

# An *ab initio* Study of the $C_{60}$ Particle-Hole Pair $C_{60}^{12+}$ and $C_{60}^{12-}$

Michael C. Böhm<sup>a</sup>, Joachim Schulte<sup>a</sup> and Robert Schlögl<sup>b</sup>

<sup>a</sup> Institut für Physikalische Chemie, Physikalische Chemie III, Technische Hochschule Darmstadt, Petersenstr. 20, D-64287 Darmstadt

<sup>b</sup> Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4 - 6, D-14195 Berlin

Z. Naturforsch. **52 a**, 331–334 (1997); received January 9, 1997

The  $C_{60}$  ions  $C_{60}^{12+}$  and  $C_{60}^{12-}$  are discussed comparatively on the basis of *ab initio* calculations. The basis set employed is of 3-21 G\* quality. By analogy with the neutral molecule the geometry of the anion is icosahedral ( $I_h$ ). Both  $I_h$  systems differ, however, in the bondlength alternation. In the neutral molecule the hexagon-hexagon bondlength exceeds the hexagon-pentagon value; vice versa in the anion.  $C_{60}^{12+}$  is of  $C_s$  symmetry with a strong intermixing in the length of the two types of CC bonds. Calculated geometries, total energies and net charges are adopted to evaluate differences in the electronic structure of  $C_{60}^{12+}$  and  $C_{60}^{12-}$ .

**Key words:**  $C_{60}$  ions, Electronic Structure of Fullerenes, Violation of Particle-hole Symmetry, *ab initio* Calculations.

The  $C_{60}$  soccerball exhibits a somewhat “hybride”  $\pi$  electron character [1]. Although this system has the topology of a polycyclic non-alternant molecule,  $C_{60}$  shows the charge distribution of an alternant network [2]. The high icosahedral point symmetry forces identical net charges  $q_c$  at any atom. The splitting of the canonical molecular orbitals (CMOs) of  $C_{60}$ , however, is characteristic for a non-alternant molecule; particle-hole symmetry is missing. Experimental investigations have shown that  $C_{60}$  is a strong electron acceptor [3, 4]. This behaviour can be traced back to the presence of pentagon defects in an otherwise graphitic structure. For an interesting theoretical analysis of this topic we refer to [5]. In a recent contribution we have evaluated a second quantity of influence to enhance the acceptor capability of  $C_{60}$ , i. e. the  $\pi^*/\sigma^*$  coupling which is allowed in the spherical molecule [6]. In solution,  $C_{60}$  can add reversibly up to six electrons [7]. The cationic counterpart of  $C_{60}^{6-}$  has been detected in an isotope resolved mass spectrum [8]. In the “anionic” series,  $Li_{12}C_{60}$  has been identified in an electrochemical study [9]. The donor-to-acceptor charge transfer (CT) in this compound leads to a high excess charge on the soccerball. In the solid state,  $C_{60}$  units approaching electron excess

charges of  $-12$  are well-known [10, 11]. They occur in solid solutions of alkaline-earth-doped  $M_xC_{60}$  materials with sufficiently large  $x$ . Concerning highly charged cations, there is some vague evidence of metastable  $C_{60}^{8+}$  and  $C_{60}^{9+}$  [12].

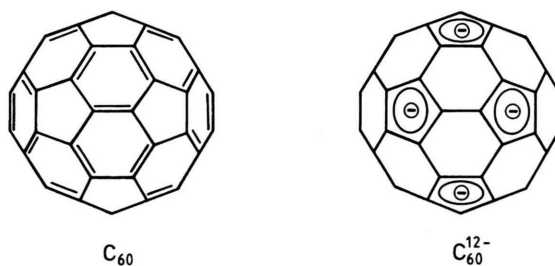


Fig. 1.  $C_{60}$   $\pi$  electron configuration formed by 30 6-6 “double” bonds and 60 6-5 “single” bonds (lhs.), as well as  $C_{60}^{12-}$   $\pi$  electron configuration with isolated  $\pi$  electron sextets per pentagon (rhs.). This distribution of the  $\pi$  electrons implies the formation of 30 6-6 “single” bonds and 60 6-5 bonds with partial “double” bond character.

