Chinese Chemical Letters Vol. 11, No. 8, pp. 693–696, 2000

Substituents Effect on the Optical Properties of Benzonitrile and Oligobenzonitriles

Ting Jun HOU, You Yong LI, Yuan Kang HE, Hui Ying CHEN, Xiao Jie XU*

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871

Abstract: The semiempirical calculations were performed to discuss the effects of different substituents on the optical properties of a series of substituted benzonitriles and their corresponding oligomers. The substituents located in *para, meta* and *ortho*-position of the benzenoid ring involve a large range of δ-π electron-donor-acceptor capability. Theoretical analysis shows that the optical property is affected by the steric and electronic characteristics of the substituents on the benzenoid ring, moreover, the third-order polarizability regularly varies with the polymerization degrees.

Keywords: Benzonitrile derivatives, oligomer, semiempirical calculation, ZINDO.

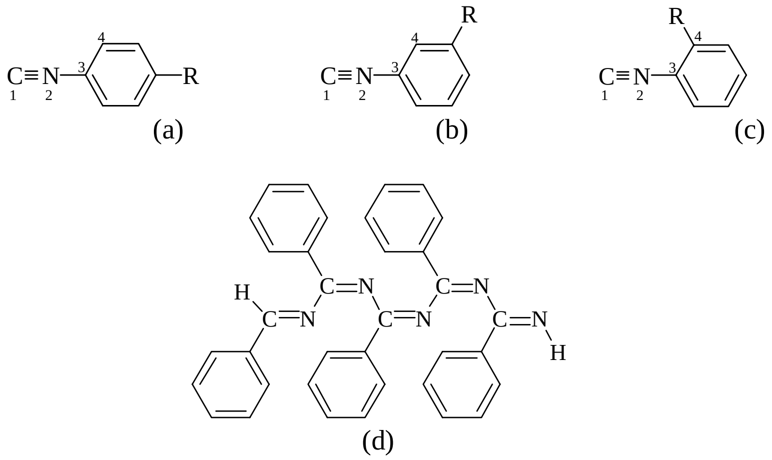
During the past decades, the organic systems with good electronic and optical property, such as oligomer and polymers, have been attracted much attention because of their optical nonlinearity, fast response, relatively low cost, ease of fabrication and integration into devices. Generally to say, the common oligomers or polymers that we usually study are all of carbon-carbon or heteroaromatic conjugated system. In previous work, the synthesis of new linear -$(C=N)_n$- conjugated systems, polynitriles have been reported[1,2]. But until now, any information on their geometrical structures and the effect of different substituents or substituted positions on geometrical and optical properties have not been known from the energy level, so it is useful to obtain some meaningful information from the theoretical calculations, which may permit the design of new organic system with optimum optical characteristics.

The aim of this work is to study the effect of different substituents and substituted positions to optical properties of oligomers. To understand the extent of the substituent effects on the structural and optical properties of benzonitrile and oligobenzonitriles, groups involved in a large δ-π electron-donor-acceptor capability range are studied, including methoxy, methyl, hydroxy, amino and nitro. Theoretical studies performed on pentabenzonitrile and pentabenzonitriles substituted in *para*, *meta* and *ortho*-position of the benzenoid ring are also reported in this work.

Methods

In **Figure 1**, structures A, B, C correspond to the benzonitrile monomers and their derivatives with substituents linked to *para*, *ortho* and *meta*-position of the benzenoid ring respectively, and structures D corresponds to the pentamer of benzonitrile.

Figure 1 Schematic representation of benzonitrile monomers and pentabenzonitrile.



(a) benzonitrile substituted in *para*-position, (b) benzonitrile substituted in *meta*-position, (c) benzonitrile substituted in *ortho*-position, (d) pentabenzonitrile.

The details of constructing the oligomer models of benzonitrile derivatives have been mentioned in our previous work[3]. We use Autsin Model 1 (AM1) method combined with molecular mechanical conformational analysis to seek their energy-lowest structures. First, geometries of the monomers are optimized. Then, the optimized benzonitrile molecules are coupled to generate dimers to pentamers and the systematic conformational analysis and Boltzmanne jump method are used to get the most stable conformers. Last, the obtained oligomers with lowest energy are further optimized by AM1[4], available in MOPAC 7.0[5].

The static (zero frequency) γ values for third-harmonic generation (THG) are deduced from the AM1 time-dependent Hartree-Fork (TDHF) method implemented in the MOPAC7.0. It has been reported that the quality of the semiempirical AM1 γ values can be expected to be on the order of that of a relatively small basis set *ab initio* calculation.

