

Atomic and electronic structure of the barrelenes $b - C_m$ with $m = 36 + 12n$

E. G. Gal'pern, I. V. Stankevich, and A. L. Chistyakov

Institute of Element-Organic Compounds, Russian Academy of Sciences, 117813, Moscow

L. A. Chernozatonskii

Institute of Chemical Physics, Russian Academy of Sciences, 117334, Moscow

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The atomic structure, the metric characteristics, and the one-electron energy levels are calculated for the barrel-shaped carbon clusters $b - C_m$, where $m = 36 + 12n$. The dianion of $b - C_{60}$ is stabler than the dianion of the footballene $f - C_{60}$.

The spherical-skeleton carbon molecules C_m have attracted considerable new interest in the past year, because of two developments. First, a method has recently been devised for producing C_{60} clusters in macroscopic quantities.¹ (The clusters themselves had been discovered² in 1985.) Second, it has been found³ that C_{60} crystals doped with alkali metal atoms exhibit superconducting properties with fairly high T_c 's (≥ 18 K).

The stablest isomer of the C_{60} cluster is footballene, which is a truncated icosahedron.⁴ Several recent experiments^{5–10} have shown, however, that C_{60} clusters exist in gaseous and solid phases, with properties which cannot be described by the footballene model: There are unidentified lines in the vibration spectra; there is a broadening of the NMR spectrum; C_{60} crystals exhibit paramagnetic properties at low temperatures, to 77 K; C_{60} crystals of orthorhombic symmetry grow; there are distinctive features in the destruction of C_{60} during the application of intense laser light; and elongated carbon entities with a diameter smaller than that of footballene are observed in molecular layers. One of the present authors has previously suggested¹¹ that a strong external excitation or a deformation in the solid state may create conditions which promote a transition from spheroidal molecules to a more oblong shape (Fig. 1). It has been shown that barrel-shaped C_{60} molecules ("barrelenes") differ from footballene molecules in being capable of forming a layered crystal structure. When such a structure is doped with an alkali metal, it becomes extremely similar to the layered structure of the high- T_c oxide superconductors.

All these circumstances led us to focus on imperfect forms of carbon clusters and to carry out a detailed study of the atomic and electronic structure of the barrelenes C_m with $m = 36 + 12n$. As in the case of footballene, the structure of the barrelenes can be described in terms of hybrid orbitals with an approximately sp^2 hybridization:⁴ Three hybrid orbitals of each atom are used to form two-center σ bonds with three neighboring carbon atoms. The fourth orbital (a ρ orbital) can be chosen in such a way that the vector which specifies its orientation makes identical angles with the

vectors from the given atom to its neighbors.⁴ When chosen in this manner, the ρ orbitals form the basis of the reducible representation Γ_ρ of the symmetry group D_{6h} in the case $n = 2k$ or the group D_{6d} in the case $n = 2k + 1$ (Fig. 1).

The system of ρ electrons of the barrelenes C_m with $m = 36, 60,$ and 72 has been studied in the Hückel topological approximation. The results of these calculations are presented in Fig. 1 as diagrams of the one-electron energy levels, expressed in units of β , where β is the resonance integral. It can be seen from this figure that the upper