In recent investigations of the electronic properties of  $M_xC_{60}$ -solids and molecular  $C_{60}$  we have analyzed the modifications in the  $\pi$  electronic structure of the soccerball as a function of the electron count [10, 11]. Our combined solid state and molecular studies have shown that the  $\pi$  electronic structure of  $C_{60}$  is changed dramatically when going from the neutral system to

Reprint requests to Prof. Dr. M. C. Böhm,  
Fax: 06151 164298.

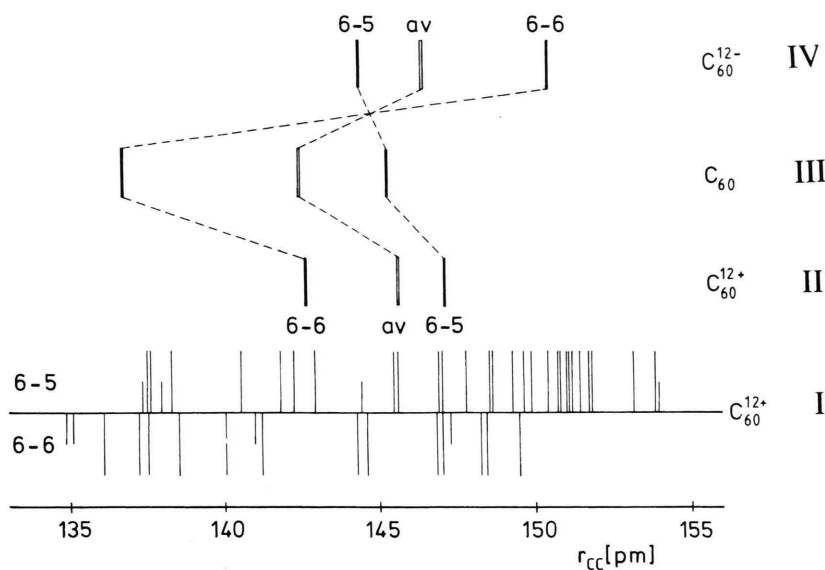


Fig. 2. Optimized bond lengths of  $C_{60}^{12+}$  (row I and II),  $C_{60}$  (row III) and  $C_{60}^{12-}$  (row IV) according to ab initio calculations in a 3-21 G\* basis set. The molecular point symmetry of  $C_{60}$  and  $C_{60}^{12-}$  is  $I_h$ , while it is reduced to  $C_s$  for  $C_{60}^{12+}$ . The height of the peaks in the  $C_{60}^{12+}$  system represents the multiplicity of the corresponding CC bonds (= 1 or 2). In row II we have displayed the mean value of the 6-6 and 6-5 bond lengths of  $C_{60}^{12+}$ . av symbolizes the mean value of the CC bond length when averaged over the 90 CC bonds of the  $C_{60}$  soccerball. All values are given in pm.

highly charged anionic states. The  $\pi$  electronic wave function of neutral  $C_{60}$  can be approximated with sufficient accuracy by a “resonance” structure formed by 30 hexagon-hexagon (= 6-6) “double” bonds and 60 hexagon-pentagon (= 6-5) “single” bonds. In the vicinity of  $C_{60}^{12-}$  this graduation is inverted. Here the 6-6 bonds have single bond character and the 6-5 bonds exhibit double bond character; see Fig. 1 for a schematical representation of these two “resonance” structures of  $C_{60}$  and  $C_{60}^{12-}$ .

This strong modification in the  $C_{60}$  electronic structure as a function of the electron count, on the one hand, and the missing particle-hole symmetry in the distribution of the CMOs, on the other, has been a strong motivation for us to discuss comparatively three  $C_{60}$  systems,  $C_{60}^{12-}$ , the neutral molecule and  $C_{60}^{12+}$ . By analogy with our previous ab initio studies of  $C_{60}$  species we have adopted the GAMESS program to optimize the geometries of the above systems and to analyze their electronic properties [13]. The basis set we have used is of 3-21 G\* quality. In the literature, several investigations of anionic  $C_{60}$  configurations can be found [14, 15]. Electronic structure calculations of cations are quite rare [12]. In the icosahedral point group of  $C_{60}$  the LUMO (= lowest unoccupied molecular orbital) and (LUMO+1) orbitals of the neutral system transform according to the irreducible representations  $t_{1u}$  and  $t_{1g}$ . In our recent contribution we have shown that the occupation of these two MOs in  $C_{60}^{12-}$  conserves the icosahedral point symmetry [10]. For  $C_{60}^{12+}$  a Jahn-Teller distortion

