. \tag{3}$$

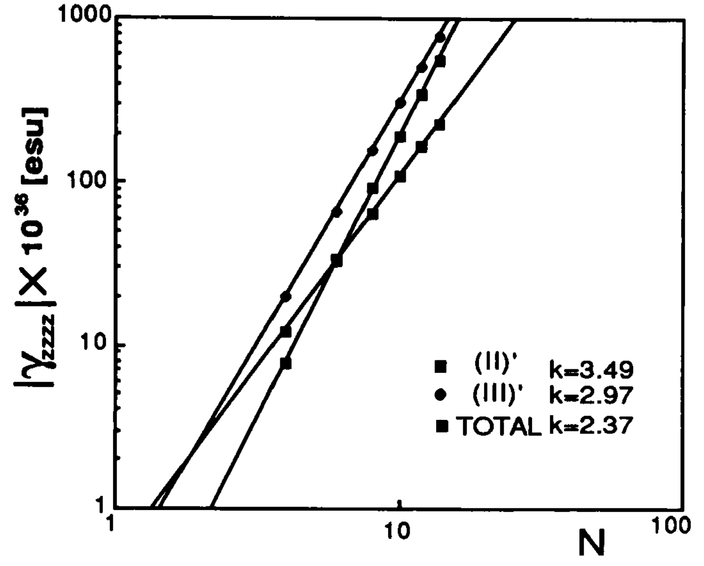

FIGURE 8 log-log Plot of $|\gamma_{zzzz}|$ versus the number of carbon atoms N for (E). k; slope.

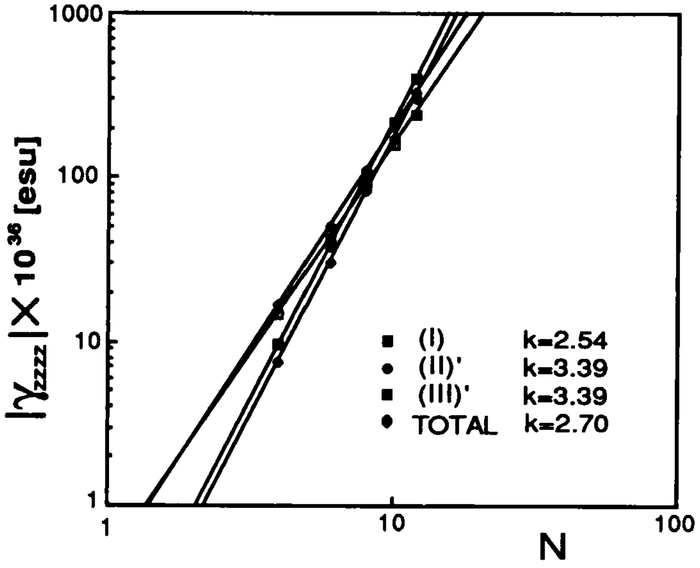

FIGURE 9 log-log Plot of $|\gamma_{zzzz}|$ versus the number of carbon atoms N for (F). k; slope.

From Figure 4, these terms have power law dependences on the number N of carbon-atom sites with exponents (k) of 4.09, 4.10 and 4.14, respectively. The results are in good agreement with previously reported results.[4,7-9]

Ab initio calculations of γ_{ijkl} in a static electric field for regular polyenes have been carried out by Hurst *et al.*[12] Their calculations using the CPHF method give γ_{ijkl} in a static electric field by differentiating the ground state energy at the Hartree-

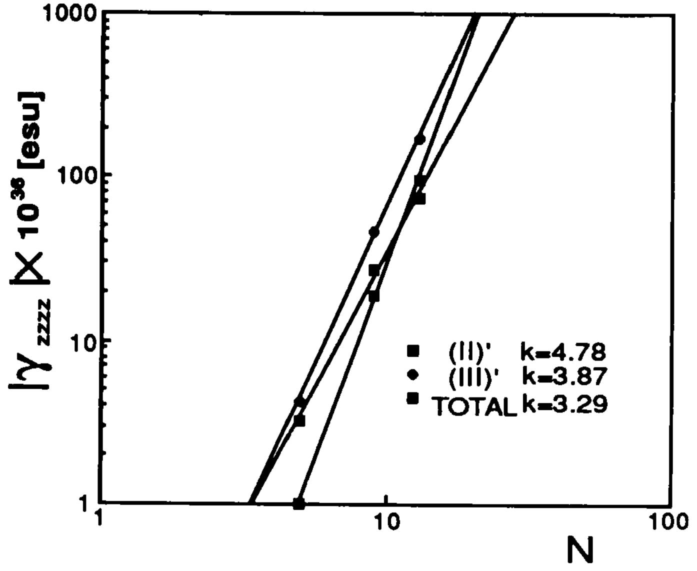

FIGURE 10 log-log Plot of $|\gamma_{zzzz}|$ versus the number of carbon atoms N for (G). k; slope.

