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UV and IR Studies on Heterofullerene $C_{76}BN$

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Twenty-two possible isomers for $C_{76}BN$ were studied by INDO methods. The two most stable geometries are 52,53- $C_{76}BN$ and 29,28- $C_{76}BN$, in which boron and nitrogen atoms are connected with each other and located at the 6/6 bond near the longest axis of $C_{78}(C_{2v})$. Electronic spectra of $C_{76}BN$ were investigated with INDO/SCI method. UV absorptions of $C_{76}BN$ are red-shifted compared with those of $C_{78}(C_{2v})$. The structures and IR spectra for the four stable isomers of $C_{76}BN$ were calculated by AM1 method. It was indicated that the substitution of the BN unit weakens the conjugation of carbon atoms, leading to the decrease of IR frequencies.

Key words: Heterofullerene, $C_{76}BN$, Electronic spectrum, IR spectrum

I. INTRODUCTION

Investigation into heterofullerenes has been attracting increasing attention, as scientists make use of the improvement on electronic properties for fullerenes. Esfarjani *et al.* studied the band structure in heterofullerenes $C_{58}BN$ [1]; Wu *et al.* calculated 10 clusters of $B_{32}N_{32}$ and verified that the most stable isomer has 28 hexagons and 6 squares by the B3LYP/6-31G* method [2]. Lau *et al.* studied equilibrium structures, the electronic and vibrational properties of B_{24} using first-principle calculations [3]. Fowler *et al.* studied BN cages using density-functional tight-binding calculations and indicated that fullerene-like B_xN_{x+4} cages can be constructed so that they have just six N-N bonds [4]. Zhao *et al.* studied energy gaps, ionization potentials and electron affinities of $C_{48}X_2$ ($X=B, N$) and $C_{50-2x}(BN)_x$ ($x=1-15$) by AM1 and MNDO methods [5,6]. Chen *et al.* calculated electronic structures and spectra of $C_{58}BN$, $C_{60-x-y}B_xN_y$ and $C_{60-2x}(BN)_x$ [7-9]. We used INDO methods to study the stability of $C_{75}N^+$, $C_{75}B^-$, $C_{77}N^+$ and $C_{76}N_2$ isomers [10-13]. In this work, we explored the structures, UV and IR spectra of $C_{76}BN$, and discussed the reason for the red-shift of UV bands relative to $C_{78}(C_{2v})$.

II. CALCULATION METHODS

Based on $C_{78}(C_{2v})$, a nitrogen atom is used to substitute for one carbon atom to get the most stable isomer $C_{77}N^+(78)$ [12]. Then a boron atom is employed to replace another carbon atom such as C(69) to get 69,78- $C_{76}BN$. Other possibly stable isomers are also investigated on the basis of $C_{77}N^+(27)$, $C_{77}N^+(26)$ and $C_{77}B^-(10)$. Full geometry optimization was carried

out using the INDO/2 method without symmetry restriction [14]. Electronic spectra were computed by the INDO/SCI method using the ZINDO program with no parameter adjustments [14-18]. There are 197 configurations, with their corresponding states, generated by exciting electrons from 14 highest occupied molecular orbitals into 14 lowest virtual molecular orbitals, in addition to the ground state. The four most stable INDO geometries, structures and IR spectra were explored by AM1 method using the Gaussian 03 program package [19].

III. RESULTS AND DISCUSSION

A. Optimized energy and geometries

The optimized geometry of 52,53- $C_{76}BN$ (whose total energy is -11789.9632 eV, making it less stable than $C_{78}(C_{2v})$ at -11807.27 eV) is shown in Fig.1. The lowest-energy isomers 52,53- $C_{76}BN$ and 29,28- $C_{76}BN$ (see Table I) are isomers in which boron and nitrogen atoms are connected with each other and located at the 6/6 bonds near the longest axis of $C_{78}(C_{2v})$. The former

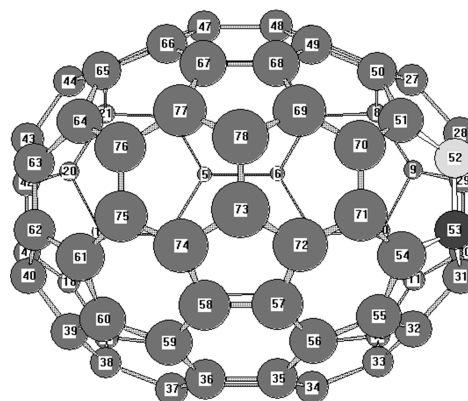


FIG. 1 The optimized geometry of 52,53- $C_{76}BN$.