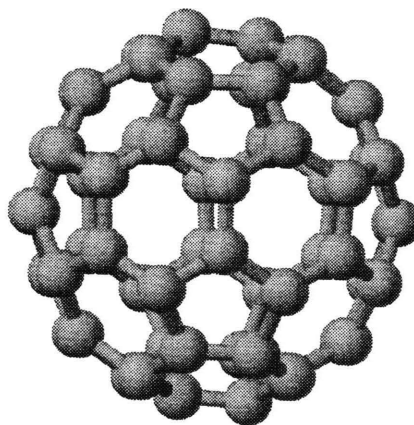


Fig. 3. Schematical representation of the optimized  $C_{60}^{12+}$  geometry. The molecular frame is symbolized by the CC bonds.

is expected. In the point group  $I_h$  the three highest occupied MOs (HOMOs) are of  $g_g$ ,  $h_g$  and  $h_u$  symmetry. Partial depopulation of the  $g_g$  (HOMO-2) orbital in  $C_{60}^{12+}$  is responsible for the Jahn-Teller distortion. Note that the  $C_{60}$  HOMO and (HOMO-1) functions are unoccupied in  $C_{60}^{12+}$ .

In Fig. 2 we have portrayed the optimized bond lengths of the three  $C_{60}$  species considered in the present report. The structural information of this diagram is supplemented in Fig. 3, which provides a schematical representation of the  $C_{60}^{12+}$  geometry. For a detailed discussion of the  $C_{60}^{12-}$  and  $C_{60}$  results we refer to [10, 11]. The conservation of the  $I_h$  symmetry of the neutral soccerball in the anion is

clearly seen in Figure 2. We wish to point out that the bondlength alternation of C<sub>60</sub> is perhaps somewhat overestimated in comparison to experiment. The calculated 6-6 and 6-5 bondlengths amount to 136.70 and 145.32 pm. Experimental bondlengths cited in the literature show a rather large splitting, an observation which indicates the difficulties to derive trustworthy structural parameters of fullerides. In the gas phase, 6-6 and 6-5 distances of 140.1 and 145.9 pm have been derived by electron diffraction measurements. The largest bondlength alternation reported for crystalline C<sub>60</sub> amounts to 11.2 pm [16]. The 6-6 and 6-5 bondlengths reported in [16] are based on an X-ray investigation; they amount to 135.5 and 146.7 pm. We are left with experimental bondlength alternations in C<sub>60</sub> within an interval between 5.7 and 11.6 pm. In consideration of this uncertainty we cannot estimate the error bars of the calculated alternation parameter of 8.6 pm. But it is well-known that bondlength alternations in  $\pi$  systems are somewhat overestimated by Hartree-Fock methods. Its correction requires calculations beyond the single-determinantal approximation [16]. In the C<sub>60</sub><sup>12-</sup> anion the bondlength alternation is inverted. Here the length of the 6-6 bonds exceeds the 6-5 values. Figure 2 indicates that the 6-5 length is slightly reduced in the transition from C<sub>60</sub> to C<sub>60</sub><sup>12-</sup>, while the 6-6 bondlength is strongly enhanced. In [10] we have demonstrated that the  $\pi$  electronic properties of C<sub>60</sub><sup>12-</sup> can be explained by the popular Hückel counting rule for annulenes [17], i.e. the discrimination between stabilized “aromatic” (4n+2)  $\pi$  electron systems (n = 0, 1, 2, ...) and destabilized “antiaromatic” 4n rings (n = 1, 2, 3, ...). In the C<sub>60</sub><sup>12-</sup>  $\pi$  electron configuration shown schematically in Fig. 1 an electronically isolated  $\pi$  electron sextet per pentagon occurs. The neutral pendant of this C<sub>60</sub><sup>12-</sup> “isolated pentagon” configuration would lead to a  $\pi$  electron quintet per pentagon, a rather unstable annulene configuration. In annulenes with a  $\pi$  electron count of 4n and (2n+1) (n = 1, 2, 3, ...) the spatial degrees of freedom of the electrons are strongly attenuated by the Pauli antisymmetry principle [18]. In neutral C<sub>60</sub> this constraint can be suppressed by the bondorder alternation symbolized in Fig. 1 (= bondlength alternation portrayed in Figure 2). The C<sub>60</sub><sup>12+</sup> counterpart of the “isolated pentagon”  $\pi$  configuration of C<sub>60</sub><sup>12-</sup> would yield an “antiaromatic” 4 $\pi$  electron system per pentagon. It is self-explanatory that such a configuration of the corresponding cation is avoided via