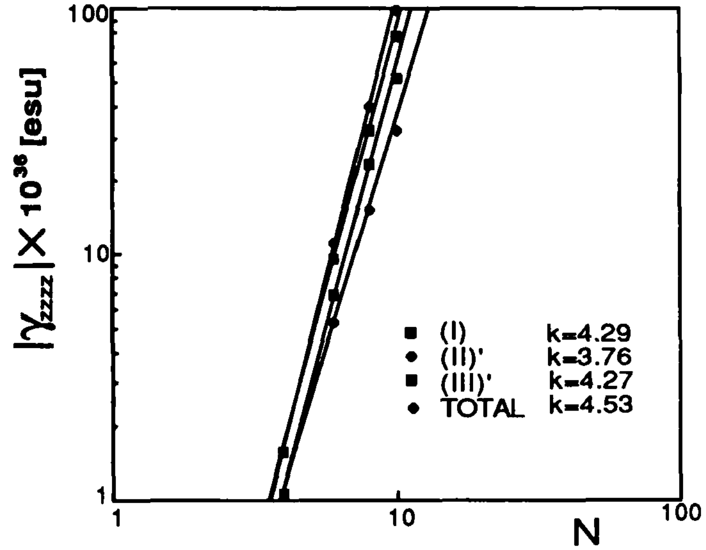

FIGURE 11 log-log Plot of $|\gamma_{zzzz}|$ versus the number of carbon atoms N for (H). k; slope.

Fock level obtained variationally in the presence of an electric field. They investigate the dependences of some basis sets on γ_{ijkl} and propose the basis set named 6-31G+PD by which reasonable results of the chain axis component can be obtained. In order to compare their results with those obtained by the present authors, the chain axis components were calculated from their equation of extrapolation and their values are plotted together with our results in Figure 13. Our γ_{zzzz} are about 60% of their values at the 6-31G+PD. As for the dependence of γ_{zzzz} on

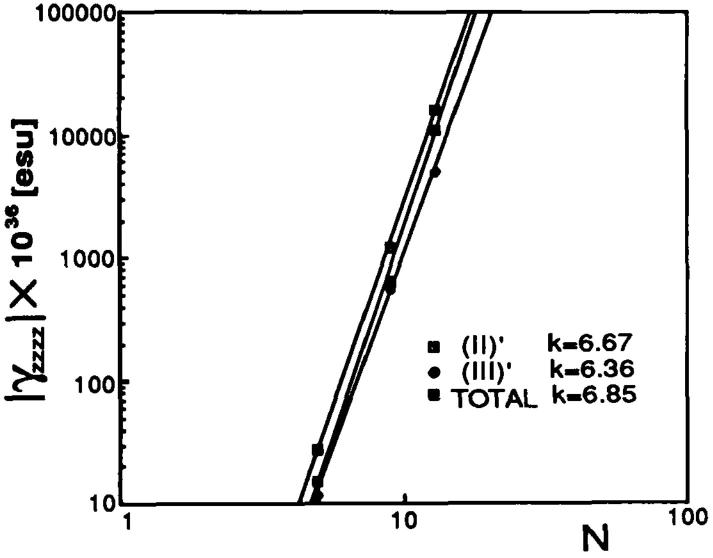

FIGURE 12 log-log Plot of $|\gamma_{zzzz}|$ versus the number of carbon atoms N for (I). k; slope.

TABLE II

More or most contributing process (according to type of contribution) to γ_{zzzz} for (A)-(I).[a]

System	(I)	(II)'	(III)'
(A)		01-10-01-10 (-39.3)	01-12-21-10 (50.0)
(B)		01-10-01-10 (-145)	01-12-21-10 (76.8)
(C)		01-10-01-10 (-184)	01-12-21-10 (107)
(D)		01-10-01-10 (-68.9)	01-12-21-10 (81.4)
(E)		01-10-01-10 (-91.6)	01-12-21-10 (102)
(F)	01-11-11-10 (87.2)	01-10-01-10 (-81.9)	01-12-21-10 (20.2) 01-13-31-10 (44.6)
(G)		01-10-01-10 (-18.3)	01-12-21-10 (19.4)
(H)	01-11-11-10 (22.2)	01-10-01-10 (-14.9)	01-12-21-10 (21.7)
(I)		01-10-01-10 (-16000)	01-12-21-10 (4870)

[a] $\gamma_{zzzz} \times 10^{36}$ [esu] values of the contributions in three parts are shown in parentheses.