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TABLE I Optimized relative energy (E_r) and LUMO-HOMO energy gap (ΔE_{L-H}) (eV) of $C_{76}BN$

Isomers	E_r	ΔE_{L-H}	Isomers	E_r	ΔE_{L-H}	Isomers	E_r	ΔE_{L-H}
52,53- $C_{76}BN$	0.0000	4.7651	10,8- $C_{76}BN$	1.9883	4.2047	27,78- $C_{76}BN$	2.3821	4.2964
29,28- $C_{76}BN$	0.0003	4.7479	7,78- $C_{76}BN$	2.0115	4.4037	28,78- $C_{76}BN$	2.3875	4.2916
10,9- $C_{76}BN$	0.2515	4.4278	10,78- $C_{76}BN$	2.0492	4.3547	9,78- $C_{76}BN$	2.4665	4.3327
73,78- $C_{76}BN$	0.3099	4.6804	10,27- $C_{76}BN$	2.0692	4.2725	1,78- $C_{76}BN$	2.4990	4.5435
10,1- $C_{76}BN$	0.3422	4.8251	25,78- $C_{76}BN$	2.2637	4.2477	10,26- $C_{76}BN$	2.6262	4.4494
29,30- $C_{76}BN$	0.4279	4.4587	29,78- $C_{76}BN$	2.2695	4.2978	70,78- $C_{76}BN$	2.6832	4.2728
69,78- $C_{76}BN$	0.7616	4.1767	51,78- $C_{76}BN$	2.3091	4.2724			
47,48- $C_{76}BN$	1.0551	4.5983	52,78- $C_{76}BN$	2.3159	4.4244			

TABLE II Several optimized bond lengths (nm) in $C_{76}BN$ isomers

Isomers	B-N	C-B	C-B	C-N	C-N	Sym.
52,53- $C_{76}BN$	0.1512	0.1649	0.1661	0.1336	0.1328	C_1
29,28- $C_{76}BN$	0.1522	0.1655	0.1644	0.1326	0.1329	C_1
10,9- $C_{76}BN$	0.1560	0.1643	0.1618	0.1330	0.1285	C_1
73,78- $C_{76}BN$	0.1495	0.1654	0.1654	0.1336	0.1336	C_s

eight stable isomers are those in which the nitrogen and boron atoms are bridged at the neighboring sites, and B and N are located near the longest axis, which are more stable than those near the shorter axis, which is consistent with Chen's calculations [7-9]. Comparison of 29,28- $C_{76}BN$ with 29,30- $C_{76}BN$ and 73,78- $C_{76}BN$ with 69,78- $C_{76}BN$ revealed the isomers where B and N are located at the 6/6 bonds are generally more stable than those at 6/5 bonds. In addition, the isomers become less stable when B and N are separated further, as seen in 51,78- $C_{76}BN$, 52,78- $C_{76}BN$, 28,78- $C_{76}BN$, 9,78- $C_{76}BN$ and 1,78- $C_{76}BN$, which is also consistent with Chen's results [7].

Some bond lengths in the four stable isomers (see Table II) indicated that B and N form a single-bond, and also form single-bonds with neighboring carbon atoms. B-N, C-B and C-N bond lengths in other isomers drop within 0.1537-0.1562, 0.1580-0.1658 and 0.1274-0.1344 nm. The cage is expanded at the boron-substituted site but compressed at the nitrogen-substituted site.

B. Electronic structures

$C_{76}BN$ is a closed-shell isoelectronic molecule relative to C_{78} . Energy of HOMO(156) and LUMO(157) for 52,53- $C_{76}BN$ is -6.5983 and -1.8332 eV, and the LUMO-HOMO energy gap is 4.7651 eV (see Table I). This is a little different from that of $C_{78}(C_{2v})$ (4.7534 eV), which means that the first absorption of the electronic spectrum for 52,53- $C_{76}BN$ will be the same as that of $C_{78}(C_{2v})$. HOMO energies of 29,28- $C_{76}BN$, 10,9- $C_{76}BN$ and 73,78- $C_{76}BN$ are -6.6141, -6.4921 and -6.5441 eV, and LUMO energies are -1.8662, -2.0643 and -1.8637 eV, so the LUMO-

HOMO energy gaps are 4.7479, 4.4278 and 4.6804 eV. Only a few isomers, such as 10,1- $C_{76}BN$, possess a larger energy gap than that of $C_{78}(C_{2v})$, resulting in the blue-shift of absorptions in electronic spectra. All of the molecular orbitals for $C_{76}BN$ are non-degenerate owing to the lower symmetry.

