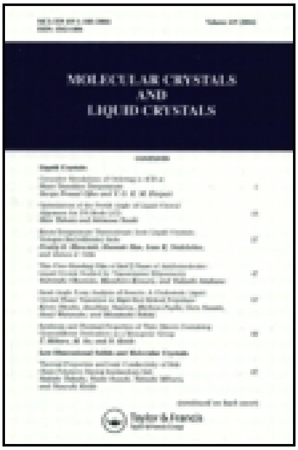

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The Frequency Dependent Nonlinear Optical Properties of Thiophene-, Furan-, Pyrrole-Nitro Polyene Systems

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THE FREQUENCY DEPENDENT NONLINEAR OPTICAL PROPERTIES OF THIOPHENE-, FURAN-, PYRROLE-NITRO POLYENE SYSTEMS

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Abstract By using the semiempirical time-dependent Hartree-Fock PM3 calculations we have studied the frequency-dependent second- and third-order polarizabilities of thiophene-, furan-, pyrrole-nitro polyene systems. The PM3 predicted limiting average second-order polarizabilities increase in the order: pyrrole-> furan-> thiophene-nitro polyene systems. The average and longitudinal third-order polarizabilties have the following order: pyrrole->thiophene->furan-nitro polyene systems. In these trends. we sugest that pyrrole group is the best donor group among the three polyene systems.

INTRODUCTION

The large second-order polarizabilities originate from strong charge-transfer interaction in the donor and acceptor molecules which enhance the electronic polarization induced by incident laser light. Bella et al.[1] reported that the second-order nonlinear optical response of model molecular 1:1 and asymmetric 2:1 organic π electron donor-acceptor(EDA) complexes is investigated using the INDO/S sum-over-excited particle-hole-states formalism. Meyers et al.[2] have reported ab initio-CPHF calculations on the series of benzodithia and dithiolene polyenals.The authors concluded that the sulfur ring groups behave as electron doners in all molecules in that study.

There are a number of semiempirical calculations of hyperpolarizabilities. For example, the NLO properties for benzene and stilbene derivatives[3] and push-pull polyenes have been performed using the Pariser-Parr-Pople(PPP) method. CNDO calculations of NLO properties have been performed on urea[4], benzene derivatives[5,6], and polyphenyls and polyenes[7].

METHODS

In this paper, the time-dependent Hartree-Fock semiempirical PM3 calculations were empolyed to obtain the second- and third-order frequency dependent polarizabilities for the thiophene-(a), furan-(b), and pyrrole-(c) nitro polyenes of the varying chain length N shown in FIGURE 1. The quantum chemistry program MOPAC'93 was used.

The limiting values for the thiophene-, furan-, pyrrole-nitro polyenes have been estimated by extrapolation. In this study, the extrapolation procedure is applied by the following formular

$$\log A(N)=a+b/N+c/N^2+d/N^3$$

where N is the number of the unit C=C bonds and where A(N) is the β and $<\gamma>$, γ_{xxxx}. To calculate the saturation, the second- and third-order polarizabilities are usually expressed as a function of chain length(n):

$$A(N)=N^k$$

where A(N) is the second- and third-order polarizabilities, N is from 1 to 9.

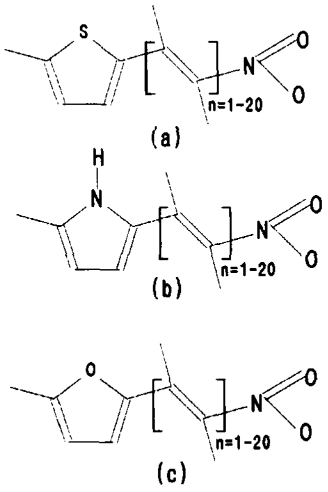

FIGURE 1 Structures of Thiophene-(a), Pyrrole-(b), Furan-(c)Nitro Polyene Systems.

RESULTS AND DISCUSSION

The PM3 predicted second-order polarizabilities of thiophene-, furan-, pyrrole-nitro polyene systems for the frequencies of the 0.5eV are represented in TABLE 1.

The limiting second-order polarizabilities(exponents values) of the thiophene-, pyrrole-, and furan-nitro polyene systems for the frequencies of the 0.5eV are 2.18E4(1.15), 3.03E4(1.02), and 2.44E4(1.04), respectively. The exponent values are about two times smaller than previous experimental studies on π-electron polyenic systems in which the estimated exponet values are 2.1[8], 2.4[9], and 3.4[10]. We predicted that the second-order polarizabilities, β, reached an optimum value in the thiophene-nitro polyene systems near N=20, These results were in agreement with the CNDOVSB-derived results on the conjugation length for dimethylamino-nitro polyene systems. On the other hand, these saturated conjugation lengths are slightly longer than dimethylamino-nitro polyphenyl systems.[11]

TABLE 1 PM3 predicted frequency-dependent second- and third-order polarizabilities($\langle\beta\rangle$, $\langle\gamma\rangle$ and γ_{xxxx} in a.u.).

