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Similarities and Differences between $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ Conformers

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In the second generation of fullerene research, polymeric structures of the carbon cages and special techniques for doping have attracted particular attention.[1,2] One-, two-, and three-dimensional polymeric configurations have been prepared in quite a considerable variety. Unfortunately, the degree of polymerization is rather uncontrolled except for the lowest possible oligomeric structures where only two monomers are covalently connected. Therefore, it is very crucial to understand the fullerene dimers that are the basic unit of new molecular arrays.

Recently, the simplest dimer, C_{120} linked by a cyclic C4 unit in a [2 + 2] cycloaddition, was synthesized by a solid-state mechanochemical reaction of C_{60} with potassium cyanide by the use of high-speed vibration milling.[3] An electron-doped C_{60} dimer dianion phase appears as a result of rapid cooling from about 500 K of alkali-metal fullerides.[4] The X-ray structure of this dimer phase suggested a single-bonded structure which is formed by direct covalent bonding between two fullerene monomers.[5] An alternative to the electron-doping procedure is the substitution of carbon atoms on the fullerene cage by more electron-rich atoms such as nitrogen.[6] In the case of doping on the cage with nitrogen, an azafullerene radical was synthesized from C_{60} and isolated as its dimer $(C_{59}N)_2$ which comprises dimeric molecular units linked by a single C−C bond formed by C atoms neighboring the N atom on each monomer. Perfectly spherical C_{60} molecules are known to spin freely at room temperature when crystallized to a solid. ^{13}C nuclear magnetic resonance experiments[7] on solid C_{60} have shown that it is only below $T = 260$ K that the free C_{60} rotation is hindered by an a-sphericity of the intermolecular potential, due to the discrete atomic positions.

Although several kinds of quantum chemical studies[8] were performed to determine the ground-state structure to $(C_{60})_2^{2-}$, only one plane wave-based density functional method (PW-DFT) with a nonlocal pseudopotential within the Becke−Lee−Yang−Parr approximation,[9a] the full potential linear muffin-tin orbital calculations,[9b] and the intermediate neglect of differential overlap methods[9c] were applied to $(C_{59}N)_2$. Normally, in the vapor or liquid states, molecules exist as an equilibrium mixture of rotational isomers. Conformational properties of flexible single bonds are of fundamental importance in determining the behavior of organic molecules and are among the fundamental principles of organic chemistry. However, as far as we know, there has been no attempt to analyze the conformers of isoelectronic $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ until now. Here, we feel that it is appropriate to use quantum chemical methods already well established for organic molecules to analyze the conformers of $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ which are the basic unit of new molecular arrays. With the advanced computational power, it is now possible to understand the free spinning around the intercage single C−C bond of fullerene dimers at ab initio levels.

To optimize the structures of the $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ conformers, we employed different theoretical methods: semiempirical parametrized method (PM3) and density functional method (using 4-21G and 6-31G* basis sets) employing Becke's three-parameter hybrid method and the Lee−Yang−Parr correlation functional (B3LYP).[10] All geometries at local minima and transition states are fully optimized using the Gaussian 98 suite of programs.[11] Although there are some variations between different methods, it can be seen from our calculations that the results are consistent. Among them, the B3LYP results should be considered to be most reliable.[12] Thus, our discussion will be based mostly on B3LYP/6-31G*//B3LYP/6-31G* (B3LYP/6-31G*) and B3LYP/6-31G*//B3LYP/4-21G results. The structures studied here are shown in Figure 1.

There are three distinct stable conformer forms with respect to rotation around a single C−C bond: two enantiomeric *gauche* forms with ACCA dihedral angle ω of about 60° (right − handed helix) and −60° (left − handed helix) and an *anti* form with ω of 180°. The others are the highest energy *syn* form with ω of 0° and the second highest energy eclipsed form with ω of about 120° which are two transition states between *gauche* (+) and *gauche* (−) and between *anti* and *gauche* (±).

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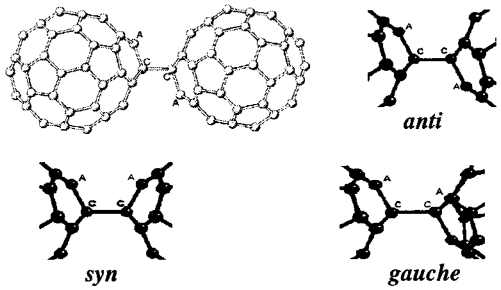

Figure 1. Molecular structures of three possible conformers of a single bonded $(C_{60})_2^{2-}$ and $(C_{59}N)_2$.

