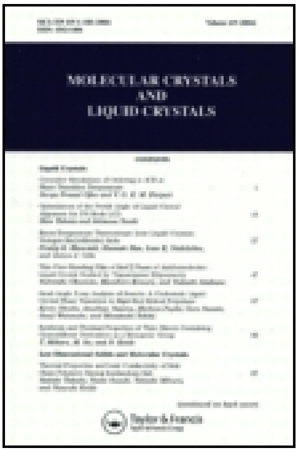

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

C_{60} Barrelene: Structure, Stability and Layered Metal-Doped C_{60} Solid

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Version of record first published: 04 Jun 2010.

To cite this article: Leonid Chernozatonskii (1993): C_{60} Barrelene: Structure, Stability and Layered Metal-Doped C_{60} Solid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 229:1, 69-74

To link to this article: http://dx.doi.org/10.1080/10587259308032178

Mol. Cryst. Liq. Cryst. 1993, Vol. 229, pp. 69–74
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Printed in the United States of America

C_{60} BARRELENE: STRUCTURE, STABILITY AND LAYERED METAL-DOPED C_{60} SOLID

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Abstract Formation, electron structure and high dianion stability of barrel-shape C_{60} cluster are considered. We also discuss unusual C_{60} distribution on the GaAs (110) surface, barrelene presence in C_{60} crystal, metal-doped barrelite.

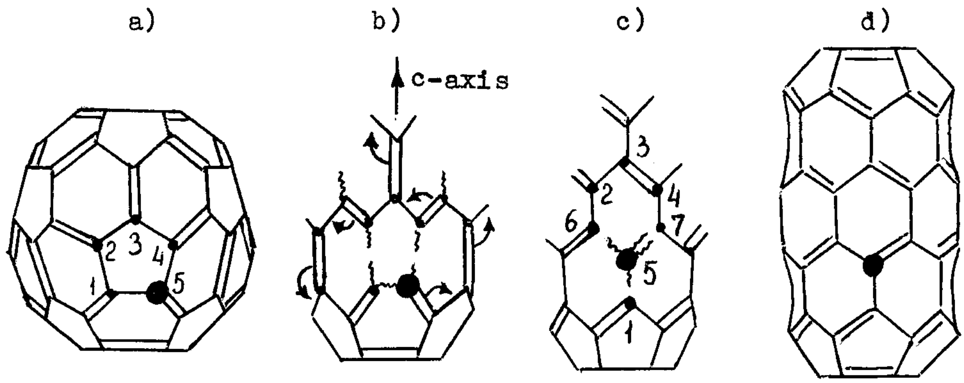
INTRODUCTION

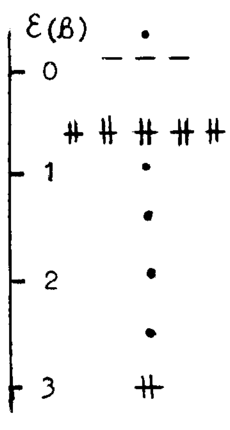
Carbon cluster of C_{60} has been the focus of many experimental and theoretic studies [1]. The most stable isomer - footballene has the form of a truncated icosahedron[2]. But a series of the latest experiments has shown that gas and solid phases of C_{60} include molecules with properties,which can't be explained by existing footballene model, such as: the presence of not identified lines in the vibration spectrum[3,4], specific C_{60} destruction character under intense laser excitation[5], NMR spectrum expansion[6] and appearance of paramagnetic properties[7] in C_{60} powder at low temperatures, observation of prolongated and thin objects in molecule layers[8,9]. We have proposed[10] a more strained form of C_{60} to explain these properties, suggesting that C_{60} footballene takes this form under the influence of forces pressing a ball along its diameter or pulling it along the c-axis, going through two parallel hexagons - Fig.1a.