C. Electronic spectra

UV absorptions of $C_{78}(C_{2v})$ [16] were consistent with the experiment. The first absorption of 52,53- $C_{76}BN$ (Table III) is at 614.2 nm, produced by a $\pi \rightarrow \pi^*$ transition from HOMO(156) to LUMO(157). The first absorptions of 29,28- $C_{76}BN$ and 10,9- $C_{76}BN$ appear at 659.2 and 795.2 nm, resulting from $\pi \rightarrow \pi^*$ excitations from (155) to (157) and (156) to (157). MO (155) and (157) of 29,28- $C_{76}BN$ are composed of p_x for C(19) and p_z for C(1) by coefficients -0.2171 and -0.2264. While 2s, $2p_x$, $2p_y$ and $2p_z$ for B(29) mainly contribute to MO(58), (134), (196) and (257) by -0.2835, 0.2923, -0.3275 and -0.2361, leading to the change in HOMO energy. MO (156) and (157) of 10,9- $C_{76}BN$ consist of p_y for C(52) and p_z for C(40). While 2s, $2p_x$, $2p_y$ and $2p_z$ for B(10) contribute to MO (50), (196), (133) and (135) by 0.2778, 0.2547, 0.2955 and 0.4212. First absorptions for 29,28- $C_{76}BN$ and 10,9- $C_{76}BN$ are red-shifted relative to that of $C_{78}(C_{2v})$ (614 nm) because of less energy gap and the decrease in symmetry, agreeing with Chen's conclusion [7].

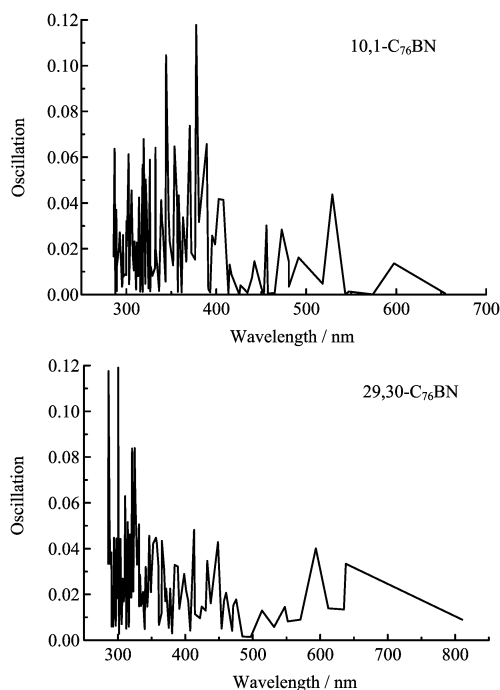
The first absorption of 73,78- $C_{76}BN$ with C_s symmetry is at 646.7 nm, owing to electronic transition from $a'(155)$ to $a''(157)$. The first strong peaks in the electronic spectra for 10,1- $C_{76}BN$ and 29,30- $C_{76}BN$ with C_s and C_1 symmetry (Fig.2) appear at 597.5 and 638.0 nm. These are produced by electronic transitions from $a''(156)$ to $a''(157)$ and (155) to (157). Compared

