

Stability and electronic spectra of $C_{76}N_2$ isomers

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Abstract: Study of geometries of 16 possible isomers for $C_{76}N_2$ based on $C_{78}(C_{2v})$ by intermediate neglect of differential overlap (INDO) series of methods indicated that the most stable geometry 25,78- $C_{76}N_2$ where two nitrogen atoms substitute two apexes C(25) and C(78) near the shortest X axis and Y axis formed by two hexagons and a pentagon. Electronic structures and spectra of $C_{76}N_2$ were investigated. The reason for the red-shift for absorptions of $C_{76}N_2$ compared with that of $C_{78}(C_{2v})$ is discussed.

Key words: $C_{76}N_2$, Electronic spectra, INDO

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INTRODUCTION

The synthesis and characterization of heterofullerenes are very challengeable research topics because of application in superconductivity, photoelectronics, organic magnetism and even nanotubes. Pradeep *et al.*(1991) studied the interaction between nitrogen and fullerenes and obtained nitrogen derivatives of C_{60} and C_{70} such as $C_{59}N_2$, $C_{59}N_4$, $C_{59}N_6$ and $C_{70}N_2$ by contact-arc vaporization of graphite in a partial N_2 or NH_3 atmosphere. Yu *et al.*(1995) synthesized carbon nanotubes and nitrogen-doped fullerenes by arcing a graphite rod in a pure nitrogen atmosphere and observed $C_{59}N^-$ by mass spectra. Hummelen *et al.*(1995) isolated the heterofullerene $C_{59}N$ as its dimer $(C_{59}N)_2$. Nuber and Hirsh (1996) found a new way to synthesize nitrogen heterofullerenes $RC_{59}N$ and $RC_{69}N$ and achieved $(C_{69}N)_2$ by heating butylamino adducts of diazafullerenes with toluene-*p*-sulfonic acid. Esfarjani *et al.*(1994) investigated the bonding and electronic properties of substituted fullerenes $C_{58}BN$. Wang *et al.*(1995) theoretically analyzed $C_{60-x}N_x$ and $C_{60-x}B_x$ ($x=1\sim 2$) and their study on the stability of heterohedral fullerenes showed that the 6/6 site is favorable for $C_{58}N_2$ while the 5/6 site is favorable for $C_{58}B_2$ according to molecular mechanics calculations. Lamparth *et al.*(1995) used bisazafulleroid as a precursor

to prepare bisadducts, which directly fragment to form the heterofullerene ions $C_{59}N^+$ and $C_{69}N^+$ —the isoelectronic heteroanalogues of C_{60} and C_{70} , and gave the resonance structures of $C_{59}N^+$ using Austin model 1 (AM1) method. We used INDO series of methods to study stabilities of isomers and electronic spectra for $C_{75}N^+$ (Wu and Teng, 2002) and $C_{75}B^-$ (Teng *et al.*, 2003), which showed that the substitution of other atoms leads to the decrease in symmetry and the red-shift of absorptions in electronic spectra. Benz *et al.*(1996) characterized $C_{78}(C_{2v})$ with 21 unique carbon atoms and $C_{78}(C'_{2v})$ with 22 unique carbon atoms by nuclear magnetic resonance (NMR), ultraviolet visible (UV), infra-red (IR) and Raman spectra, and indicated that the properties of higher fullerenes must be treated on an individual basis when they share the same number of atoms and symmetry. Based on $C_{78}(C_{2v})$, here we study $C_{76}N_2$ to predict electronic structures and stabilities of isomers and calculate electronic spectra. We also discuss electronic transition theoretically and the red-shift of absorption peaks of $C_{76}N_2$ relative to that of $C_{78}(C_{2v})$.

CALCULATIONAL METHODS

We used standard bond lengths as an initial input for $C_{78}(C_{2v})$ and implemented full geometry optimi-

zation with the INDO/2 method without any symmetry restriction and obtained $C_{78}(C_{2v})$ (Fig.1). Then we used a nitrogen atom to substitute 21 unique carbon atoms to get the most stable isomer where C(78) is substituted. After that we replaced other carbon atoms such as C(69), C(68) and so on using the second nitrogen atom to get 16 possible isomers. Full geometry optimization was carried out using the same method as described above to obtain equilibrium geometries. Electronic spectra were computed by intermediate neglect of differential overlap/configuration interaction for singlet (INDO/CIS) (Wu and Teng, 2002; Teng *et al.*, 2003) as in the INDO program improved by Michael C. Zerner without any parameter adjustments. One-hundred ninety-seven configurations were generated by exciting electrons from the 14 highest occupied molecular orbitals (HOMO) into the 14 lowest unoccupied molecular orbitals (LUMO).