TRANSFORMATION OF f-C_{60} INTO b-C_{60}

Under external forces 6 atoms of f-C_{60} change their place and 6 pentagons form "rosettes" around each of two "lid" hexagons - Figure 1. The cylindrical surface of the b-C_{60}

- "barrel" is essentially a fragment of rolled graphite surface. Let us discuss in detail the motion dynamics of a jumping atom and reorganization of the Kekule' structure while a footballene transforms into a barrelene. Such reorganization process can be conditionally divided into three stages: 1) first a break of two single bonds (1-2 and 4-5) in a second belt pentagon of the f-C_{60} takes place under the forces pressure - Fig.1b ; 2) atoms 2,3,4 - "hinges" move and connecting them bonds turn so that the construction lengthens along the c-axis, simultaneously the hexagon adjacent to the lid is deformed which causes pushing out of its right (or its left) atom 5 into the created hollow space - Fig.1c ; 3) the pushed out atom achieves the place





E(β)	f-C_{60}	b-C_{60}
E/60	1.55	1.54
E^{1-}	92.86	92.76
E^{2-}	92.72	93.17
E^{1+}	92.38	91.94
E^{2+}	91. 16	91.52

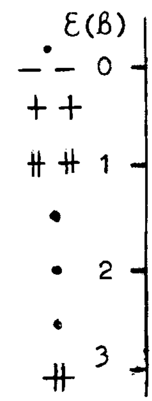


FIGURE 1. f-b transformation of C_{60}

of local balance, which determines the cylindrical graphite fragment configuration, and is fastened there forming single bonds with atoms 1,6 and a double bond with atom 7 of created pentagon "rosette" - Fig.1d.

ELECTRON STRUCTURE AND STABILITY OF b-C_{60}

As it was shown by calculations[11] this very distribution - - Fig.1d - is acquired presupposing conservation of D_{6h} symmetry group of the cluster b-C_{60}. Electron structure was examined in valency approximation by extended Hukkel method. It is showed that neutral b-C_{60} has a closed electron shell but the gap dividing the fulled energy level and the nearest valency one is very small (0.02eV) - lower part of Fig.1d. This proves paramagnetism of b-C_{60} and its ability to form stable dianion and dication. On the base of experimental f-C_{60} data[1] of the first ionization potential 7.6eV and the energy of its affinity 2.6eV the values of Coulomb (α= -3.5eV) and resonance (β= -6.6eV) integrals were calculated. It is possible to estimate the stability of footballene and barrelene ions, that is their energy and energy difference in various charge positions of these two C_{60} forms - table on Fig.1 . Following conclusions can be drawn from the table: 1) barrelene ionization potential is about 1.4eV less than footballene one and its value is close to the non indentified line 6.3eV, discovered in the absorption spectrum of considerably excited C_{60} synchrotron radiation [4]; 2) barrelene dianion's energy is lower than that of f-C_{60} dianion ($E_f^{2-}-E_b^{2-}$= 2.97eV); 3) in case of double ionization barrelene also possesses lower energy ($E_f^{2+}-E_b^{2+}$= 2.36eV). So b-C_{60} is characterized by a greater acceptor and donor ability as compared to f-C_{60}.

C_{60} MONOLAYER ON (110) GaAs SURFACE

On the base of the 2) conclusion we can explain the unusual picture of C_{60} monolayer distribution on the (110) surface of GaAs[12]. Two types of the distribution were observed: a row of "deeply" sitting A clusters each surrounded by protruding on the reorganized GaAs surface As atoms (such monomolecule islands were $\sim 7A^{o}$ high); a row of more closely packed B clusters each surrounded by Ga atoms, and protruding over A clusters up to $\sim 1A^{o}$. Our explanation is as follows: C_{60} footballene finds itself in a cell of the reorganized surface, it is charged positively and makes a stable compound with four As^{-} anions; C_{60} barrelene falls into a pit and is toughly joint to four Ga^{+}, it is charged negatively. As barrelenes are longer and thinner (the cage sizes are $D^{b} \simeq 5A^{o}$, $L^{b} \simeq 8.5A^{o}$ [10,11]) than footballenes ($D^{f} = 7.1A^{o}$ [1]), they are higher $\sim 1A^{o}$ than f-C_{60} rows even after their "fall".