changes in the bondlengths. The ab initio geometry optimizations of C<sub>60</sub><sup>12+</sup> converged to the point group C<sub>s</sub>. In this low symmetry, a clear discrimination between the two types of CC bonds of the C<sub>60</sub> unit is no longer established. Short CC bonds occur both in the 6-6 and 6-5 manifold. Below 140 pm ten 6-6 and eight 6-5 bonds are predicted. Figure 3, however, indicates that the intermixing in the lengths of the 6-6 and 6-5 bonds does not lead to a strong deviation from an overall spherical symmetry. Deviations towards “prolate” or “oblate” arrangements occur in C<sub>60</sub> anions with excess charges exceeding 12 [11]. The total number of short CC “double” bonds in C<sub>60</sub><sup>12+</sup> is 18, a value that is expected on the basis of simple electron counting arguments. Remember that the  $\pi$  configuration of the neutral network is defined by 30 6-6 “double” bonds. 12 excess holes will reduce the number of “localized”  $\pi$  double bonds to 18. The label “localized” has been employed to describe the two-center character of the corresponding bonds. In contrast to this localized “two-center” picture of the  $\pi$  bonds in C<sub>60</sub> and C<sub>60</sub><sup>12+</sup> “double bond localization” is not possible in C<sub>60</sub><sup>12-</sup>. The electron count in icosahedral C<sub>60</sub><sup>12-</sup> is incompatible with the well-known Hund localization criterion which defines the possibility to represent molecular orbitals in a localized two-center picture [19]. The bondlength distribution displayed in Fig. 2 is a clear evidence of the missing particle-hole symmetry in the ion pair C<sub>60</sub><sup>12-</sup> and C<sub>60</sub><sup>12+</sup>. The mean values of the 6-6 and 6-5 bondlengths in the cation reproduce the graduation of the two bondlengths of the neutral system. The length of the 6-5 bonds exceeds the 6-6 values. C<sub>60</sub><sup>12-</sup> has an exceptional position in the series of C<sub>60</sub> ions which is not shared by the corresponding hole pendant C<sub>60</sub><sup>12+</sup>. The symmetry reduction from I<sub>h</sub> to C<sub>s</sub> in C<sub>60</sub><sup>12+</sup> is accompanied by a sizeable charge polarization. In the framework of a Mulliken population analysis [20] net charges q<sub>c</sub> between roughly 0.40 and -0.02 are predicted for the Jahn-Teller distorted C<sub>60</sub><sup>12+</sup> ion. In icosahedral C<sub>60</sub><sup>12-</sup> the point symmetry forces a q<sub>c</sub> value of -0.20 at any atom.

Finally let us consider the total energies of C<sub>60</sub><sup>12-</sup> and C<sub>60</sub><sup>12+</sup> to reemphasize the violation of the particle-hole symmetry of this ion pair. C<sub>60</sub><sup>12+</sup> is by 308.31 eV above the energy of the neutral molecule. The population of “antibonding” states in C<sub>60</sub><sup>12-</sup> does not lead to such a strong destabilization as encountered for the depopulation of bonding states in C<sub>60</sub><sup>12+</sup>. With the

3-21 G\* basis set employed in the present study we predict C<sub>60</sub><sup>12-</sup> to be only by 195.52 eV above the neutral C<sub>60</sub> molecule. The energy difference between the C<sub>60</sub> particle-hole pair C<sub>60</sub><sup>12-</sup> and C<sub>60</sub><sup>12+</sup> amounts to 112.79 eV. This result indicates that the “antibonding” character of the C<sub>60</sub> LUMO and (LUMO+1) states is less pronounced than the bonding character of the highest filled CMOs. In [10, 11] we have demonstrated that the LUMO and (LUMO+1) functions of C<sub>60</sub> are by no means antibonding. Population of the corresponding MOs leads to the aforementioned change in the character of the 6-6 and 6-5 bonds under conservation of the net bondstrength. The destabilization of C<sub>60</sub><sup>12-</sup> relative to the neutral molecule is more or less a bare electrostatic effect (= classical Coulomb repulsion as a result of the non-zero atomic net charges) which is attenuated in doped solids (= Madelung stabilization). The bonding character of all occupied MOs in C<sub>60</sub><sup>12-</sup> explains the higher stability of C<sub>60</sub><sup>12-</sup> relative to C<sub>60</sub><sup>12+</sup>.