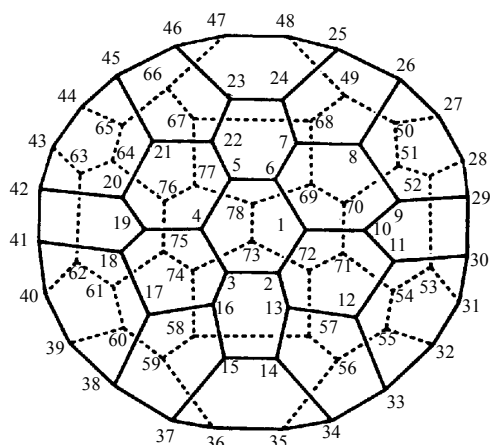


Fig.1 The optimized geometry of $C_{78}(C_{2v})$

RESULTS AND DISCUSSION

Stabilities of isomers

The relative energy and LUMO-HOMO energy gap of 16 isomers for $C_{76}N_2$ are given in Table 1 showing that the most stable isomer is 25,78- $C_{76}N_2$ where two nitrogen atoms locate at two apexes of two hexagons and a pentagon near the shortest X axis and Y axis of $C_{78}(C_{2v})$ because the apexes are connected with relatively weak 6/5 bonds. Lengths of C-N bonds were 0.1312, 0.1317 and 0.1325 nm and bond orders were 1.0844, 1.0678 and 1.0496, forming C-N single

bonds. The second stable isomer is 49,78- $C_{76}N_2$, N(49), which also substitutes near the X axis, and more stable than 28,78- $C_{76}N_2$ by 0.1949 eV; N(28) locates near the longest Z axis of $C_{78}(C_{2v})$. The next four stable isomers are those where two nitrogen atoms are separated from each other. From 71,78- $C_{76}N_2$ and 73,78- $C_{76}N_2$ we can see that 1,4-substitution is more stable than 1,2-substitution on the hexagon. It is noted that the unstable isomers are those where two nitrogen atoms are connected with each other, which leads to higher energies from 29,30- $C_{76}N_2$ to 1,10- $C_{76}N_2$. Bond lengths and orders for C-N bonds in other isomers are 0.1281~0.1348 nm and 1.0138~1.1879.

Table 1 Relative energy and LUMO-HOMO energy gap (eV) of $C_{76}N_2$

Isomers	Energy	L-H gap	Isomers	Energy	L-H gap
25,78- $C_{76}N_2$	0	3.4578	68,78- $C_{76}N_2$	0.7798	3.3710
49,78- $C_{76}N_2$	0.1910	3.5315	29,30- $C_{76}N_2$	2.4413	3.5174
28,78- $C_{76}N_2$	0.1949	3.4883	70,71- $C_{76}N_2$	3.0077	3.5430
24,78- $C_{76}N_2$	0.2201	3.4749	69,78- $C_{76}N_2$	3.3090	3.1795
6,78- $C_{76}N_2$	0.4185	3.4804	73,78- $C_{76}N_2$	3.5660	3.5516
7,78- $C_{76}N_2$	0.5220	3.4461	52,53- $C_{76}N_2$	4.0588	3.4670
48,78- $C_{76}N_2$	0.6620	3.5040	47,48- $C_{76}N_2$	4.1177	3.6110
71,78- $C_{76}N_2$	0.6708	3.4325	1,10- $C_{76}N_2$	4.8244	3.3802

Electronic structures

25,78- $C_{76}N_2$ is a stable closed-shell molecule where LUMO-HOMO energy gap is 3.4578 eV. Other isomers in Table 1 possess much less LUMO-HOMO energy gap than that of $C_{78}(C_{2v})$ (4.7534 eV). Molecular orbitals for $C_{76}N_2$ isomers are non-degenerate owing to the lower symmetry. In 25,78- $C_{76}N_2$, two nitrogen atoms carry positive Mülliken charges 1.589 and 1.590 whereas the adjacent carbon atoms are of negative charges from -0.467 to -0.557 , leading to the formation of polar covalent bonds. At the same time, the positive charge is chiefly concentrated on two nitrogen atoms, which makes them become further reaction centers for nucleophilic reagents. For the rest of the isomers, Mülliken charges of nitrogen atoms and successive carbon atoms are within the regions of 1.171~1.602 and -0.443 ~ -0.620 .