C_{60} ORTHOROMBIC CRYSTAL

Barrelene dianion stability causes the possibility of appearance of mixed f-b complexes, for example, $(f\text{-}C_{60}^{1+})_2 b\text{-}C_{60}^{2-}$ or $b\text{-}C_{60}^{2+}$ $b\text{-}C_{60}^{2-}$. The unusual orthorombic structure of a C_{60}crystal can be explained by presence of the latter one b-b complex in the middle of its 8 molecules unique cell[13] (usual fcc structure of f-C_{60} is destroyed). The complexes form a rod of standing on each other C_{60_b} "barrels" covalent ($a \cong 1.5A^{o}$) bound by lid hexagons. $L_{cov} \cong L^{b} + a \cong 10A^{o}$ is the period of such a rod, which equals to the structure period along the c-axis [13].

METAL-DOPED C_{60} BARRELITE - POSSIBLE HT SUPERCONDUCTOR

Stability of b-C_{60} dianion makes it possible to suppose that doping by metal atoms results in appearance of a complicated hexagonal close packed structure of $A^{1+} b\text{-}C_{60}^{2-} A^{1+}$ complexes - quasidielectric layer, where A atoms are in tetrahedral sites, and sublattice of quasimetal layers, where B atoms are in orthohedral sites. So the $A_2Bb\text{-}C_{60}$

compound is very much like layered high T_c superconducting oxides. The plane of B layer is deprived of mirror symmetry - Fig.2 . Thus propagating along the layer phonons (having

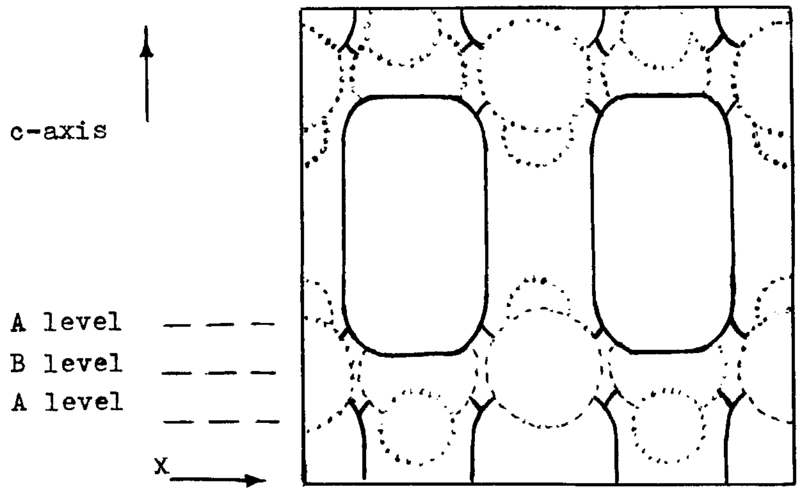


FIGURE 2. A_2BC_{60} barrelite.

along the c-axis polarization of A and carbon atoms displacements u_z) must be accompanied by along layer electric polarization $P_x \sim e_{xij} u_{ij}$, where e_{xij} are "piezo" bond constants[14]. It is this local piezo-like effect that determines high electron-phonon interaction. Note that "piezo" constant should increase with the growth of the differece between the atomic number of carbon and that of doping atoms, which causes still greater nonmirror symmetry of "metal" plane. Besides empty A sites in C_{60} barrelite should be filled by atoms with a small ion radius ~1A° and B sites may be filled by atoms a larger radius ~2A°. Thus for example III group atom ions: Ga, In (r_i =1.13, 1.32Å correspondingly) are rather suitable for empty A sites. So high enough T_c can be predicted for compounds like $RbIn_2C_{60}$ and $CsGa_2C_{60}$. The layered structure of such a material leads to energy state density localization in electron and phonon subsystems. This fact together with high "piezo" constants determines the high value of the electron-phonon interaction and after all the high T_c of superconducting transition.

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