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Theoretical Studies on Electronic Spectra and Second-order Nonlinear Optical Properties of N-methyl-2-(2′-thiophene)-pyrrolo[3,4]C_{60}

Ying LIU[1], Yong Jun LIU[2]*, Cheng Bu LIU[2]

[1]Department of Chemistry, Qufu Normal University, Qufu 273165
[2]Institute of Theoretical Chemistry, Shandong University, Jinan 250100

Abstract: By using AM1 method, the structures and electronic properties of N-methyl-2-(2′-thiophene)-pyrrolo[3,4]C_{60} (MTPC) and N-methyl-pyrrolo[3,4]C_{60} (MPC) have been studied. Based on the AM1 geometry optimizing, the electronic spectra and second-order nonlinear optical polarizabilities (β) of MTPC and MPC were calculated by using INDO/SCI method combined with Sum-Over-States (SOS) expression.

Keywords: C_{60} derivatives, electronic spectra, and second-order nonlinear optical properties.

Since C_{60} was synthesized, the theoretical predications and experimental observations about the structures and properties of C_{60} derivatives[1~5] were attracted great interest. Many new types of C_{60} derivatives, which have potential application in material and biological science[6,7], have been synthesized *via* different reactions. Liu[11] *et al.* successfully prepared a series of N-methyl-pyrrolo[3,4]C_{60} derivatives and their optical and electro chemical properties were determined. But, up to now, no systematic theoretical investigations on the structure, electronic spectra and second-order nonlinear optical properties of these C_{60} derivatives were reported. The present work is concerned with N-methyl-2-(2′-thio-phene)-pyrrolo[3,4]C_{60} (MTPC) derivatives and systematical theoretical investigations.

Methodology

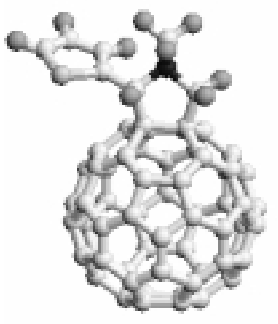
In the calculations, the molecular geometries were fully optimized by using AM1 method. INDO/SCI technique was applied to obtain photoexcited states. The components of the molecular second-order polarizability tensors (β_{ijk}) were obtained by means of the Sum-Over-States (SOS)[12,13] expression. β is a third-order tensor, while β_μ is its projector on the direction of dipole moment.

β_μ is usually sampled by EFISH (electric-field induced second harmonic generation) experiments. In order to compare with the experimental results, β_μ is usually calculated by using the following expression:

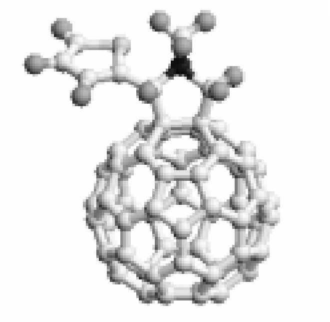
$$\beta_\mu(-2\omega;\omega,\omega) = (\mu_x\beta_x + \mu_y\beta_y + \mu_z\beta_z)/(\mu_x^2 + \mu_y^2 + \mu_z^2)^{\frac{1}{2}} \tag{1}$$

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i\neq j}(\beta_{jii} + \beta_{iji} + \beta_{iij}) \qquad i, j=(x, y, z) \tag{2}$$

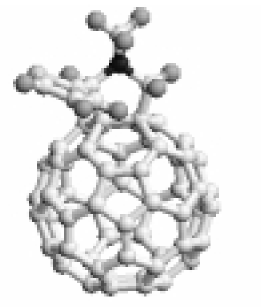
Figure 1 The atom series number and structures of MTPC isomers (A type)



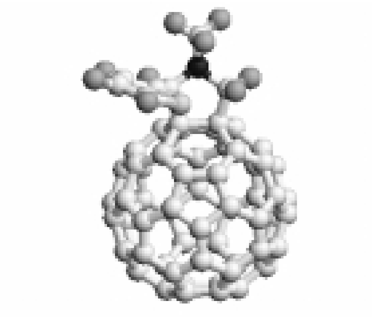
MTPC-1A



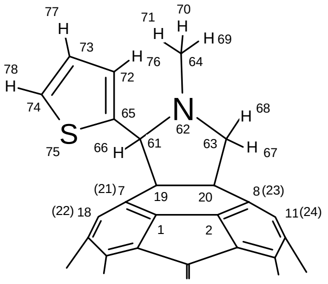
MTPC-2A



MTPC-3A



TPC-4A



Results and Discussion

The optimizing of the structures

The geometries of N-methyl-pyrrolo[3,4]C_{60} (MPC) and N-methyl-2-(2′-thiophene)-pyrrolo[3,4]C_{60} (MTPC) were fully optimized on the basis of AM1 Hamiltonian in the MOPAC package. The PRECISE option was used as convergence criterion.

Because of the unsymmetry of thiophene moiety and the relatively larger rotational energy barrier of C61-C65 bond between thiophene and pyrrolidine, eight stable MTPC isomers were obtained by geometry optimizing. These MTPC isomers can be divided into two series, A and B, and can be named as MTPC-1A, MTPC-2A, MTPC-3A, MTPC-4A, MTPC-1B, MTPC-2B, MTPC-3B, and MTPC-4B respectively. A and B type isomers constitute enantiomeres. Their geometry and atom series numbers, taking A type isomers as example, are shown in **Figure 1**. Because of the completely equivalency on the properties of enantiomeres, only A type isomers were studied. The calculated results showed that the changes of bond lengths of C_{60} moiety, from beginning of additive reaction to the end, are great for the C19 or C20-containing six- or five-member ring. Bond C19-C20 changed from single to double. Besides, we find that the changes of bond lengths of five- or six-member ring that containing C19 and C20 of MTPC isomers are less than that of MPC. It probably implies that the interaction between C_{60} and additive group of MPC is more intense than that of MTPC. The introduction of thiophene ring decreases partly the interaction between C_{60} and pyrrolidine, and thus led to the decrease of net charge of C_{60} moiety in MTPC isomers.

