

## 폴리엔의 HOMO-LUMO Gap, THG, DC-EFISHG, IDRI, OKE들에 대한 이론적 연구

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(1996. 7. 6 접수)

## Theoretical Study of the HOMO-LUMO Gap, THG, DC-EFISHG, IDRI, and OKE in Polyenes

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(Received July 6, 1996)

**요 약.** 폴리엔의 HOMO-LUMO gap, 정적 및 동적인 3차 편극율을 시간의존 Hartree Fock 반경험적 PM3, AM1, MNDO, MINDO/3 방법을 이용하여 구하였다.  $C_2H_4$ 로부터  $C_{32}H_{34}$ 까지 모든 계산이 수행되었다. HOMO-LUMO gap은 MINDO/3>MNDO>PM3>AM1 순서로 증가하였으며, THG, DC-EFISHG, IDRI, OKE효과는 AM1>MNDO>PM3 순서로 증가하였다. 다양한 3차 효과는 THG>DC-EFISHG>IDRI>OKE 순서로 증가함을 보여주고 있다.

**ABSTRACT.** The HOMO-LUMO gap, and static and dynamic third-order polarizabilities for the polyenes are evaluated by means of the time-dependent Hartree Fock(TDHF) semiempirical PM3, AM1, MNDO, and MINDO/3 calculations. All calculations have performed on the series  $C_2H_4$  to  $C_{32}H_{34}$ . The HOMO-LUMO gap increases in the order: MINDO/3>MNDO>PM3>AM1 levels. THG, DC-EFISHG, IDRI, and OKE for the various calculations show the order: AM1>MNDO>PM3 levels. The various third-order effects for the polyenes have the following order: THG>DC-EFISHG>IDRI>OKE.

### INTRODUCTION

A number of  $\pi$ -conjugated polymers with highly nonlinear optical characteristics have attracted in relation to their nonlinearities. Recently, experimental and theoretical studies have carried out to investigate the nonlinear optical properties for polyenes systems. The  $\chi^{(3)}$  behavior of *trans*-polyacetylene has been investigated by third-harmonic generation,<sup>1</sup> pump-probe transient absorption, and degenerate four wave mixing.<sup>2</sup>

A number of theoretical studies have been performed to investigate of the  $\gamma$  evolution as a function of chain length in polyenes.<sup>3-5</sup> In particular, Craig *et al.*<sup>6</sup> reported that the effective third-order polarizability of the copolymers at 1.34  $\mu\text{m}$  varied

with nominal conjugation length to the exponents 2.9 and 3.0 in the case of the alternating and all-trans isomers, respectively. The CNDO/S approximation including the single-excitation configuration interaction(SCI) is employed to calculate  $\gamma_{xxxx}$  values.<sup>7</sup> Ab initio calculations of  $\gamma_{xxxx}$  in a static electric field for regular polyenes have been carried out by Hurst *et al.*<sup>8</sup> Rustagi *et al.*<sup>9</sup> showed that the third-order polarizability of linear system has a length dependence as  $N^5$ . This value are nearly similar to that(5.3) of result reported by Hameka *et al.*<sup>10</sup>

In this study, the HOMO-LUMO gaps, Third-Harmonic Generation(THG), DC-electric field induced Second-Harmonic Generation(EFISHG), in-

tensity dependent refractive index(IDRI), and optical kerr effect(OKE) are evaluated for all-*trans* polyenes by means of the PM3,<sup>11</sup> AM1,<sup>12</sup> MNDO,<sup>13</sup> and MINDO/3<sup>14</sup> time-dependent Hartree-Fock methods(MOPAC'93).

### THEORETICAL APPROACH

The polyene geometries are optimized with the PM3, AM1, MNDO, and MINDO/3 Hamiltonians, in  $C_{2h}$  symmetry. The  $C_{2h}$  molecular structure of  $C_6H_8$  is shown in Fig. 1.

