Unconventional Bonding of Azafullerenes: Theory and Experiment

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Azafullerenes are a new and fascinating discovery in the class of C_{60}-based materials. Stemming from the synthesis of $C_{59}N$ in the dimer form[1] and of the potassium-intercalated $K_6C_{59}N$ solid,[2] a new class of compounds is starting to be born, opening up new avenues in materials science and organic chemistry and raising new fundamental questions about their stability, morphology, and electronic behavior. Further progress now requires the solution of the molecular structure and a full understanding of the basic features of the chemical bonding. We have studied this for the parent radical $C_{59}N$ and two closed-shell systems, $(C_{59}N)_2$ and $C_{59}HN$, through *ab initio* calculations and experiments. A picture emerges, which allows us to identify trends and peculiarities of the $C_{59}N$ family, and especially to understand how, and to what extent, the nitrogen substitution distinguishes them from isoelectronic C_{60} derivatives.

Our calculations are based on density functional theory (DFT) and use gradient-corrected exchange and correlation functionals,[3,4] which guarantee accurate results for the key quantities of interest, such as structural parameters, vibrational frequencies, cohesive energies, ionization potentials, and electron affinities.

$(C_{59}N)_2$ is the most interesting case. Even though dimerization is not new in fullerenes, for C_{60} itself this only takes place after rapid quenching in alkali-intercalated AC_{60} solids.[5] $(C_{59}N)_2$ is, instead, stable in solution[1] and in the solid state.[6] The question arises: How and how strongly do the two radical units bind to each other? Certain characteristics of the chemical bonding emerged in ref 1. Cyclic voltammetry suggested a weak coupling of the two units, whose structure was difficult to assess. ^{13}C NMR revealed a relatively high symmetry, but no sp^3 carbon was detected (30 signals in the range of 124−157 ppm), which made one wonder about the possibility of an "open" C−N configuration. Vibrational spectra did not allow an unambiguous interpretation either. IR absorption was observed in regions where C_{60} was silent, namely at ∼845 and at ∼1580 cm^{-1}.

Our search for the energetically favored conformation in DFT has followed several routes, namely via local relaxation of a number of geometries and via Car−Parrinello molecular dynamics.[7] The optimized structure in Figure 1a (*trans*-configuration) has only one intermolecular bond and C_{2h} symmetry, consistent with the NMR signals. That the link is made by that specific nearest neighbor (C′) of nitrogen, at the hexagon−hexagon fusion (see Table 1), is evident from the knowledge of the distribution of the unpaired electron in $C_{59}N$,[2] which has its largest amplitude there. The intermolecular bond is more than 0.05 Å longer than that between two sp^3 carbons, and accordingly, the electron density is relatively low on the intermolecular axis (see Figure 1a). The binding energy in BLYP−DFT is ∼18 kcal/mol,[8] a value in the range of the formation enthalpies of dimers of C_{60} with monoalkyl radical adducts.[9] Note that the spin density on the monomer also has its maximum at the C′ position but steric factors make dimerization happen at different sites.[9]

The *trans*-configuration of the nitrogens minimizes the repulsion of the electron clouds. One additional factor appears to contribute to its stabilization, namely the coupling of the σ intermolecular bond and the p_z orbitals of the atoms (N, C_b, C_b in Table 1) bonded to the two bridging carbons that are coplanar, as shown in the distribution of the HOMO (see Figure 1b). Rotation about the molecular axis by 120° transforms the system to a quasi-degenerate isomer (higher by less than 1 kcal/mol), with a loss in symmetry but retention of the same type of conjugation. These minima are separated by an energy barrier of ∼4 kcal/mol, corresponding to a torsional angle of 60°, so that isomerization should be hindered at room temperature, at least in the gas phase. The *cis*-configuration also corresponds to an energy maximum, as a function of the torsion angle, and lies at ∼5 kcal/mol. Away from the minima, the special electron conjugation of the optimal structures is lost.

