

Quantum-Chemical Studies of Superconducting Fullerene Derivatives†

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Various derivatives of the fullerene C_{60} have been reported as prosperous superconductors. A charge transfer in the derivatives implies Jahn-Teller distortion of the icosahedral fullerene cage. This can be well documented by quantum-chemical calculations. Computational illustrations are given on the fullerene interactions with Cl_2 , alkaline metals, and sodium azide NaN_3 based on the semiempirical quantum-chemical methods AM1 and SAM1. Treated are also structures based on boron nitride. The results of computations could be used in search of structure/activity correlations with the T_c temperature.

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Discovery of the fullerene superconductivity, exemplified [1] by K_3C_{60} with the critical temperature T_c of 18 K, has placed [2,3] fullerene derivatives into the focus of interest of the superconductivity research. Although there is no generally accepted theory [4-6] of the fullerene superconductivity quantum-chemical computations can be of a considerable use in the research. The usage is related to two well working empirical correlations of the fullerene superconductivity with the material properties. One deals with Raman spectra [7,8] of A_xC_{60} mixtures where a vibrational shift is related to stoichiometry x (only $x=3$ is superconductive and the stoichiometry can be deduced from the vibrational shift). The other correlation is a linear relationship [9] between the lattice constant of A_3C_{60} and its critical temperature T_c . The lattice constant can also be deduced from quantum-chemical computations. Hence, quantum chemistry can serve as an alternative source of molecular parameters, especially in screening new materials.

The computations have primarily been performed with semiempirical quantum-chemical methods, especially SAM1[10], implemented in AMPAC [11] and other program packages [12-14]. Geometry optimizations were carried out without symmetry constraints in Cartesian coordinates and with analytically constructed energy gradient. In the optimized geometries, the harmonic vibrational analysis was done by a numerical differentiation of the analytical energy gradient. The treatment supplied structure, energetics, and vibrational spectra of the systems studied.

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A charge transfer to or from the fullerene cage implies its Jahn-Teller distortion owing to the degeneracies present in the frontier orbitals (unless we deal with a special number of electrons, like in hexa-anion [4]). The effect reduces symmetry and activates various spectral transitions. Duclos et al. [8] reported that the vibrational shift in $A_x C_{60}$ species was only slightly influenced by the atom A nature. This suggests that simple charged cage C_{60}^{z-} is a good approximation of the fullerene part of the system. Therefore we computed several charged C_{60} species (Table I shows systems with reasonable SCF convergence properties). The geometrical parameters are not too different from the neutral cage but spectral consequences are substantial (Table II). The experiment treats a Raman line at 1458 cm^{-1} (which is not particularly strong in the IR spectra surveyed in Table II). If we take into account transfer from the solid to gas phase and computational overestimation of stretching modes, we can suggest experimental equivalents of the SAM1 vibrational frequencies at about $1757, 1741, \text{ and } 1723 \text{ cm}^{-1}$ for $C_{60}, C_{60}^{3-}, \text{ and } C_{60}^{6-}$, respectively. In our SAM1 computations we have several lines at $1756, 1711\text{-}1730, 1652\text{-}1691 \text{ cm}^{-1}$ for $C_{60}, C_{60}^{2-}, \text{ and } C_{60}^{4-}$, respectively. Although numerical difficulties still prevent a direct experiment-theory comparisons, the trends are apparently correct.

Interaction of C_{60} with alkali metals can also be computed with more elaborated models (though closed shells). We have studied charged species $X.C_{60}^+$, especially with lithium complexes [15]. From methodical point of view one should consider both, endohedral (internal) and exohedral (external) complexes. In fact, the obvious location of the X atom in the very centre of the cage exhibits the highest energy among all the structures studied (1078 kcal/mol). If n-e allow for an internal location closer to the cage surface, two different minimum-energy structures have been found, either location above a carbon atom (1053.9 kcal/mol ; $\text{Li-C}=2.29 \text{ \AA}$) or above a hexagon (1053.7 kcal/mol ; $\text{Li-C}=2.41 \text{ \AA}$). On the other hand, we were unable to locate a minimum-energy structure above a pentagon. However, the energy drops still more dramatically if we allow for the outside location, i.e. the situation

TABLE I. The SAM1 computed geometrical characteristics of the neutral and charged C_{60} .

Species	r_{min}	r_{max}	$I_A \times 10^{37}$	$I_B \times 10^{37}$	$I_C \times 10^{37}$
	\AA	\AA	gcm^2	gcm^2	gcm^2
C_{60}^b	1.406	1.487	10.407	10.407	10.407
C_{60}^{4+}	1.398	1.495	10.459	10.459	10.306
C_{60}^{2-}	1.408	1.491	10.442	10.442	10.410
C_{60}^{4+}	1.394	1.512	10.499	10.443	10.337
C_{60}^{4-}	1.407	1.512	10.489	10.488	10.450

^a The shortest and the longest C-C bond, and the principal moments of inertia.

^b Two types of bonds only owing to the I_h symmetry.