TABLE III Electronic spectra for 52,53-C₇₆BN, 29,28-C₇₆BN and 10,9-C₇₆BN

52,53-C ₇₆ BN (C ₁)				29,28-C ₇₆ BN (C ₁)				10,9-C ₇₆ BN (C ₁)			
λ/nm	f	Trans.	nature coeffic.	λ/nm	f	Trans.	nature coeffic.	λ/nm	f	Trans.	nature coeffic.
614.2	0.0122	(156)→(157)	0.8349	659.2	0.0008	(155)→(157)	0.8520	795.2	0.0234	(156)→(157)	0.9263
576.0	0.0195	(155)→(157)	-0.6066	612.7	0.0089	(156)→(157)	0.8138	621.8	0.0007	(156)→(158)	-0.4950
563.7	0.0036	(156)→(158)	-0.5871	575.1	0.0048	(154)→(157)	-0.5312	610.4	0.0110	(156)→(158)	-0.7519
550.8	0.0019	(154)→(157)	-0.5715	554.0	0.0212	(154)→(157)	0.6449	570.2	0.0083	(156)→(159)	-0.7193
541.7	0.0074	(156)→(159)	-0.7462	533.3	0.0024	(156)→(159)	-0.5602	563.3	0.0116	(154)→(157)	-0.7023
507.6	0.0052	(153)→(157)	-0.4860	522.4	0.0224	(154)→(158)	-0.5335	563.3	0.0116	(154)→(157)	-0.7023
499.0	0.0044	(156)→(160)	-0.4772	519.9	0.0270	(155)→(158)	-0.4954	531.3	0.0315	(154)→(158)	0.6420
496.3	0.0034	(155)→(159)	-0.6559	510.3	0.0181	(155)→(158)	-0.5398	524.3	0.0101	(153)→(157)	0.5686

TABLE IV Wavelengths and oscillation of absorptions in electronic spectra for other C₇₆BN (C₁) isomers

λ/nm	f	λ/nm	f	λ/nm	f	λ/nm	f	λ/nm	f	λ/nm	f
69,78-C ₇₆ BN		47,48-C ₇₆ BN		10,8-C ₇₆ BN		7,78-C ₇₆ BN		10,78-C ₇₆ BN		10,27-C ₇₆ BN	
835.8	0.0005	730.2	0.0338	900.5	0.0303	741.9	0.0409	796.3	0.0213	885.5	0.0178
811.9	0.0429	647.2	0.0182	791.8	0.0153	649.9	0.0114	687.1	0.0068	687.0	0.0101
741.2	0.0399	625.2	0.0022	693.3	0.0015	639.5	0.0020	625.6	0.0051	651.7	0.0012
25,78-C ₇₆ BN		29,78-C ₇₆ BN		51,78-C ₇₆ BN		52,78-C ₇₆ BN		27,78-C ₇₆ BN		28,78-C ₇₆ BN	
743.6	0.0051	888.4	0.0068	787.7	0.0097	823.8	0.0138	747.7	0.0144	872.2	0.0062
731.5	0.0340	734.4	0.0134	756.3	0.0110	769.8	0.0188	738.6	0.0109	774.4	0.0189
711.3	0.0257	668.2	0.0428	631.6	0.0272	659.5	0.0060	648.5	0.0196	705.7	0.0244

FIG. 2 Electronic spectra of C₇₆BN.

with the C₇₈ molecule, there is blue-shift in the first peak for 10,1-C₇₆BN.

Electronic spectra for other C₇₆BN isomers in Table IV indicate that first peaks are red-shifted relative to

that of C₇₈(C_{2v}). We attribute this to narrow LUMO-HOMO energy gaps. The first band of 10,8-C₇₆BN is located at 900.5 nm in the NIR region but it is impossible to be observed because the isomer in which B and N are separated is unstable in the experiment.

D. AM1 optimization and IR spectra

Mülliken charges of B in 52,53-C₇₆BN, 29,28-C₇₆BN, 10,9-C₇₆BN and 73,78-C₇₆BN are 0.252, 0.250, 0.215 and 0.277; while those for N are -0.108, -0.105, -0.075 and -0.098, showing the formation of a polar covalent B-N bond. Energy gaps for C₇₈(C_{2v}), 52,53-C₇₆BN, 29,28-C₇₆BN and 10,9-C₇₆BN are 5.5299, 5.6581, 5.3430 and 5.2962 eV, which is consistent with that of the INDO calculation. The AM1 energy gap for 2,1-C₅₈BN was 5.83 eV, less than that of C₆₀ (6.69 eV), supporting our conclusion [7]. 52,53-C₇₆BN has less total energy than 29,28-C₇₆BN and 10,9-C₇₆BN by 0.0626 and 0.5551 eV, respectively, and is more stable. Relative formation enthalpies for 52,53-C₇₆BN, 29,28-C₇₆BN and 10,9-C₇₆BN are 61.94, 62.01 and 62.49 eV. Free energies are 60.02, 60.08 and 60.56 eV.