The bond pattern in the individual units is also rather special. Changes with respect to C_{60} mainly concern the pyracylene structure around the C′−N bond (Table 1). Whereas the single replacement in $C_{59}N$ keeps the bond lengths close to the C_{60} values (1.40 and 1.45 Å), dimerization has strong effects as expected. The charge redistributes itself to weaken the intramolecular bonds of the tetracoordinated C′ and to strengthen both the N−C bonds on the pentagon and the "double" bonds in the hexagons containing C′−N. This bond turns out to be a relatively weak one, as the electron density distribution in Figure 1a emphasizes. In combination with the weak intermolecular C′−C′ bonding, this results in an electronic environment for C′ remarkably different from that of a typical sp^3 atom. This fact should account for the missing NMR signal in the sp^3 region. Accurate calculations of the carbon chemical shifts would be highly desirable.

The calculated vibrational spectrum of $(C_{59}N)_2$ reflects these structural characteristics. In agreement with experiment, in the gap of C_{60}, around 850 cm^{-1}, a whole new band emerges, which is dominated by stretching modes of the C−N and C−C bonds on the pentagonal rings and new modes appear at higher frequencies, which involve the stretching of the reinforced "double" C−C bonds in the proximity of the C′−N bond. Once compared to the calculated spectrum of the monomer, we recognize as sign of the dimerization the appearance of vibrational density below 200 cm^{-1} and down to ∼50 cm^{-1}, the softest being torsional modes.

Finally, a natural and interesting comparison is that between $(C_{59}N)_2$ and the isoelectronic $(C_{60}^-)_2$ system. Our calculations predict a very similar structure for the latter (*anti*-conformation), apart from the much elongated intermolecular distance (1.675

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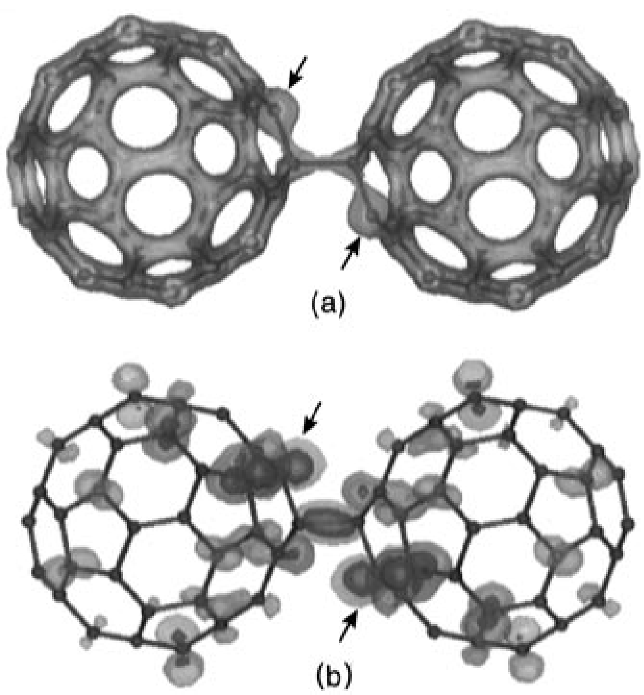
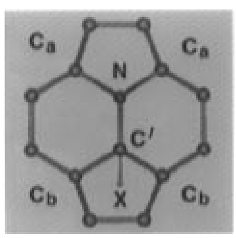


Figure 1. For $(C_{59}N)_2$: Isodensity hypersurfaces of (a) the electron density and (b) the HOMO. Values (in au) are 0.2 (a); 0.002 (dark) and 0.0005 (light) (b).

Table 1. Bond lengths (Å) and bond angles (deg): X = C′ in the dimer; X = H in $C_{59}HN$



	$C_{59}N$	$C_{59}HN$	$(C_{59}N)_2$
C′-N	1.405	1.523	1.520
C_a-N	1.429	1.423	1.425
C′-C_b	1.430	1.546	1.550
C′-X		1.100	1.609
$\widehat{C_bC'C_b}$	109	111	100
$\widehat{C_bC'N}$	120	112	111
$\widehat{NC'X}$		113	114
$\widehat{C_bC'X}$		108	108

Å). The *anti*-conformation has been determined also by less sophisticated calculations[10] and confirmed in $(K,Rb)C_{60}$ solids.[11] Owing to the dominant Coulomb repulsion, this isolated dimer is not bound with respect to the charged monomers,[10,12] by as much as 44 kcal/mol. Its stabilization in the fulleride solids, then, is provided by the alkali counterions.