Table 1. Energies of $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ Conformers Relative to Their *anti* Conformers (as Energy of $(C_{60})_2^{2-}$, Energy of $(C_{59}N)_2$)[a]

structure (symmetry) dihedral angle (deg)	*syn* (C_{2v}) 0.0	*gauche* (C_2) ∼60	*eclipsed* (C_2) ∼120.0	*anti* (C_{2h}) 180.0
PM3	3.4, 2.6	1.0, −0.7	1.8, 1.9	0.0, 0.0
HF/STO-3G	6.1, 6.8	1.1, 0.4		0.0, 0.0
B3LYP/4-21G	6.7, 7.4 (1.649, 1.617)[b]	0.1, −0.4 (1.610, 1.565)[b] (54.9, 60.6)[c]		0.0, 0.0 (1.612, 1.570)[b]
B3LYP/6-31G*// B3LYP/4-21G	6.5, 6.7	0.2, −0.4		0.0, 0.0
B3LYP/6-31G*	6.4, 6.8 (1.652, 1.627)[b]	0.4, −0.4 (1.616, 1.577)[b] (63.2, 59.8)[c]		0.0, 0.0 (1.618, 1.581)[b]

[a] Energies are in kcal/mol. [b] The intercage C−C bond lengths (Å). [c] The optimized dihedral angles (deg).

Table 1 shows the relative stability for four conformers of $(C_{60})_2^{2-}$ and $(C_{59}N)_2$, respectively. At all levels of theory we find that the most stable conformer for the singlet state of $(C_{60})_2^{2-}$ is the *anti* conformer with C_{2h} symmetry, while for $(C_{59}N)_2$ the *gauche* conformer with C_2 symmetry is the most stable except for the result of HF/STO-3G at the HF/STO-3G-optimized structure.

In terms of energy differences, at the PM3 level we find that the *anti* form of $(C_{60})_2^{2-}$ is more stable than the *gauche* conformer by 1.0 kcal/mol, while in the case of $(C_{59}N)_2$ the *gauche* conformer is 0.7 kcal/mol more stable than the *anti* conformer. This is confirmed by the B3LYP/6-31G* calculations where the *gauche* form of $(C_{59}N)_2$ is 0.4 kcal/mol more stable than the *anti* form, while the *gauche* form of $(C_{60})_2^{2-}$ is 0.4 kcal/mol less stable than the *anti* form. Here, the *syn* energy barrier of $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ conformers is 6.5 and 6.7 kcal/mol using the B3LYP/6-31G*// B3LYP/4-21G calculations, respectively. Also, the energy calculations using B3LYP/6-31G* show that the *syn* energy barrier of $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ conformers is 6.4 and 6.8 kcal/mol, respectively. Thus, consistent results for the relative stability of conformers are obtained with the different methods employed.

For $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ conformers, the rotational potential surfaces have the two minima (*anti* and *gauche*) and two transition states (*syn*, C_{2v} and *eclipsed*, C_2). The pattern of this rotational potential surface is the same as that of *n*-butane.[13] Also considering the barriers computed, we suggest that these molecules exist as an equilibrium mixture of *anti* and *gauche* conformers.

For $(C_{59}N)_2$, our results show that the *gauche* conformer is the lowest-energy state. This is different from the former PW-DFT result,[9] which showed that the *anti* form is less than 1 kcal/mol lower than the *gauche*. Our result could be understood with a *gauche* effect which is a tendency to adopt that structure which has the maximum number of *gauche* interactions between the adjacent electron pairs and polar bonds.[14] *Gauche* conformations about the C−C bond are also favored in $NCCH_2CH_2CN$ and $H_3COCH_2CH_2OCH_3$.[15]

Considering the existence of the mixture of *anti* and *gauche* conformers would be helpful to interpret the unusual line positions for the recently reported Raman spectra.[16] The difference of the rotational potential surface between $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ would explain that the intercage mode for $(C_{60})_2^{2-}$ was highly dependent on the increase of temperature, while the behavior of the corresponding lines of $(C_{59}N)_2$ appeared highly independent of temperature in Raman spectra.

The theoretically predicted intercage center-of-mass (c.m.) separation distances (B3LYP/6-31G*) in the single-bonded conformers of $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ are about 9.34 and 9.22 Å, respectively. These are almost the same as the X-ray structures that predict intercage c.m. separations of 9.34 and 9.41 Å for $(C_{60})_2^{2-}$ and $(C_{59}N)_2$, respectively. But by using the B3LYP/6-31G* method, the predicted intercage c.m. separation distance of $(C_{59}N)_2$ is a little short. The intercage bond distance of single C−C bonds of the *gauche* form of $(C_{59}N)_2$ is 1.577 Å which is a little longer than the approximate $C(sp^3)-C(sp^3)$ bond length 1.54 Å, while the intercage bond length 1.618 Å of $(C_{60})_2^{2-}$ is much longer than 1.54 Å. Thus, the intercage distance difference of single C−C bonds between the *gauche* form of $(C_{59}N)_2$ and the *anti* form of $(C_{60})_2^{2-}$ may contribute to the explanation that the breaking of the intercage bond [17] of $(C_{59}N)_2$ occurs at 500 K, while breaking of the intercage bond of $(C_{60})_2^{2-}$ occurs below room temperature. It could be supported by a general bond energy−bond length relation for C−C bonds,[18] which suggests that the energy difference of single C−C intercage bonds of the $(C_{60})_2^{2-}$ and $(C_{59}N)_2$ might be 6.9−11.3 kcal/mol.

In conclusion, by analyzing the rotational potential energy surfaces of $(C_{60})_2^{2-}$ and $(C_{59}N)_2$, we suggest that these fullerene and hetero-fullerene dimer molecules exist as equilibrium mixtures of *anti* and *gauche* conformers, which should be considered when interpreting the experimental measurements.

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