N, our k value (4.14) agrees well with theirs ($k = 3.91$) at 6-31G + PD. This suggests that the three type approximation with CNDO/S-CI method is appropriate to reproduce the dependences of γ_{zzzz} on chain length of medium-size polyenes, which are obtained by the large scale ab initio CPHF method with the augmented basis sets.

The calculated results for the charged polyenes (+) (B) show that the |type (I)| values are zero because of the centrosymmetric structure as in the case of regular polyenes, while the |type (II)'| values are larger than |type (III)'| values unlike the regular polyene, resulting in a γ_{zzzz} that is negative in sign. The result is in good accord with the calculated result for the charged soliton (+) reported by Silbey *et al.*[7-9] From Figure 5, it is seen that |type (II)'|, |type (III)'| and $|\gamma_{zzzz}|$ of charged polyene (+) have power law dependences on N with the exponents 4.57, 4.61 and 4.44, respectively. Similarly, Figure 6 shows that |type (II)'|, |type (III)'| and $|\gamma_{zzzz}|$ of charged polyene (−) exhibit similar power law dependences with the exponents 4.25, 4.26 and 4.25, respectively.

The system (F) represents the largest $|\gamma_{zzzz}|$ value among the disubstituted systems: (D) with amino groups as electron donors, (E) with nitro groups as acceptors and (F) with both amino and nitro groups. The γ-values decrease in the order:

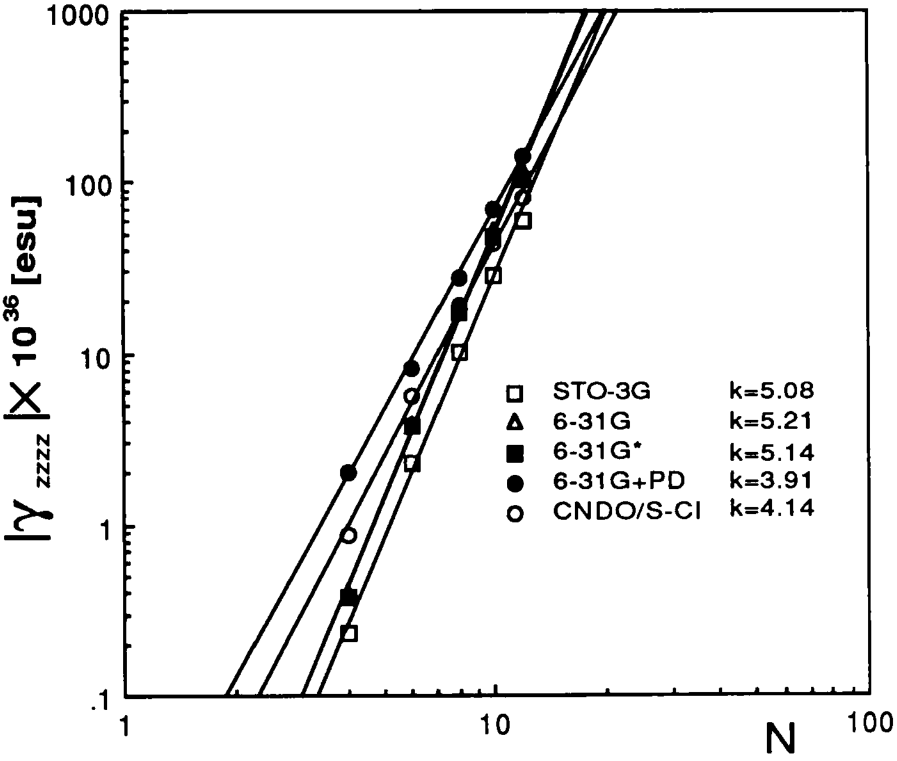

FIGURE 13 log-log Plot of $|\gamma_{zzzz}|$ versus the number of carbon atoms N. The results of ab initio calculations are taken from reference 12.

(*F*) > (*E*) > (*D*), as shown in Table I. However, the N dependences of $|\gamma_{zzzz}|$ in Figures 7–9 show that the k values for (*D*), (*E*), and (*F*) are 3.64, 2.37 and 2.70, respectively. From comparison with the N dependence of each part for the regular polyenes (*A*), it is found that system (*D*) exhibits smaller N dependences of E_{10} and E_{20} than system (*A*), and that the N dependences of E_{10}, E_{20} and $|\mu_{12}|$ for system (*E*) are smaller than those of system (*A*). Since *D*-*A* disubstituted system (*F*) is not centrosymmetric in structure, the contribution of type (*I*) to (*F*) is non-zero, whereas types (II)′ and (III)′ contributions are nearly cancelled as shown in Figure 9. Therefore, the N dependence of the |type (I)| contribution seems to be reflected mainly in the N dependence of the total $|\gamma_{zzzz}|$ value of (*F*).