Results and Discussion

It is well-known that the evaluation of the third-order polarizability γ is an ongoing problem. The evaluation of third-order polarizability γ can only be performed on small systems, moreover, because the third-order polarizability γ vary remarkably in a large range according to the change of the environments in experiments, the results from the theoretical calculations may exist large deviations from the experiments. But if one is merely interested in establishing trends in the nonlinear optical properties among a series of structurally related molecules, the results from the theoretical calculations are reliable in this respect.

Table 1. Calculated γ ($\times 10^{-37}$esu) values for a series of benzonitriles and their derivatives (from nomomers to pentamers)

	$\gamma_{n=1}$	$\gamma_{n=2}$	$\gamma_{n=3}$	$\gamma_{n=4}$	$\gamma_{n=5}$	*r**
H	2.70	17.89	28.34	29.32	38.36	0.947
p-NH_2	6.76	43.94	79.48	74.84	93.72	0.942
m-NH_2	4.24	19.41	41.91	32.64	43.27	
o-NH_2	3.93	18.28	24.61	28.43	39.77	
p-CH_3	4.99	27.50	41.72	44.89	71.08	0.966
m-CH_3	3.88	20.00	27.23	34.79	44.91	
o-CH_3	2.86	16.95	14.88	27.08	35.91	
p-OCH_3	6.22	34.87	51.82	77.62	88.72	0.974
m-OCH_3	4.54	22.48	42.74	32.28	43.88	
o-OCH_3	4.12	18.20	24.63	35.20	54.93	
p-OH	4.44	27.69	40.80	59.91	68.05	0.969
m-OH	4.05	18.82	27.96	32.23	47.95	
o-OH	3.13	17.42	27.24	34.26	39.46	
p-NO_2	6.37	30.98	90.71	107.34	109.56	0.971
m-NO_2	3.34	25.55	41.29	43.80	54.04	
o-NO_2	4.07	12.29	20.62	24.27	44.48	

* The linear regression coefficient between lg(γ) and lg(n)

The theoretical results for benzonitriles and their derivatives n=1 to n=5 are shown in **Table 1**, which gives the static third-order polarizability γ of all studied systems with various groups substituted in *para*, *meta* and *ortho*-position of the benzenoid ring. From **Table 1**, it is obvious that the values of γ of the oligomers with different groups substituted in *para*-position of the benzenoid ring is larger than those oligomers with different groups substituted in *meta* and *ortho*-position. From the results of previous work, we know that when different groups are substituted in different position of the benzenoid ring, the geometrical structures of the oligomers change regularly. **Table 1** shows that the changeable regularity of the third-order polarizabilty is totally in accordance with that of the geometrical structures of oligomers. When different groups are substituted in *meta* and *ortho*-position of the benzenoid ring, due to the steric effect of the substituents, the conjugation system between the benzenoid and the C-N main chain will be partly destroyed and the values of γ inevitablly change smaller. From **Table 1**, it can be found that the molecules substituted by nitro or amino group in *para*-position of the benzenoid ring possess relatively large γ values, which can be understood by the conjugation effects. The additions of nitro and amino groups on benzenoid ring are favorable to produce larger conjugation region. From the experimental results, the molecules with hydroxy group substituted in *para*-position of the benzenoid also possess large γ values. To the oligomers with hydroxy group on the benzenoid ring, the intermolecular and intramolecular hydrogen bonds should be formed, which will influence their geometrical and optical properties significantly.

Our analysis shows that the pentamers with different substituents in *para*-position of the benzenoid ring have similar geometries, and the electronic property of the substituents may be very important to the third-order polarizability. From the studied system, the calculated results evidence a linear dependence of lg(γ) versus lg(n) and the linear regression coefficient for the systems with substituents in *para*-position on the benzenoid ring are listed in **Table 1**. Previous work have validated that the γ values were greatly influenced by the conjugation state, and there existed a linear relationship between lg(γ) and lg(n)[2], which agree with the calculation results in this paper.

Aknowledgments

This project is supported by the National Natural Science Foundation of China (NSFC) 29992590-2 and 29573095.

References

1. X. Y. Zhao, Q. Xu, Y. K. He, *et al. Chin. Chem. Lett.*, **1996**, *7*, 71.
2. Q. Wang, Y. Y. Li, W. W. Pei, *et al. Mat. Res. Soc. Symp. Proc.*, Vol. 488.
3. T. J. Hou, Y. Y. Li, X. J. Xu, *et al. Acta Chimica Sinica* (In press)
4. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, *et al. J. Am. Chem. Soc.*, **1985**, *107*, 3902.
5. Mopac ver 7.0, Quantum Chemistry Program Exchange, Bloomington, U.S.A. **1995**.

Received 21 February 2000