The IR spectrum of C₇₈(C_{2v}) matches the experimental results within the 500-900 cm⁻¹ narrow bands, the 900-1300 cm⁻¹ flat region and the 1300-1500 cm⁻¹ broad bands [20]. The first peaks for C₇₈(C_{2v}) and 52,53-C₇₆BN are 1896.7 and 1892.9 cm⁻¹, the stronger absorptions for C₇₈(C_{2v}) are 1892.9, 1829.2, 1765.9, 1714.9, 1668.4 and 1544.3 cm⁻¹, and the correspond-

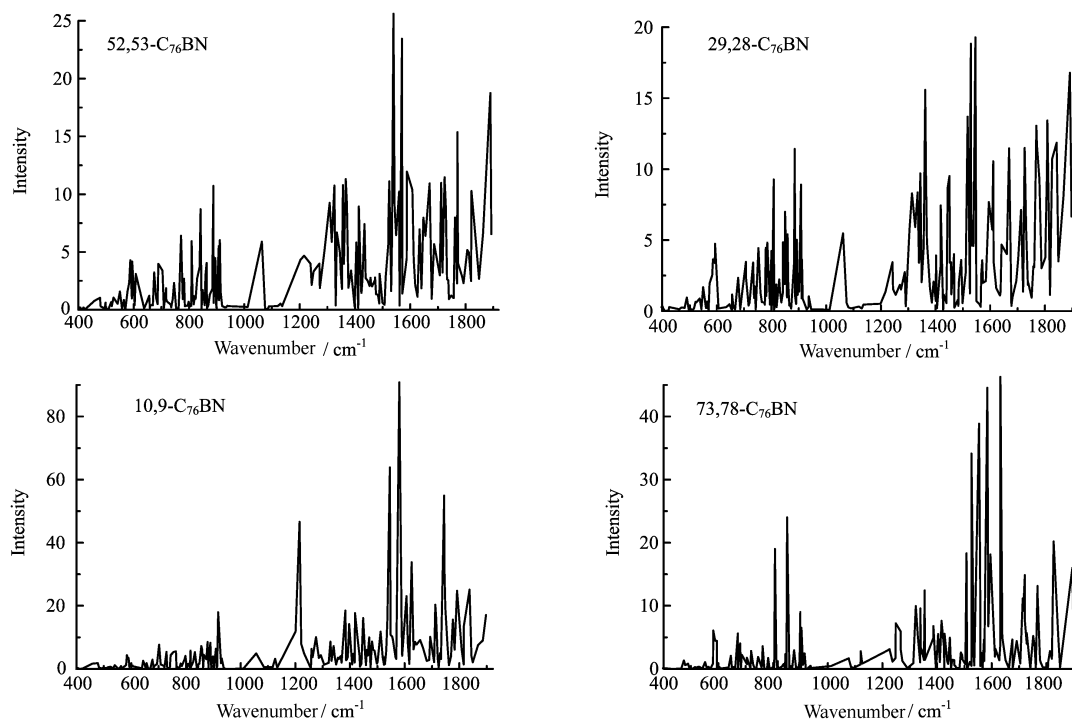


FIG. 3 IR spectra for four stable isomers of $C_{76}BN$.

ing absorptions for 52,53- $C_{76}BN$ are 1889.9, 1821.6, 1761.9, 1706.7, 1655.1 and 1539.1 cm^{-1} (Fig.3), indicating that the substitution of the BN unit leads to a decrease in frequencies of these peaks. IR frequencies in 29,28- $C_{76}BN$ generally lessen, compared to $C_{78}(C_{2v})$, illustrating that C–C bonds in the whole conjugated system, rather than merely C–C bonds near the substituted sites, are weakened. Most of IR absorptions in 10,9- $C_{76}BN$ and 73,78- $C_{76}BN$ are red-shifted relative to those of $C_{78}(C_{2v})$ due to the destruction of the conjugated system and the weakening of C–C bonds.

The INDO method can be used to study the geometries and electronic spectra of $C_{76}BN$. The most stable geometries are 52,53- $C_{76}BN$ and 29,28- $C_{76}BN$ where B and N are connected and located at 6/6 bonds near the longest axis of $C_{78}(C_{2v})$. The red-shifts of absorptions in electronic spectra and IR frequencies for $C_{76}BN$ relative to those of $C_{78}(C_{2v})$ take place because of less energy gap and the weakening of C–C bonds in the conjugated system after the substitution of the BN unit.

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