Electronic structures

The frontier molecular orbital energies of MTPC isomers and MPC were calculated by using AM1 method. The calculated results reveal that the frontier molecular orbitals of these C_{60} derivatives were decided mainly by that of C_{60} moiety. Thiophene and pyrrolidine only play a perturbation role in the whole molecular orbitals. Compared with that of MPC, the energy difference between LUMO and HOMO (namely $\Delta E_{LUMO-HOMO}$) of MTPC isomers increase about 0.7~1.0 eV but still less than that of C_{60} (6.70 eV). The values of $\Delta E_{LUMO-HOMO}$ and net charge of C_{60} moiety are listed in **Table 1**. From **Table 1** showed that the net charge of C_{60} moiety is always negative. So, in the intramolecular electron transfer, C_{60} moiety is always electron acceptor while pyrrolidine and thiophene parts are electron donor. The nearer the atoms from additive group in C_{60} moiety, the larger the changes of their electron density are. Besides, the net charges of C_{60} moiety of MTPC isomers are always less than that of MPC. In other words, the introduction of thiophene does not enhance the intramolecular electron transfer between C_{60} moiety and additive group. This may be mainly due to the mutual interaction between thiophene and pyrrolidine.

Table 1 The net charge of C_{60} moiety and $\Delta E_{LUMO-HOMO}$ of MTPC isomers and MPC

	MTPC-A	MTPC-2A	MTPC-3A	MTPC-4A	MPC
q_{C60}	-0.1418	-0.1419	-0.1394	-0.1457	-0.1541
$\Delta E_{LUMO-HOMO}$ (eV)	5.6092	5.6904	5.6112	5.9024	4.9414

Table 2 Electronic spectra of MTPC isomers and MPC calculated using INDO/SCI

Excited states	MTPC-1A		MTPC-2A		MTPC-3A		MTPC-4A		MPC	
	λ (nm)	f	λ (nm)	f	λ (nm)	f	λ (nm)	f	λ (nm)	f
$1 \longrightarrow 2$	763	0.0078	747	0.0078	767	0.0078	724	0.0088	1045	0.0069
$1 \longrightarrow 10$	569	0.0029	556	0.0030	570	0.0028	532	0.0028		
$1 \longrightarrow 18$	484	0.0113	474	0.0115	485	0.0114	452	0.0112	583	0.0087
$1 \longrightarrow 22$	442	0.0269	434	0.0312	442	0.0310	416	0.0356		
$1 \longrightarrow 23$	438	0.0075	429	0.0038	439	0.0029	411	0.0032	514	0.0522
$1 \longrightarrow 25$	422	0.0067	413	0.0029	423	0.0061				
$1 \longrightarrow 26$			413	0.0057						
$1 \longrightarrow 27$									471	0.0194
$1 \longrightarrow 28$					403	0.0033				
$1 \longrightarrow 33$									424	0.0202
$1 \longrightarrow 35$									416	0.0540
$1 \longrightarrow 36$									415	0.0892
$1 \longrightarrow 37$									413	0.0866

Electronic spectra

The electronic spectra of MTPC and MPC were calculated by using INDO/SCI method on the basis of AM1geometrical optimization. In the INDO/SCI method, an active space of 14 occupied and 14 virtual orbital with 197 single-electron excitation configurations and the ground state were included. The calculated results show that the strong absorption areas of MTPC isomers and MPC are between 200~240 nm, near the strong absorption peaks 215 nm, 236 nm and 250 nm[14] of C_{60}. In addition, there exist weak absorption peaks above 400 nm (see **Table 2**). These weak absorption peaks above 400 nm can be taken as the characteristic absorption peaks of MTPC and MPC.

Second-order nonlinear optical polarizability

Because of the stronger intramolecular electron transfer and unsymmetric center and highly delocalized π-conjugated electron systems, MTPC and MPC may exhibit good nonlinear optical properties. So, in this paper, the second-order nonlinear optical polariza- bilities β_{ijk} and β_0 (β_0 is the static polarizability at zero frequency) of MTPC and MPC were calculated by using INDO/SCI method combined with SOS expression. The calculated results are shown in **Table 3**. **Table 3** show that the introduction of thiophene decreases the dipole moment and the second-order nonlinear optical polarizability. This may be mainly due to the decrease of the quantity of the intramolecular electron transfer (see **Table 1**). For MTPC, the values of β vary with different isomers. MTPC-3A possesses the largest β value of all the stable isomers.

Table 3 Values of μ, β_0 and $\mu\beta_0$ of MTPC isomers, MPC and MATPC

	MPC	MTPC-1A	MTPC-2A	MTPC-3A	MTPC-4A
μ (D)	4.77	4.41	4.16	4.71	3.94
β_0 (10^{-30}esu)	76.7	49.1	63.8	66.2	51.4
$\mu\beta_0$ (10^{-48}esu)	365.3	216.3	265.1	311.4	202.3

In summary, comparing with other C_{60} derivatives, MTPC, MPC and its derivatives exhibit good second-order optical nonlinearity. This opens a route to explore new type of nonlinear optical materials based on C_{60} derivatives.

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