Electronic spectroscopy

The INDO/CIS method can be used successfully for computing electronic spectra of carbon clusters

(Wu and Teng, 2002; Teng *et al.*, 2003). UV bands of $C_{78}(C_{2v})$ are at 289.9, 310.2, 328.8, 370.7, 434.4, 466.7, 527.6 and 614.0 nm, and are consistent with the experiment values of 290, 310, 330, 370, 430, 470, 530 and 590 nm (Benz *et al.*, 1996). The first absorption of 25,78- $C_{76}N_2$ is at 1484.6 nm (Table 2), generated by electronic transition from HOMO (157) to LUMO (158). Strong absorption appearing at 913.2 nm, resulted from electronic excitation from (157) to (161). The first peak of 49,78- $C_{76}N_2$ locates at 1456.6 nm, generated by electronic transition from (157) to (158). The absorptions for 25,78- $C_{76}N_2$ and 49,78- $C_{76}N_2$ are red-shifted relative to that of $C_{78}(C_{2v})$ due to less LUMO-HOMO energy gaps.

Table 2 The calculated electronic spectra for 25,78- $C_{76}N_2$ and 49,78- $C_{76}N_2$

Isomers	λ (nm)	Oscill.	Trans. nature and coeffic.
25,78- $C_{76}N_2$	1484.6	0.0297	(157)→(158) 0.7700
25,78- $C_{76}N_2$	1209.7	0.0033	(157)→(159) 0.7527
25,78- $C_{76}N_2$	985.2	0.0381	(157)→(160) 0.8554
25,78- $C_{76}N_2$	913.2	0.1334	(157)→(161) -0.7561
25,78- $C_{76}N_2$	807.6	0.0279	(157)→(162) -0.8754
25,78- $C_{76}N_2$	692.3	0.0032	(157)→(163) 0.6966
49,78- $C_{76}N_2$	1456.6	0.0205	(157)→(158) 0.7914
49,78- $C_{76}N_2$	1183.6	0.0135	(157)→(159) 0.7251
49,78- $C_{76}N_2$	952.2	0.0339	(157)→(160) -0.8013
49,78- $C_{76}N_2$	891.4	0.1236	(157)→(161) -0.8059
49,78- $C_{76}N_2$	787.9	0.0195	(157)→(162) 0.8972
49,78- $C_{76}N_2$	630.0	0.0609	(156)→(158) 0.8019

The first peak of 28,78- $C_{76}N_2$ is at 1387.7 nm (Table 3), generated by electronic transition from (157) to (159). The strong band is at 928.4 nm, owing to electronic transition from (157) to (161). The first band of 24,78- $C_{76}N_2$ is at 1559.2 nm, generated by electronic transition from (157) to (158). The near infra-red (NIR) absorptions for 25,78- $C_{76}N_2$ and 24,78- $C_{76}N_2$ are caused by decrease in LUMO-HOMO energy gaps.

First peaks of electronic spectra for 6,78- $C_{76}N_2$ and 7,78- $C_{76}N_2$ (Fig.2) appearing at 1534.4 and 1518.0 nm are produced by electronic transitions from (157) to (158) and (157) to (159). The red-shift of the first peaks for 6,78- $C_{76}N_2$ and 7,78- $C_{76}N_2$ compared with that of $C_{78}(C_{2v})$ happens owing to less LUMO-HOMO energy gaps.

Table 4 indicates that first peaks of electronic spectra for other $C_{76}N_2$ isomers are red-shifted relative to that of $C_{78}(C_{2v})$, which is attributable to less LUMO-HOMO energy gaps. These NIR peaks are characteristics for recognizing different isomers in the experiment.

Table 3 The calculated electronic spectra for 28,78- $C_{76}N_2$ and 24,78- $C_{76}N_2$

Isomers	λ (nm)	Oscill.	Trans. nature and coeffic.
28,78- $C_{76}N_2$	1387.7	0.0329	(157)→(159) 0.9023
28,78- $C_{76}N_2$	1325.4	0.0263	(157)→(158) -0.9534
28,78- $C_{76}N_2$	990.7	0.0280	(157)→(160) 0.8837
28,78- $C_{76}N_2$	928.4	0.1211	(157)→(161) 0.8932
28,78- $C_{76}N_2$	762.2	0.0243	(157)→(162) -0.9014
28,78- $C_{76}N_2$	700.5	0.0057	(157)→(163) -0.6439
24,78- $C_{76}N_2$	1559.2	0.0226	(157)→(158) 0.9109
24,78- $C_{76}N_2$	1187.0	0.0233	(157)→(159) 0.8704
24,78- $C_{76}N_2$	990.3	0.0254	(157)→(160) -0.9220
24,78- $C_{76}N_2$	930.4	0.1057	(157)→(161) -0.8769
24,78- $C_{76}N_2$	793.6	0.0431	(157)→(162) 0.8832
24,78- $C_{76}N_2$	701.9	0.0107	(157)→(163) 0.7287