The PM3, AM1, and MNDO calculations were carried out to investigate the frequency-dependent third-order polarizabilities on the series  $C_2H_4$  to  $C_{32}H_{34}$ . The averaged  $\gamma$  value is defined as  $\langle\gamma\rangle = 1/5(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xyxy} + 2\gamma_{xzzz} + 2\gamma_{yyzz})$ . In the cases of the frequency-dependent THG, EFISHG, IDRI, and OKE are expressed as  $\gamma(-3\omega; \omega, \omega, \omega)$ ,  $\gamma(-2\omega; 0, \omega, \omega)$ ,  $\gamma(-\omega; \omega, -\omega, \omega)$ , and  $\gamma(-\omega; 0, 0, \omega)$ , respectively. In order to obtain the limiting  $\langle\gamma\rangle$ , and  $\gamma_{xxxx}$  value with respect to the intermolecular distances, we used the equation  $\{A(N) = a + b/N + c/N^2 + d/N^3$ , where  $A(N) = \langle\gamma\rangle$ (THG,

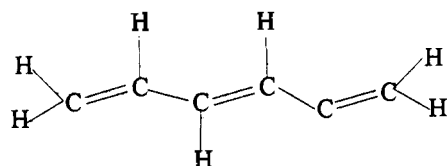


Fig. 1. Structure of hexatriene.

DC-EFISHG, IDRI, OKE), and  $\gamma_{xxxx}$ (THG, DC-EFISHG, IDRI, OKE),  $n$  is the number of C=C bonds}.

### RESULTS AND DISCUSSION

The results of the difference data between HOMO and LUMO fitted by the linear equation( $A(n) = a_0 + b_0/n$ ) are given in Table 1. The PM3, AM1, MNDO, and MINDO/3 limiting energy gaps are 5.959, 6.062, 6.204, and 6.256 respectively. PM3 limiting energy gaps are smallest among the four cases. When we comparing with the VEH band gaps for the short chain lengths, PM3 and AM1 calculated energy gaps are 2 times smaller. On the other hand, for long chain lengths, these values are 3~4 times are smaller.

The chain-length( $N=1-16$ ) and frequency(0.65 eV)-dependent average and longitudinal third-order polarizabilities are represented in Fig. 2. In particular, the static  $\gamma$  values of polyenes are about 16 and 5 times larger than those of the corresponding PPV and PTV oligomers, respectively. The asymptotic  $\langle\gamma\rangle$ ( $\gamma_{xxxx}$ ) values for the frequency of 0.65 eV are 1.47e7(7.41e7), 1.43e7(7.20e7), and 1.35 e7(6.80e7) predicted by PM3, AM1, and MNDO levels, respectively. The asymptotic third-order polarizabilities increase in the order: PM3>AM1>MNDO levels. PM3 asymptotic average and longitudinal third-order polarizabilities are similar to ab initio 6-31G\* asymptotic values for the poly-

Table 1. PM3, AM1, MINDO/3, and MNDO HOMO-LUMO gaps

|         |      | 4      | 5      | 6      | 7      | 8      | 9      | 10     | 12     | 14     | 16     | $\infty$ |
|---------|------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|----------|
| PM3     | HOMO | -8.551 | -8.376 | -8.214 | -8.149 | -8.052 | -8.032 | -7.963 | -7.909 | -7.874 | -7.850 |          |
|         | LUMO | -0.574 | -0.756 | -0.912 | -0.989 | -1.082 | -1.114 | -1.180 | -1.241 | -1.282 | -1.130 |          |
|         | Eg   | 7.977  | 7.620  | 7.302  | 7.160  | 6.970  | 6.918  | 6.783  | 6.668  | 6.592  | 6.540  | 5.959    |
| AM1     | HOMO | -8.379 | -8.124 | -8.034 | -7.983 | -7.868 | -7.864 | -7.777 | -7.722 | -7.687 | -7.663 |          |
|         | LUMO | -0.429 | -0.616 | -0.788 | -0.864 | -0.971 | -0.999 | -1.077 | -1.144 | -1.198 | -1.220 |          |
|         | Eg   | 7.950  | 7.598  | 7.246  | 7.119  | 6.951  | 6.865  | 6.700  | 6.578  | 6.493  | 6.443  | 6.062    |
| MINDO/3 | HOMO | -8.607 | -7.819 | -7.969 | -7.635 | -7.516 | -7.501 | -7.415 | -7.353 | -7.313 | -7.285 |          |
|         | LUMO | 0.243  | 0.046  | -0.101 | -0.188 | -0.270 | -0.311 | -0.364 | -0.422 | -0.460 | -0.487 |          |
|         | Eg   | 8.310  | 7.937  | 7.595  | 7.447  | 7.246  | 7.190  | 7.051  | 6.853  | 6.853  | 6.798  | 6.256    |
| MNDO    | HOMO | -8.320 | -8.198 | -8.040 | -8.010 | -7.909 | -7.916 | -7.838 | -7.796 | -7.769 | -7.751 |          |
|         | LUMO | -0.414 | -0.557 | -0.730 | -0.793 | -0.888 | -0.908 | -0.979 | -1.035 | -1.072 | -1.099 |          |
|         | Eg   | 7.906  | 7.621  | 7.310  | 7.217  | 7.021  | 7.008  | 6.859  | 6.761  | 6.697  | 6.652  | 6.204    |