The distribution of the unpaired electron in $C_{59}N$ also makes C′ the most natural candidate for the attachment of hydrogen, which, in contrast with the case of a second $C_{59}N$, is able to form a strong σ bond. This leads to $C_{59}HN$, an especially stable member of the $C_{59}N$ family with a calculated binding energy of ~72 kcal/mol. The structure of the $C_{59}N$ moiety is very similar to that in the dimer (Table 1), although the strong C′−H bond forms at the expense of a slight weakening of the bonds of the C′ atom on the ball. The C′ atom has a unique electronic environment, different than that in the dimer, being closer to sp^3. Accordingly, NMR detects it at 72.1 ppm. In agreement with these theoretical results, the proton−carbon-coupled NMR experiment gave $^1J_{CH} = 162.0$ Hz for this resonance. $^1J_{CH}$ is directly proportional to the degree of s character of a C−H bond and is used to assign hybridization of carbon atoms when uncertain. The observed high value indicates a higher s character than a similar bond of $C_{60}HCN$ ($^1JCH = 143.4$ Hz). The $^1J_{CH}$ of 162 Hz is high, even if one considers that attachment of the carbon in question to nitrogen could increase J by 5−10 Hz. In addition, the calculated frequency of the C′−H stretching mode at 2888 cm^{-1} lies in the expected range for a saturated carbon atom. Compared to $(C_{59}N)_2$, the vibrational spectrum of $C_{59}HN$ resembles more closely that of C_{60}. A detailed comparison will be reported elsewhere.

Focusing on the electronic properties, Kohn−Sham (KS) energy diagrams show that dimerization as well as hydrogenation are accompanied by the opening of a large HOMO−LUMO gap. In both cases the KS-BLYP value is 1.2 eV, 0.4 eV lower than that calculated for C_{60}. Comparison with experiments in solid $(C_{59}N)_2$ can be made, keeping however in mind what is known for C_{60}. Namely, due to the neglect of self-energy corrections, the KS value strongly underestimates the quasi-particle energy gap (2.3−2.6 eV),[13] and the first observed excitation is significantly lower than the latter (1.8−1.9 eV), dominated by excitonic effects. Electron energy loss spectroscopy (EELS)[14] detects the first excitation in $(C_{59}N)_2$ at 1.4 eV, also 0.4 eV lower than in C_{60}, showing that the global "correction" to the KS estimate amounts to a similar value in the two systems. In contrast, but consistent with the lack of stability, the "ideal" dimer of the C_{60} anion has a much smaller gap (0.4 eV). Consistent with this finding, the dimer phase of the RbC_{60} solid exhibits a small gap (0.5 eV).[15]

In conclusion, replacing one carbon with nitrogen on the Bucky cage, emerges as a clever way of adding an electron to the π system of C_{60} by keeping it neutral, perturbing its structure not too strongly, and avoiding the "cumbersome" addition of a radical. $C_{59}N$ is shown to be a very reactive radical which readily saturates through regioselective reactions, in which one specific carbon either takes up a hydrogen or binds to a like $C_{59}N$ radical. In this way, new stable molecules form, which we have characterized through experiment and with the aid of *ab initio* calculations. Electronic energy spectra are easily derivable from those of C_{60}, but significantly differ from those of isoelectronic nitrogen free systems, and show that interesting properties can be expected for azafullerene anions.[16] Concerning redox properties, we calculate ionization potentials much lower than in C_{60} (6.3 eV in $(C_{59}N)_2$ and 6.1 eV in $C_{59}HN$, respectively) but comparable electron affinities (2.8 and 2.5 eV, respectively). Vibrational spectra still bear fingerprints of the individual molecules. Finally, the chemical bonding of the stable azafullerenes is unique among all the stable fullerene derivatives known so far. This suggests the paths to the synthesis of novel interesting fullerene-based materials.

Supporting Information Available: Optimized structures of $(C_{59}N)_2$ and $C_{59}HN$ (4 pages). See any current masthead page for ordering and Internet access instructions.

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