

## Bonding and Delocalization in C<sub>60</sub> via Topographical Analysis of the Electrostatic Potential and Electron Density

Tom A. Claxton,<sup>a</sup> Rajendra N. Shirsat<sup>b</sup> and Shridhar R. Gadre\*<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Leicester, Leicester, UK LE1 7RH

<sup>b</sup> Department of Chemistry, University of Poona, Pune 411007, India

Analysis of the *ab initio* electron density distribution of C<sub>60</sub> show that all *exo* bonds to the five-membered rings have partial double-bond character with all molecular electrostatic potential minima located outside the molecular cage.

Ever since the discovery of fullerene allotropes of carbon, there has been much debate over the structure, interpretation of the bonding and applications as gauged from the 1300 or more papers published so far on the subject.<sup>1</sup> The description of bonding in such large molecules, particularly those which can potentially show extensive conjugation, has traditionally been controversial. The most studied fullerene, C<sub>60</sub>, distinguished in that all carbon atoms are equivalent, shows just two types of bond. Resonance theory in the simplest form<sup>2</sup> engenders 12 500 structures of which the C–C bonds in the five-membered rings are predicted to have less double bond character,<sup>3</sup> by a factor of 7/11, to those of the six-membered rings. This distinction correlates with<sup>1</sup> the so-called Mills–Nixon effect<sup>4</sup> *viz.* presence of double bonds further shortens the already strained C–C bonds in five-membered rings. It is well known that the number of resonance structures alone does not indicate aromaticity<sup>5</sup> so it is important to present results in as many different ways as possible to contribute to and widen the debate. Here we present molecular electrostatic potential (MESP) results derived from both STO-3G and 6-31G basis sets using the optimized geometries corresponding to STO-3G and 3-21G basis sets respectively.

The MESP,  $V(r)$ , at a reference point  $r$ , due to a molecular electronic charge distribution  $\rho(r')$ , is given by eqn. (1), where

$$V(r) = \sum_{A=1}^N \frac{Z_A}{|r - R_A|} - \int \frac{\rho(r')}{|r' - r|} d^3r' \quad (1)$$

$N$  is the total number of nuclei and  $Z$  the charge of the nucleus at  $R$ . MESP has not only been used as a tool to investigate molecular electronic structure but also chemical reactivity,<sup>6</sup> for example, sites of electrophilic<sup>7,8</sup> and nucleophilic<sup>9</sup> attack. This may be attributed to rich topographical features exhibited by the MESP due to the delicate balance between the nuclear and electronic terms in eqn. (1). The study of maximal and minimal characteristics of the MESP topography<sup>10,11</sup> has

led to definition of sizes and shapes of anions, molecular structural parameters such as lone pairs, C–C double bonds *etc.* These investigations<sup>10,11</sup> also shows that, for the molecules so far studied, only carbon–carbon double bonds are characterized by two minima one each on the opposite sides with respect to the C–C double bond. Correspondingly, there has been great interest in locating such minima for the study of conjugation. Recently, an efficient parallel program<sup>12</sup> has been developed for locating not only minima but all the other types of critical points as well in the scalar field of MESP.

The supposition that C<sub>60</sub> can be construed as a collection of poorly conjugated ethenic type bonds is not supported. For the ethene molecule, the STO-3G MESP minima (–53.50 kJ mol<sup>–1</sup>) appear on both sides of the C–C bond, whereas in C<sub>60</sub> the minima are much less pronounced (–4.59 kJ mol<sup>–1</sup>) and occur only above (*i.e.* 'outside' the molecular surface) the *exo* bond of the five-membered rings. These minima are shown in Fig. 1 along with the MESP contours for five of them. The MESP textured on the van der Waals surface is shown in Fig. 2. This figure clearly shows that *exo* bonds to five-membered rings possess more negative potential than the corresponding five-membered ring bonds. The 6-31G results are similar although the MESP minima are consistently deeper (–10.86 kJ mol<sup>–1</sup> for C<sub>60</sub> as against –85.69 kJ mol<sup>–1</sup> for ethene). For C<sub>60</sub>, all MESP minima occur outside the cage for all basis sets used. Inside the cage the MESP is always positive indicating that some part of the electron density resides outside the cage. However, the MESP minima values are typically 12% of the ethene counterpart suggesting that C<sub>60</sub> will be rather unreactive towards electrophiles in agreement with Taylor and Walton.<sup>1</sup>