In the present report we have extended our previous ab initio studies of the C<sub>60</sub> system to a highly charged particle-hole pair. We have demonstrated a sizeable violation in the particle-hole symmetry between C<sub>60</sub><sup>12-</sup>, which is exceptional in the C<sub>60</sub> series, and C<sub>60</sub><sup>12+</sup>. The simple  $\pi$  electron counting rule of Hückel, which we have introduced in the case of C<sub>60</sub><sup>12-</sup>, can be transferred to the C<sub>60</sub><sup>12+</sup> system. The Hückel rule is helpful to understand the electronic building principles of this cation. The stabilization of C<sub>60</sub><sup>12-</sup> relative to C<sub>60</sub><sup>12+</sup> can be traced back to the formation of “aromatic” sextets in the pentagon units of the anion. “Antiaromatic” 4 $\pi$  pentagon configurations in C<sub>60</sub><sup>12+</sup> are avoided by strong modifications in the lengths of the 6-6 and 6-5 bonds relative to their values in the icosahedral neutral C<sub>60</sub> molecule.

This work has been supported by the Fonds der Chemischen Industrie and the Bundesministerium für Bildung und Forschung. We are grateful to Mrs. S. Breide for the preparation of the figures.

- [1] M. Okada and O. Goscinski, in International Winterschool on Electronic Properties of Novel Materials, Progress in Fullerene Research, Kirchberg, Tyrol 1994.
- [2] C. A. Coulson and C. S. Rushbrooke, Proc. Cambridge Phil. Soc. **36**, 193 (1940).
- [3] Q. Xie, E. Pérez-Cordero, and L. Echegoyen, J. Amer. Chem. Soc. **114**, 3978 (1992).
- [4] R. C. Haddon, Acc. Chem. Res. **25**, 127 (1992).
- [5] P. W. Fowler and A. Ceulemans, J. Phys. Chem. **99**, 508 (1995).
- [6] M. C. Böhm and J. Schulte, Mol. Phys. **87**, 735 (1996).
- [7] J. Fagan, J. C. Calabrese, and B. Malone, Acc. Chem. Res. **25**, 134 (1992).
- [8] R. J. Doyle and M. M. Ross, J. Phys. Chem. **95**, 4954 (1991).
- [9] Y. Chabre, D. Djurado, M. Armand, W. R. Romanov, N. Coustel, J. P. McCauley, Jr., J. E. Fischer, and A. B. Smith III, J. Amer. Chem. Soc. **114**, 764 (1992).
- [10] M. C. Böhm, T. Schedel-Niedrig, H. Werner, R. Schlägl, J. Schulte, and J. Schütt, Z. Naturforsch. **51a**, 283 (1996); erratum **51a**, 884 (1996).
- [11] M. C. Böhm, J. Schulte, J. Schütt, T. Schedel-Niedrig, H. Werner, and R. Schlägl, submitted for publication.
- [12] J. Cioslowski, S. Patchkovskii, and W. Thiel, Chem. Phys. Lett. **248**, 116 (1996).
- [13] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Hensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).
- [14] J. Hutter and H. P. Lüthi, Int. J. Quantum Chem. **46**, 81 (1993).
- [15] J. Kohanoff, W. Andreoni, and M. Parrinello, Chem. Phys. Lett. **198**, 472 (1992).
- [16] G. E. Scuseria, in W. Billups and A. Ciutolini (ed.), Buckminsterfullerenes, VCH, Weinheim 1993.
- [17] E. Hückel, Z. Physik **76**, 628 (1932).
- [18] J. Schütt and M. C. Böhm, Phys. Lett. A **219**, 79 (1996).
- [19] F. Hund, Z. Physik **73**, 1, 565 (1931).
- [20] R. S. Mulliken, J. Chem. Phys. **23**, 1833, 1841 (1955).