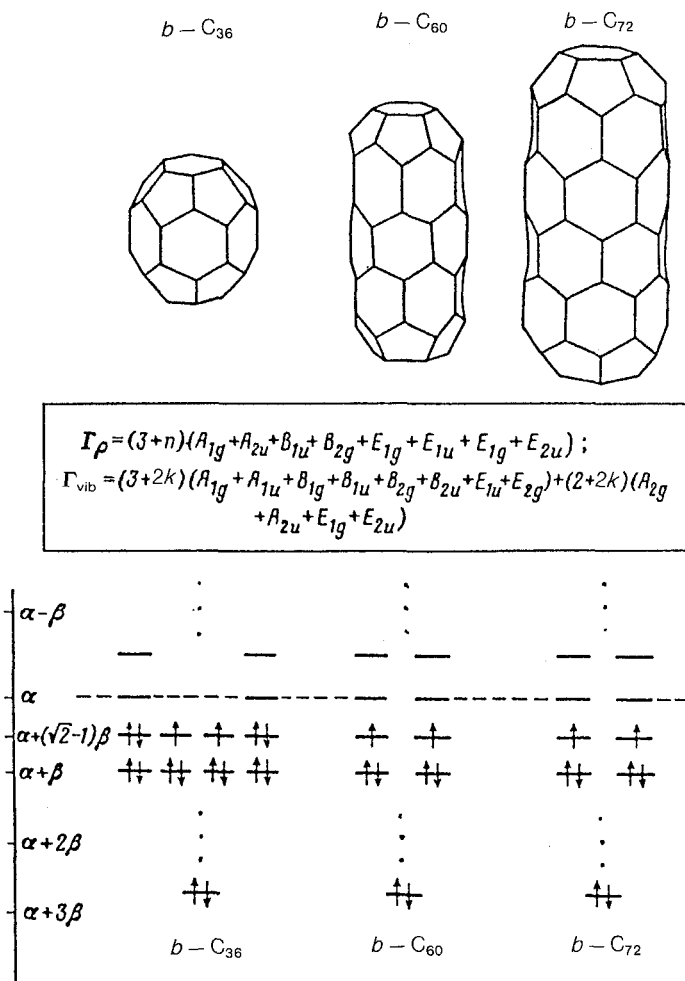


FIG. 1. Structure and one-electron energy levels of $b - C_{36+12n}$. The filled energy levels of the ground state and of several low-lying states are shown. The components of various representations Γ_ρ of the symmetry group D_{6h} ($n = 2k$) generated by the ρ orbitals are shown. The symmetry types of the vibrations of $b - C_{36+12n}$ (Γ_{vib}) are also shown. The diameter of a barrelene is $d = d_s + 2l_v$, where $d_s = 5 \text{ \AA}$ is the diameter of the skeleton, and l_v is the van der Waals radius of carbon ($2l_v = 3.35 \text{ \AA}$). The height of a barrelene is $L_n = (d + 2rn)$, where r is the length of the C-C bond ($\approx 1.4-1.5 \text{ \AA}$) ($L_{36} \approx 8 \text{ \AA}$, $L_{60} \approx 11 \text{ \AA}$, $L_{72} \approx 14 \text{ \AA}$). Here α is the Coulomb integral, and β is the resonance integral ($\alpha < 0$, $\beta < 0$).

filled energy level ϵ_{UFL} is degenerate, but two electrons are not enough to fill it. Since this is a binding energy level, with $\epsilon_{\text{UFL}} < \alpha$, the barrelenes should tend to form dianions. We would expect the ρ -electron system of the dianion of the barrelene $b - C_{60}$ to be stabler than the ρ -electron system of footballene, since the lower vacant energy level of footballene satisfies $\epsilon_{\text{LVL}} > \alpha$.

Analysis of the symmetry properties of the molecular orbitals of the upper filled energy level shows that its degeneracy is accidental. The only nonzero coefficients in these molecular orbitals are those which correspond to the carbon atoms on the "covers" of the "barrel" and the atoms of the nearest carbon layer which are bound directly to these cover atoms. Since the barrelenes exhibit acceptor properties, we estimated the structural parameters of the dianion of the simplest barrelene: the cluster of $b - C_{36}^{2-}$. These calculations were carried out in the valence approximation by a version of the method of neglect of differential overlap.¹² The total energy was optimized with respect to bond lengths, valence angles, and dihedral angles. It was assumed that the D_{6h} symmetry group of the cluster was preserved.