Similarly, by subjecting the molecular electron density (MED) to topographical analysis, similar trends are evident. The 6-31G MED at the bond critical point (BCP) corresponding to the *exo* bonds is 0.31 au whereas in the five-membered rings it is only 0.26 au. The corresponding bond orders calculated from these densities using Bader's<sup>13</sup> formula are

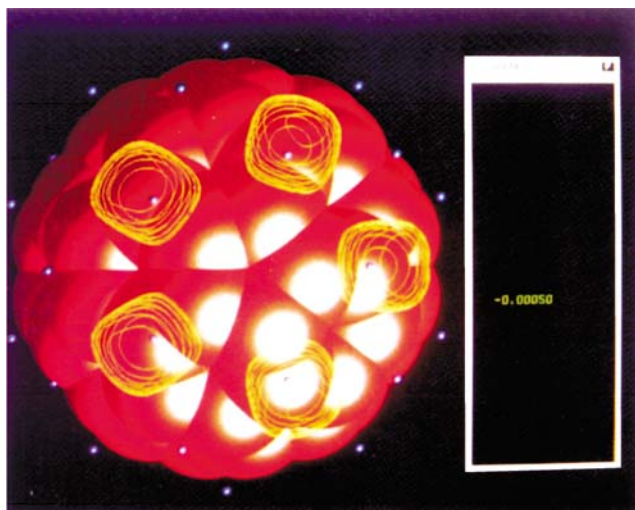


Fig. 1 The relative positions of MESP minima (using 6-31G basis) for C<sub>60</sub> superposed on van der Waals surface. Blue dots indicate the position of MESP minima. The contours correspond to MESP value of –1.31 kJ mol<sup>–1</sup>.

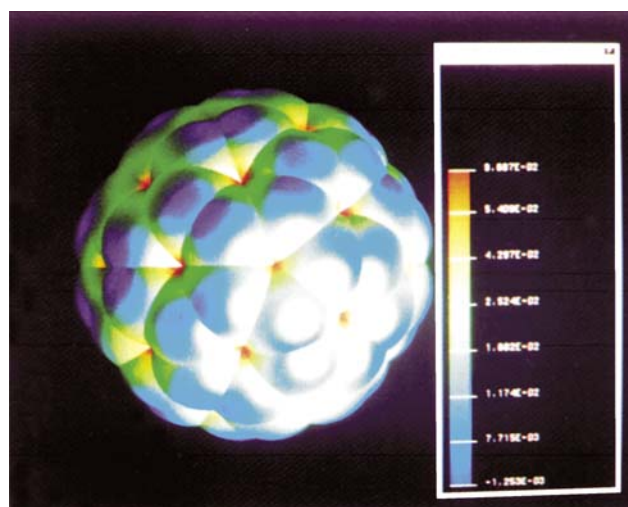


Fig. 2 The MESP (using 6-31G basis) textured on the van der Waals surface of C<sub>60</sub>

1.84 and 1.42 respectively. C<sub>60</sub> itself is electronically hollow, no doubt enabling muonium to be accommodated without significant disruption.<sup>14</sup> Bond ellipticities of the *exo* bonds are 0.179 compared to 0.101 in the five-membered ring reinforcing the view that the former bear a higher  $\pi$ -character.

A topographical study of MESP and MED is thus seen to be useful in obtaining a unified picture of bonding and electron delocalization in the C<sub>60</sub> molecule. Further studies on higher fullerenes are in progress.

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