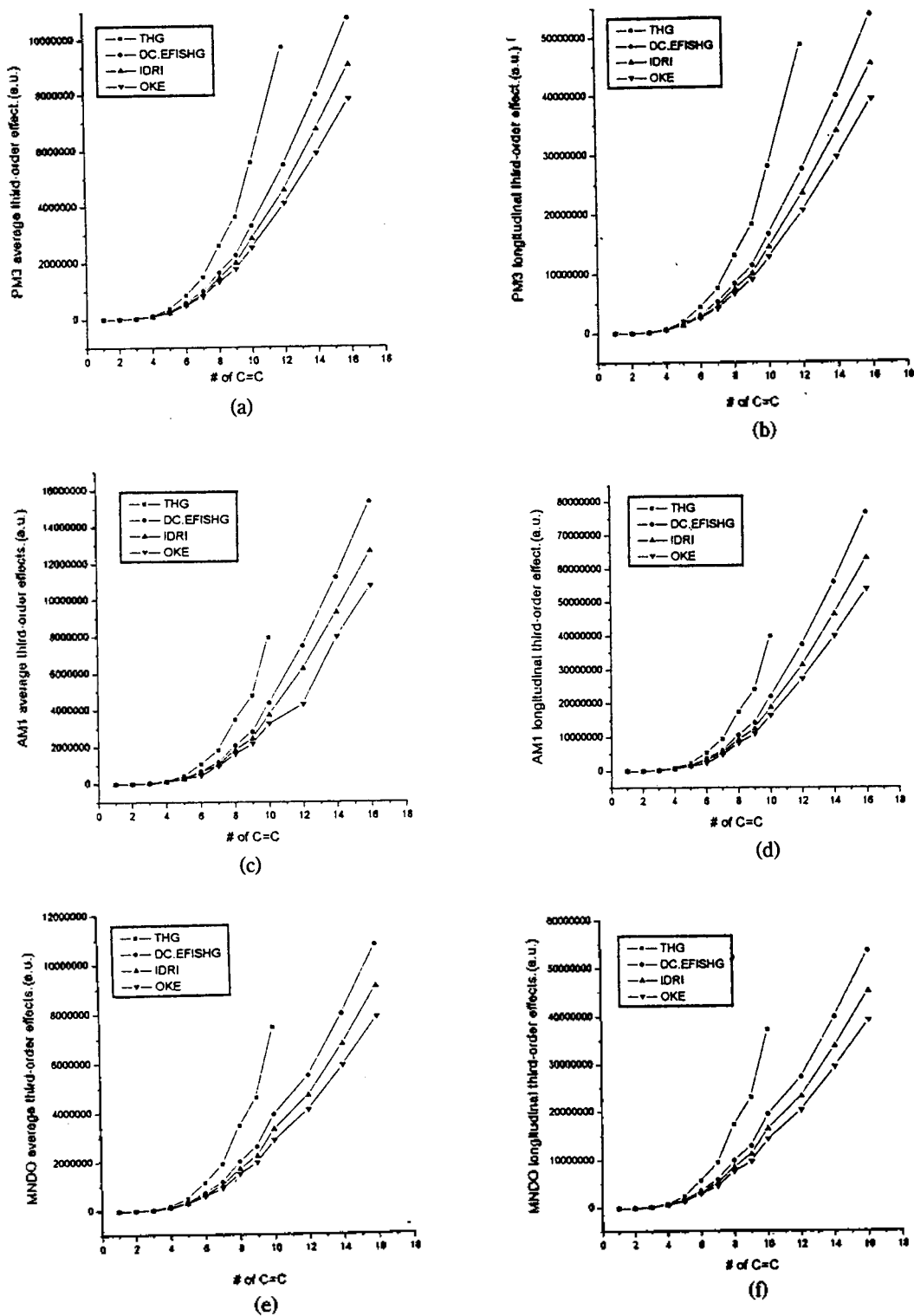


Fig. 2. The chain-length dependent average and longitudinal various third-order effects.