It seems that the dipole moment difference ($\Delta\mu$) most contributing to type (I) contributions, is not simply proportional to the number N of carbon-atom sites. This behavior of $\Delta\mu$ is responsible for the smaller N dependence of $|\gamma_{zzzz}|$ for system (*E*). In fact, in the *D*-*A* disubstituted polyene, the charge displacement by the 0-1 transition increases linearly with N in the case of short chains, whereas the charge for long chains is more or less localized in the vicinity of the carbon-atom sites connected with *D* and *A* substituted groups, rather than showing a direct charge transfer from a *D* to an *A* group. Consequently, $\Delta\mu$ causes the saturation for long chains.

For the system (*G*) with a carbonyl group in the middle of the chain, $|\gamma_{zzzz}|$ values are positive in sign. In this system, the $|\mu_{01}|$ and $|\mu_{12}|$ are smaller than those for the charged polyenes. In Figure 10, |type (II)′| exhibits a larger *N* dependence than does |type (III)′|. Hence, the *N* dependence of $|\gamma_{zzzz}|$ is calculated to be small ($k = 3.29$).

γ_{zzzz} values for system (*H*), which has a C═N backbone, become larger than those of the regular polyene. From Figure 11, the *N* dependence of $|\gamma_{zzzz}|$ is the largest with $k = 4.53$ among all the calculated systems except for the polydiacetylene. This large third-order hyperpolarizability is probably due to the large polarization in the main chain. Ab initio calculations such as CPHF are necessary to confirm this tendency.

The *k* values for the polydiacetylene (I) are found to be 6.67, 6.36 and 6.85, respectively, from the *N* dependences of |type (II)′|, |type (III)′| and $|\gamma_{zzzz}|$ shown in Figure 12. The magnitudes of *k* are the largest among all the calculated systems. The γ_{zzzz} values for system (I) are, however, enormously negative. This is attributable to the *N* dependences of the transition moments ($|\mu_{01}|$, $|\mu_{12}|$) and the excitation energies (E_{10}, E_{20}); *i.e.*, the $|\mu_{01}|$ values are much larger than $|\mu_{12}|$ and the *N* dependences of $|\mu_{01}|$ and E_{20} are larger than those of $|\mu_{12}|$ and E_{10}, respectively. Probably these differences are the origins of the characteristic behavior of γ_{zzzz} values for the polydiacetylene system (I).

IV. DISCUSSION AND CONCLUSIONS

These CNDO/S-CI calculations show that the approximate formula Equation (2) is sufficiently reliable in reproducing the tendencies for γ_{zzzz} observed for relatively short π conjugated linear chains.[5] Table III summarizes the dependences of |type (II)′|, |type (III)′| and total $|\gamma_{zzzz}|$ on the number *N* of the carbon-atom sites, and the signs of γ_{zzzz} for all the systems treated here.

From Table III, it is seen that the signs of γ_{zzzz} for the charged polyenes (*B*) and (*C*) are opposite to those for the regular polyenes and that their dependences (*k*) are larger than those for the regular polyenes. These tendencies seem to be attributable mainly to the fact that $|\mu_{01}|$ is smaller than $|\mu_{12}|$ in the case of the regular polyenes, while $|\mu_{01}|$ for charged polyenes becomes large owing to the charge transfer from the neutral carbon sites to the charged site, so that |type (II)′| dominates over |type (III)′|.

For the systems disubstituted by donor (*D*) and acceptor (*A*) groups, it is proved that $|\gamma_{zzzz}|$ values are larger than those for the regular polyenes, although the *N* dependences become smaller for the former systems. The present calculations demonstrate that the $|\gamma_{zzzz}|$ values for *D*-*A* disubstituted polyenes are determined mainly by the type (I) contribution because of the cancellation of type (II)′ and (III)′ contributions. The calculations also indicate that the type (I) contribution is affected primarily by the $|\Delta\mu|$ value. It suffers saturation in long chain systems because the charge localization in the vicinity of the carbon-atom sites connected with the *D*- and *A*- groups occurs with the increase of the number *N* of carbon-atom sites. This tendency probably leads to the characteristic behaviors of γ_{zzzz} concluded for *D*-*A* disubstituted polyenes.