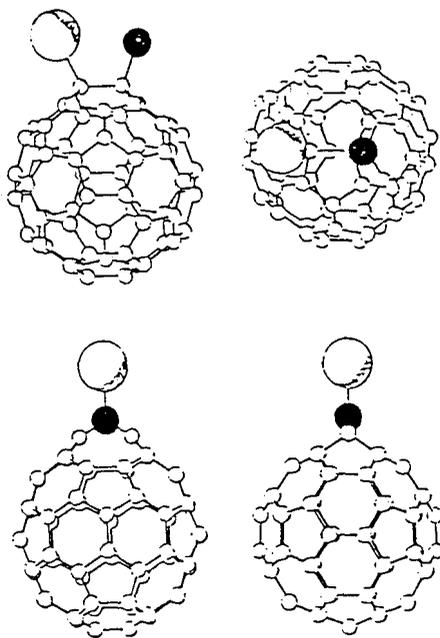


FIG. 1. Two orthogonal views of the SAM1 optimized structures of $C_{60}CH(5/6)$ (top) and $C_{60}CH(6/6)$ (• denotes the Cl atom).

TABLE II. The SAM1 computed twelve IR most intense^a harmonic vibrational wavenumbers ω_i (in cm^{-1}) of the neutral and charged C_{60} .

Species	ω_i					
C_{60}^a	493			761		
	1343			1722		
C_{60}^{2+}	201	205	528	529	590	591
	673	673	704	704	827	828
C_{60}^{2-b}	502	591	592	755	755	923
	923	1132	1387	1387	1473	1473
C_{60}^{4+}	923	1065	1149	1154	1189	1253
	1275	1385	1438	1457	1536	1550
C_{60}^{4-}	308	400	1195	1215	1219	1276
	1451	1482	1507	1567	1585	1604

^a There are only four IR active modes for the icosahedral C_{60} .

^b Two imaginary frequencies - a saddle point.

pertinent to the superconductive phenomena. Here, two minimum-energy structures have been computed, either above a pentagon (973 kcal/mol; Li-C=2.29 Å) or above a hexagon (971 kcal/mol; Li-C=2.33 Å).

Recently, thermal decomposition of sodium azide NaN_3 has been used [16] to prepare Na-doped fullerene, though the superconductive-phase (12-15 K) composition ($\text{Na}_x\text{N}_y\text{C}_{60}$) is not clear. We have performed [15] related computations at the MNDO level on lithium azide LiN_3 systems. We have studied conditions for a decomposition of the azide (the Li-N distance in the free azide is computed as 1.763 Å, the inner and outer N-N bond as 1.195 and 1.144 Å, respectively). If we try an approach of the N end towards a C atom, the optimized structure is rather high in the heat of formation scale (935 kcal/mol). The approach with the Li end is more convenient and we have localized four optimum structures; the Li-N bond is always elongated comparing to the free molecule. The highest in energy is the orthogonal approach to a five-membered ring (903 kcal/mol; Li-N=1.802 Å), being followed by a six-membered ring orthogonal approach (900 kcal/mol; Li-N=1.802 Å). The energy drops further if we allow for a parallel (stacked) orientation, while the Li-N is weakened further. There are two such orientations, one with the Li atom above a C atom (898 kcal/mol; Li-N=2.495 Å), the other above a five-membered ring center (895 kcal/mol; Li-N=2.164 Å). The last mentioned (i.e., the thermodynamically most convenient) orientation is connected with a significant enthalpy decrease along the reaction: $\text{LiN}_3 + \text{C}_{60} = \text{LiN}_3 \cdot \text{C}_{60}$, $\Delta H_{298}^\circ = -34.7$ kcal/mol. Hence, our computations suggest the azide decomposition.

Another promising doping is represented [17] by iodine monochloride CII with transition temperature possibly between 60 and 70 K. We have localized two different minimum energy structures for the ICI & C_{60} adduct (Fig. 1) - addition to a 6/6 or 5/6 bond. The 6/6 addition is connected with a substantial energy decrease (Table III). The ICI fate in both complexes is considerably different. In the 6/6 case the CC1 bonds are 1.238 Å long and the distance between the two carbons connected to the Cl atom is 2.106 Å. In the 5/6 complex the C-C bond between the two adjacent carbons is a long single bond (1.766 Å); the C-Cl and C-I bonds are 1.766 and 2.203 Å, respectively. Hence, the computations

TABLE III. The SAM1 computed energetics^a of the CII and C_{60} association.

Reaction	$r_{\text{Cl-I}}^b$	$\Delta H_{r,298}^\circ$	$\Delta H_{rel,298}''$
	Å	kcal/mol	kcal/mol
$\text{C}_{50}(\text{g}) + \text{CII}(\text{g}) = \text{C}_{60}\text{CII}(5/6; \text{g})$	3.220	2.36	77.15
$\text{C}_{60}(\text{g}) + \text{CII}(\text{g}) = \text{C}_{60}\text{CII}(6/6; \text{g})$	2.109	-74.79	0.0

^aThe reaction enthalpy $\Delta H_{r,298}^\circ$ and the relative reaction enthalpy $\Delta H_{rel,298}^\circ$ at room temperature.

^bThe SAM1 computed bond in a free CII molecule is 2.211 Å.

reveal a strong interaction.

Finally, boron-nitrides with metals exhibit superconductivity though structural aspects need to be clarified [18]. This finding recalls discussions on a possible superconductivity of boron-nitride nanotubes [19]. This context calls for a further study the B-N cage alternative structural pattern (hexagon/square) [20].

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