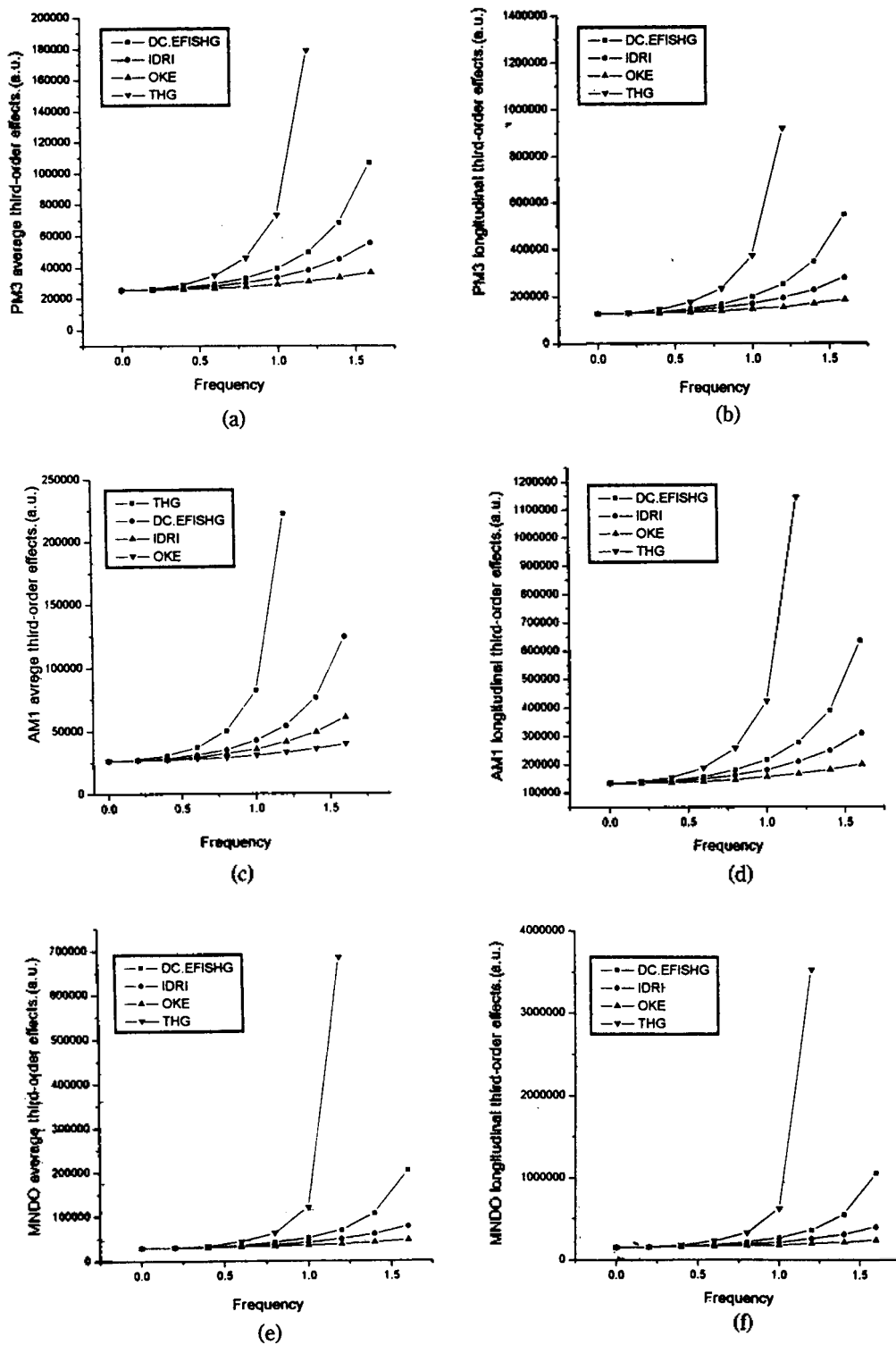


Fig. 3. The frequency-dependent various third-order effects of  $C_3H_6$ .