1	5	10	15	20	$\langle\beta\rangle$(k)	$\langle\gamma\rangle$(k)	γ_{xxxx} (k)
$\langle\beta\rangle$							
thiophene-nitro							
6.12E2	6.67E3	1.30E4	1.56E4	1.67E4	2.18E4(1.15)		
pyrrole-nitro							
1.21E3	1.92E4	1.92E4	2.26E4	2.37E4	3.03E4(1.02)		
furan-nitro							
9.41E2	8.01E3	1.37E4	1.77E4	1.88E4	2.44E4(1.04)		
$\langle\gamma\rangle$							
thiophene-nitro							
4.07E4	1.46E6	6.65E6				1.26E7(2.27)	
pyrrole-nitro							
4.95E4	1.72E6	6.85E6				1.28E7(2.17)	
furan-nitro							
4.76E4	1.45E6	6.40E6				1.23E7(2.19)	
γ_{xxxx}							
thiophene-nitro							
2.07E5	7.37E6	3.34E7					6.34E7(2.27)
pyrrole-nitro							
2.54E5	8.66E6	3.43E7					6.40E7(2.57)
furan-nitro							
2.41E5	7.34E6	3.25E7					6.14E7(2.18)

The limiting value of pyrrole-nitro polyene system is slightly larger compared with the limiting values of thiophene-nitro polyene systems. On the other hand, the exponent value is slightly smaller than that of thiophene-nitro polyene system. On the other hand, the limiting value of the furan-nitro polyene systems is sightly smaller than that of thiophene-nitro polyene systems. The PM3 predicted limiting average second-order polarizabilities showed the following order: thiophene-<furan-<pyrrole-nitro polyene systems. We pridicted

that the pyrrole group is superior to a furan and thiophene group for achieving a large second-order polarizability.

The PM3 predicted average and longitudinal third-order polarizabilities of thiophene-, furan-, pyrrole-nitro polyene systems for the frequencies of the 0.5eV are represented in TABLE 1 The PM3 asymptotic average(longitudinal) third-order polarizabilities of the thiophene-, pyrrole-, furan-nitro polyene systems for the frequency of 0.5eV are 1.28E7(6.40E7), 1.26E7(6.34E7), and 1.23E7(6.14E7), respectively. The third-order asymptotic average and longitudinal polarizabilities of the furan-nitro polyenes are the smallest values among the three polyenes. The averge third-order polarizabilities of thiophene-, furan-, and pyrrole-nitro polyenes are two order of magnitude larger than amino-nitro polyenes, methyl-fluoro polyenes, and nonsubstituted polyens.[12]

In conclusion, the PM3 predicted limiting average second-order polarizabilities increase in the order: pyrrole->furan->thiophene-nitro polyenes. The average and longitudinal third-order polarizabilities have the order: pyrrole->thiophene->furan-nitro polyenes. In these trends, we sugest that pyrrole group is the best donor group among the three polyene systems.

REPERENCES

1. S.D. Bella, M.A. Ratner and T. J. Marks, J. Am. Chem. Soc., 114, 5842.(1992).
2. F. Meyers, J.L. Bredas and J. Zyss, J. Am. Chem. Soc., 114, 2914. (1992).
3. D. Li, T.J. Marks and M.A. Ratner , Chem. Phys. Lett., 131, 370. (1986).
4. E.N. Svendsen, C.S. Willard and A.C. ALbrecht, J. Chem. Phys., 83, 5760. (1985).
5. S.J. Lalama and A.F. Gartio, Phys. Rev. A., 20, 1179. (1979).
6. J.O. Morley, V.J. Docherty and D.J. Pugh, Chem. Soc., Perkin Trans., 2 1357. (1987).
7. J.O. Morley, V.J. Docherty and D.J. Pugh, Chem. Soc., Perkin Trans., 2 1351.(1987).
8. K.C. Rustagi and Ducuing, J. Opt. Commun., 10 , 258-261. (1974).
9. M. Barzoukas, M. Blanchard-Desce, D. Josse, J.M Lehn and Zyss, J. Chem. Phys., 133, 323-329. (1989).
10. R.A. Huijts and G.L. Hesselink, J. Chem. Phys. Lett., 209-212. (1989).
11. J.O. Morley and D. Pugh, Spec. Publ.-R. Soc. Chem., 69, 28. (1989).
12. U.S. Choi and K.S. Kim, Bull. Korean Chem. Soc., 14, 14. (1993).