It was found that the C-C bond lengths in a hexagon on a cover of $b - C_{36}^{2-}$ are 1.431 Å. This figure is close to the C-C bond length in a monolayer of graphite. Each pentagon has C-C bonds of three types. The common bond with a cover hexagon has a length of 1.431 Å; the adjacent bond with two pentagons has a length of 1.497 Å; and the common bond with a hexagon which does not lie on a cover is 1.449 Å. In the same hexagon there is a C-C bond with a length of 1.454 Å. These metric characteristics of the dianion $b - C_{60}^{2-}$ were used to model the structure of $b - C_{36}^{2-}$. The electronic structure of $b - C_{60}$ was studied in the valence approximation by an expanded Hückel method.¹³ Analysis of the one-electron energy levels of $b - C_{60}$ shows that the neutral cluster $b - C_{60}$ has a closed electron shell. The energy gap separating the filled energy levels from the vacant ones is small (0.02 eV), however, confirming the conclusion, reached in the Hückel approximation, that $b - C_{60}$ is paramagnetic and tends to form dianions.

This circumstance may play a significant role in stabilizing $A^{1+}(b - C_m)^{2-}A^{1+}$ complexes in (for example) C_{60} crystals doped with atoms of alkali metals A. This circumstance also suggests some new superconducting layered crystals with the general formula AB_2C_{36} , with a hexagonal lattice with lattice constants $a = d$, $c = 1.6a$ ($d = 8$ Å is the diameter of $b - C_{36}$).

For the ionization potential we found the estimate $I_b = 7.7$ eV. This figure is about 0.6 eV lower than the ionization potential found for footballene in the same approximation. The ionization potential of a barrelene can be estimated in a different way, by comparing the results calculated for footballene and barrelene by the simple Hückel method. Using the experimental data¹⁴ on the first ionization potential of footballene ($I_f = 7.61$ eV) and on its electron affinity ($A_f = 2.65$ eV), we find the parameter values $\alpha = -3.5$ eV and $\beta = -6.6$ eV. Using these figures and the formula for the energy of the upper filled level of $b - C_{60}$, we find that the ionization potential of a barrelene should be lower than that of footballene by about 1.4 eV: $I_b = 6.2$ eV. This value is close to the energy ($\epsilon = 6.3$ eV) of an unidentified line which has been observed in the absorption spectrum of synchrotron radiation.¹⁵

In the limit $n \rightarrow \infty$, the structure of the barrelene C_{36+12n} can be described as an infinite cylindrical surface tiled with hexagons. Calculations carried out by the crystal-orbital method have shown that a macromolecule of this sort—a quasi-one-dimensional solid—has a spectrum typical of a semimetal.

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- ¹W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature* **347**, 354 (1990).
²H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, *Nature* **318**, 162 (1985).
³A. F. Hebard, M. J. Rosseinsky, R. C. Haddon *et al.*, *Nature* **350**, 600 (1991).
⁴D. A. Bochvar and E. G. Gal'pern, *Dokl. Akad. Nauk SSSR* **209**, 610 (1973).
⁵D. S. Bethune *et al.*, *Chem. Phys. Lett.* **179**, 181 (1991).
⁶S. C. O'Brien *et al.*, *J. Chem. Phys.* **88**, 220 (1988).
⁷R. S. Ruoff *et al.*, *J. Phys. Chem.* **95**, 3457 (1991).
⁸C. S. Yannoni *et al.*, *J. Phys. Chem.* **95**, 9 (1991).
⁹A. A. Zachidov *et al.*, *Proceedings of the International Conference M₂S HTSC-III* (Kanazawa, Japan, 1991); *Phys. C*, in press.
¹⁰S. Wang and P. R. Buseck, *Chem. Phys. Lett.* **182**, 1 (1991).
¹¹L. A. Chernozatonskii, *Phys. Lett. A* **160**, 392 (1991).
¹²M. J. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4899 (1977).
¹³R. Hoffman, *J. Am. Chem. Soc.* **39**, 1397 (1963).
¹⁴H. W. Kroto, A. W. Allaf, and S. P. Baum, *Chem. Rev.* **91**, 1213 (1991).
¹⁵Y. Achida *et al.*, *Chem. Lett. (Tokyo)*, 1234 (1991).

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