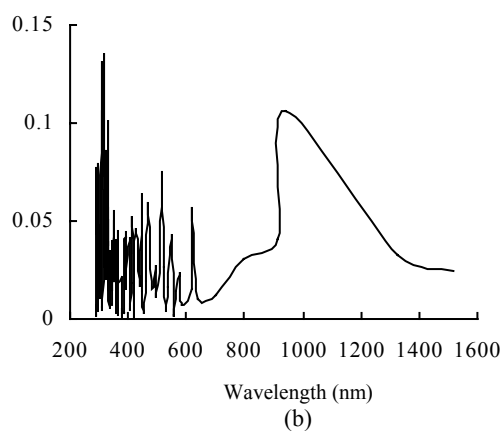
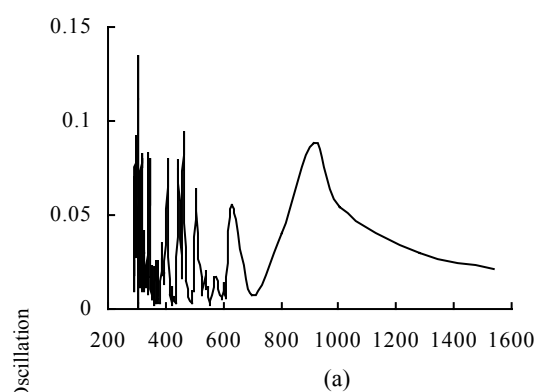


Fig.2 Electronic spectra of 6,78- $C_{76}N_2$ (a) and 7,78- $C_{76}N_2$ (b)

Table 4 Wavelength (nm) and oscillation of other isomers for C₇₆N₂

Isomers	λ (nm)	Oscill.
48,78-C ₇₆ N ₂	1474.4	0.0196
48,78-C ₇₆ N ₂	1250.8	0.0220
48,78-C ₇₆ N ₂	972.3	0.0346
71,78-C ₇₆ N ₂	1587.7	0.0191
71,78-C ₇₆ N ₂	1297.7	0.0160
71,78-C ₇₆ N ₂	1023.9	0.0221
68,78-C ₇₆ N ₂	1711.7	0.0174
68,78-C ₇₆ N ₂	1449.9	0.0158
68,78-C ₇₆ N ₂	1039.3	0.0384
29,30-C ₇₆ N ₂	1306.9	0.0028
29,30-C ₇₆ N ₂	1042.9	0.0123
29,30-C ₇₆ N ₂	1032.1	0.0258
70,71-C ₇₆ N ₂	1463.6	0.0178
70,71-C ₇₆ N ₂	1061.1	0.0031
70,71-C ₇₆ N ₂	957.7	0.0107
69,78-C ₇₆ N ₂	2399.5	0.0122
69,78-C ₇₆ N ₂	1593.6	0.0033
69,78-C ₇₆ N ₂	1251.2	0.0658
73,78-C ₇₆ N ₂	1344.1	0.0103
73,78-C ₇₆ N ₂	989.6	0.0017
73,78-C ₇₆ N ₂	861.6	0.2220
52,53-C ₇₆ N ₂	1647.5	0.0289
52,53-C ₇₆ N ₂	1054.8	0.0229
52,53-C ₇₆ N ₂	927.6	0.0427
47,48-C ₇₆ N ₂	1280.3	0.0293
47,48-C ₇₆ N ₂	935.0	0.0320
47,48-C ₇₆ N ₂	894.0	0.1232
1,10-C ₇₆ N ₂	1470.3	0.0120
1,10-C ₇₆ N ₂	1253.0	0.0266
1,10-C ₇₆ N ₂	1126.3	0.0012

CONCLUSION

ZINDO methods can be successfully used for optimizing geometries and electronic spectra of C₇₆N₂ isomers. The most stable isomer is 25,78-C₇₆N₂

where two nitrogen atoms are separated and located near two shorter axes. The red-shift of absorptions in electronic spectra for C₇₆N₂ compared with that of C₇₈(C_{2v}) takes place because of less LUMO-HOMO energy gap for C₇₆N₂.

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