TABLE III

k Values and the signs of γ_{zzzz} for (A)-(I).

System	k(I)	k(II)	k(III)	k(Total)	Sign of γ_{zzzz}
(A)		4.09	4.10	4.14	+
(B)		4.57	4.61	4.44	−
(C)		4.25	4.26	4.25	−
(D)		3.40	3.46	3.64	+
(E)		3.49	2.97	2.37	+
(F)	2.54	3.39	3.39	2.70	+
(G)		4.78	3.87	3.29	+
(H)	4.29	3.76	4.27	4.53	+
(I)		6.67	6.36	6.85	−

However, in the system (*G*), which might be expected to show the same characteristics as do the *D-A* disubstituted system, it is found that a large charge displacement in the main chain provides a large $|\gamma_{zzzz}|$ value, and furthermore, that the *N* dependence of $|\gamma_{zzzz}|$ does not exhibit so much saturation in contrast to the case of *D-A* disubstituted polyenes. It is suggested that synthesis of type (*G*) compounds is worth attempting.

For the polydiacetylene system (I), the calculated γ_{zzzz} values are found to be negative in sign, and their magnitudes and the *N* dependences exhibit the largest values in all the calculated systems. According to recent experiments[10,11], the signs of γ observed for this system are variable from plus to minus, depending on the experimental conditions. This suggests that the γ value of the system is very sensitive to subtle changes in the molecular structure and environmental effects. As can be seen from Equation (2), small changes for relationships of the magnitudes between type (II)′ contributions and the other types can induce an inversion of the sign of γ_{zzzz}. In fact, the present calculations do indicate that the introduction or elimination of charge at the center of polyene, which corresponds to the case of charged polyenes here, can change the sign, magnitude and the dependence of γ_{zzzz} on *N*. Therefore, it is not surprising that the inversion of the sign of γ_{zzzz} occurs with small changes of the molecular structure for the polydiacetylene systems.

In conclusion, the approximate formula Equation (2) derived here is suitable for effective computation and analysis of the third-order hyperpolarizability $\gamma_{ijkl}(-3\omega;\omega,\omega,\omega)$ for organic molecules, such as long chain polyenes with donor and acceptor groups. The CNDO/S-SCI method employed in these calculations provides reasonable results at least in a qualitative sense. However, more careful examination of the contributions of double excitations[4,5] will be necessary in the case of long polyenes. Ab initio calculations are also desirable for confirmation of the qualitative tendencies revealed by the present CNDO/S-SCI calculations. They are in progress in this laboratory.

References

1. J. A. Armstrong, N. Bloembergen, J. Ducuing and P. S. Pershan, *Phys. Rev.* **127**, 1918 (1962).
2. M. Nakano, K. Yamaguchi and T. Fueno, 'CNDO/S-CI Calculations of Hyperpolarizabilities. I.': in Nonlinear Optics of Organics and Semiconductors, edited by T. Kobayashi, Springer Proceedings in Physics. **36**, 98 (1989).
3. M. Nakano, K. Yamaguchi and T. Fueno, 'CNDO/S-CI Calculations of Hyperpolarizabilities. II.': in Nonlinear Optics of Organics and Semiconductors, edited by T. Kobayashi, Springer Proceedings in Physics. **36**, 103 (1989).
4. J. R. Heflin, K. Y. Wong, O. Zamani-Khamiri and A. F. Garito, *Phys. Rev.* **B38**, 1573 (1988).
5. A. F. Garito and J. R. Heflin, K. Y. Wong and O. Zamani-Khamiri, in: Organic Materials for Nonlinear Optics, edited by D. J. Ando and D. Bloor (1988).
6. J. Del Bene and H. H. Jaffe, *J. Chem. Phys.* **48**, 1807 (1968).
7. C. P. de Melo and R. Silbey, *Chem. Phys. Lett.* **140**, 537 (1987).
8. C. P. de Melo and R. Silbey, *J. Chem. Phys.* **88**, 2558 (1988).
9. C. P. de Melo and R. Silbey, *J. Chem. Phys.* **88**, 2567 (1988).
10. F. Kajar and J. Messier, in: Polydiacetylenes, NATO ASI ser. **E102**, 325, eds. D. Bloor and R. R. Chance (Nijhoff, The Hague, 1985).
11. G. M. Carter, Y. J. Chen and S. K. Tripathy, *Appl. Phys. Lett.* **43**, 841 (1983).
12. G. J. B. Hurst, M. Dupuis and E. Clementi, *J. Chem. Phys.* **89**, 385 (1988).