enes, while AM1 results are similar to ab initio 6-31G+PD values.<sup>15</sup>

Many theoretical method were used to evaluate the exponent values of the effects of THG(Third Harmonic Generation), they varied from 3 to 5.4. The exponent value with the VEH method varies from 6.0 for N=6 to 3.3 for N=30, while Heflin *et al.*<sup>11</sup> reported that the exponent values of *trans* and *cis* conformations for the polyenes were  $5.4 \pm 0.2$  and  $4.7 \pm 0.2$ , respectively. The evolution of the static and dynamic  $\gamma$  values from N=2 to N=32 are represented in Fig. 2. From Fig. 2, we find that the  $k(\langle \gamma \rangle (\gamma_{xxx}) \sim N^k)$  value varies from 4.96(5.20) for N=4 to 4.06(4.05) for N=20 at PM3 level, while for AM1 and MNDO calculations, it varies 5.15(5.33)–4.78(4.77) and 5.12(5.19)–4.58(4.56), respectively. These value are larger than that of PPV oligomers(4.8–2.8).<sup>16</sup> On the other hand, the exponent values of PM3 and AM1 results are about two times smaller than those of Pariser-Parr-Pople results and ab initio 6-31G, 6-31G\*, and 6-31G+PD results for polyenes.<sup>15</sup>

The PM3, AM1, and MNDO calculated various third-order nonlinear optical propertis for the pristine polyenes have the following order: THG>DC-EFISHG>IDRI>OKE. As shown in Fig. 2, the effects of THG increase the steeply with increase in the frequency. On the other hand, compared with the THG, the effects of DC-EFISHG, IDRI, and OKE increase slowly with the increasing the frequency. The PM3 limiting average(longitudinal) DC-EFISHG, IDRI, and OKE values for the frequency of 0.65 eV are 1.39e7(6.98e7), 1.18e7(5.92e7), and 1.02e7(5.12e7), respectively. At 0.65 eV, the AM1 limiting average(longitudinal) DC-EFISHG, IDRI, and OKE values are 1.96e7(9.83e7), 1.63e7(8.15e7), and 1.35e7(6.99e7), respectively. On the other hand, the MNDO limiting average(longitudinal) DC-EFISHG, IDRI, and OKE values for the frequency of 0.65 eV are 1.41e7(7.05e7), 1.19e7(5.97e7), and 1.03e7(5.18e7), respectively. AM1 values are slightly larger than those of PM3 and MNDO calculations. The PM3 and AM1 calculated various third-order nonlinear optical propertis for the pristine polyenes have the following order: THG>DC-

EFISHG>IDRI>OKE. The exponent values(k) of DC-EFISHG, IDRI, and OKE for the frequency of 0.65 eV are 4.08(3.76), 4.00(3.69), and 3.95(3.62) at PM3 level, 4.67(3.94), 4.60(3.86), and 4.53(3.81) at AM1 level, 3.64(3.64), 3.58(3.56), and 3.54(3.54) at MNDO level, respectively.

The frequency-dependent various third-order effects of  $C_6H_8$  are depicted in Fig. 3. The MNDO average first-order polarizabilities for  $C_6H_8$  as a function of frequencies are three times larger than those of PM3 and AM1 calculations. The average and longitudinal first-order polarizabilities have the following order: MNDO>AM1>PM3 levels. The effect of THG increases steeply as frequency increase compared with DC-EFISHG, IDRI, OKE. In particular, IDRI and OKE increase slowly with increasing the frequency. However, there is no difference between the various nonlinear optical processes in the static cases( $\omega=0$ ).

In conclusion, PM3 limiting HOMO-LUMO gaps are smallest among the four calculations. The average and longitudinal third-order polarizabilities increase in the order: AM1>MNDO>PM3 levels. However, in all calculations, THG shows the strongest chain length and frequency dependency among the four third-order effects. Therefore, we suggest that the choice of semiempirical calculations is somewhat important role to investigate the nonlinear optical properties of polyene systems.

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