Octahedral C48 and Uniform Strain

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Octahedral C_{48} and Uniform Strain

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The geometry of octahedrally symmetric C_{48} has been optimized using a local density functional. All the atoms are equivalent by symmetry, so the molecule has a unique radius. This radius, the vertical ionization potentials, and electron affinity of C_{48} are compared to the corresponding values for C_{60}.

An octahedral isomer of C_{48} can be constructed entirely of 3-fold-coordinated carbon atoms, and its surface is composed of four-membered, six-membered, and eight-membered carbon rings.[1] It may be constructed from C_{60} by removing six pairs of carbon atoms, which fuse two six-membered rings at the ends of three mutually perpendicular axes, and connecting the ensuing dangling bonds (*cf.* the formation of a C_{58} isomer.[2] As in the case of C_{60},[3] all of its atoms are equivalent by symmetry. The molecule should therefore give a single-line ^{13}C NMR spectrum, but the resonance should appear more downfield than that for C_{60}[4] due to the increased strain.[1] The high symmetry of the structure should give rise to a very simple IR spectrum and, due to the high strain of the molecule (which is predicted by Hückel MO calculations to have greater bond fixation than C_{60}[4], should be more reactive than C_{60}, undergo electron addition more readily, and give rise to both more stable cycloadducts and charge-transfer complexes; addition of a symmetrical reagent can in principle give rise to 12 diadducts.[1] We now present the results of local density functional (LDF) calculations.

The molecule is drawn in Figure 1, and the corresponding Schlegel diagram (with numbering) is shown in Figure 2. (It is not possible to number in a contiguous spiral from one pole of the molecule through to the other; *cf.* ref 5.) The geometry of the molecule has been optimized using an all-electron, self-consistent, LDF method.[6] The LDF used is the Perdew–Zunger[7] (PZ) fit that interpolates between the essentially exact Monte Carlo Calculations.[8] The Gaussian basis set used is the same triple-zeta with polarization basis that was used to optimize C_{60} (and both $C_{60}H_{60}$ and $C_{60}F_{60}$).[9] The optimized C_{48} geometry is given in Table 1. The coordinates of a given atom can be used to generate those of the other 47, by permuting any pair of coordinates and changing the sign of any coordinate.

Whereas C_{60} has two distinct bonds, namely, 6–6 bonds which connect hexagons and 6–5 bonds which connect hexagons to pentagons, C_{48} has three distinct bonds. From shortest to longest, the 6–8 bonds connect hexagons to octagons, the 4–8 bonds connect squares to octagons, and the 4–6 bonds connect squares to hexagons. Table 2 compares the LDF bond distances to those recently computed using several semiempirical programs and three different parametrizations.[10] The semiempirical results are all quite similar independent of parametrization, so only the MNDO results are listed in the table. Table 3 compares experimental,[11] LDF,[12] and MNDO[13] bond distances for C_{60}. The LDF 6–8 bond is 0.003 Å shorter than the LDF 6–6 "double" bond of C_{60}. The 4–8 bond is 0.002 Å longer
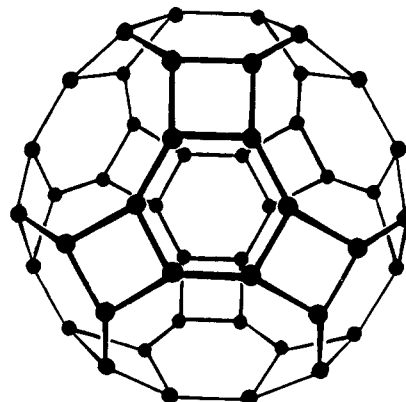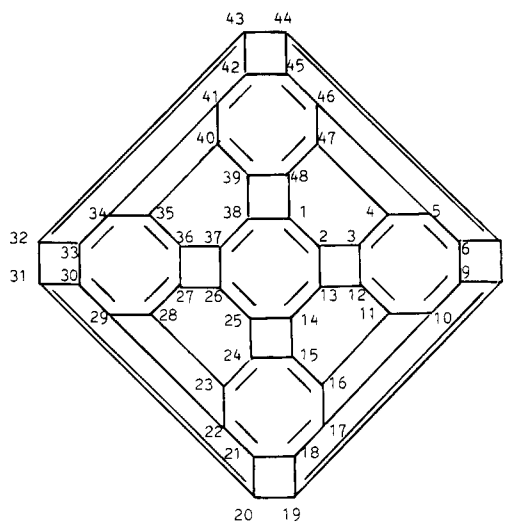
Figure 1. Structure of O_h-C_{48}.

Figure 2. Schlegel diagram with numbering for O_h-C_{48}.

TABLE 1: Coordinates of One Atom in the O_h Symmetric C_{48} Fullerene, Which Is Oriented So That the 4-fold Axes Coincide with the Coordinate Axes

X, Å	Y, Å	Z, Å
0.723	1.702	2.737

than the 5–6 "single" bond of C_{60}, whereas the 4–6 bond is almost 0.02 Å longer still and is clearly a single bond. The MNDO 6–8 bond is almost 0.04 Å shorter than the MNDO 6–6 bond of C_{60}.[12] The 4–8 bond is 0.02 Å longer than the 6–5 bond of C_{60}. The 4–6 bond is even longer. In C_{48} the "single" and "double" bonds alternate around both the hexagons

Letters

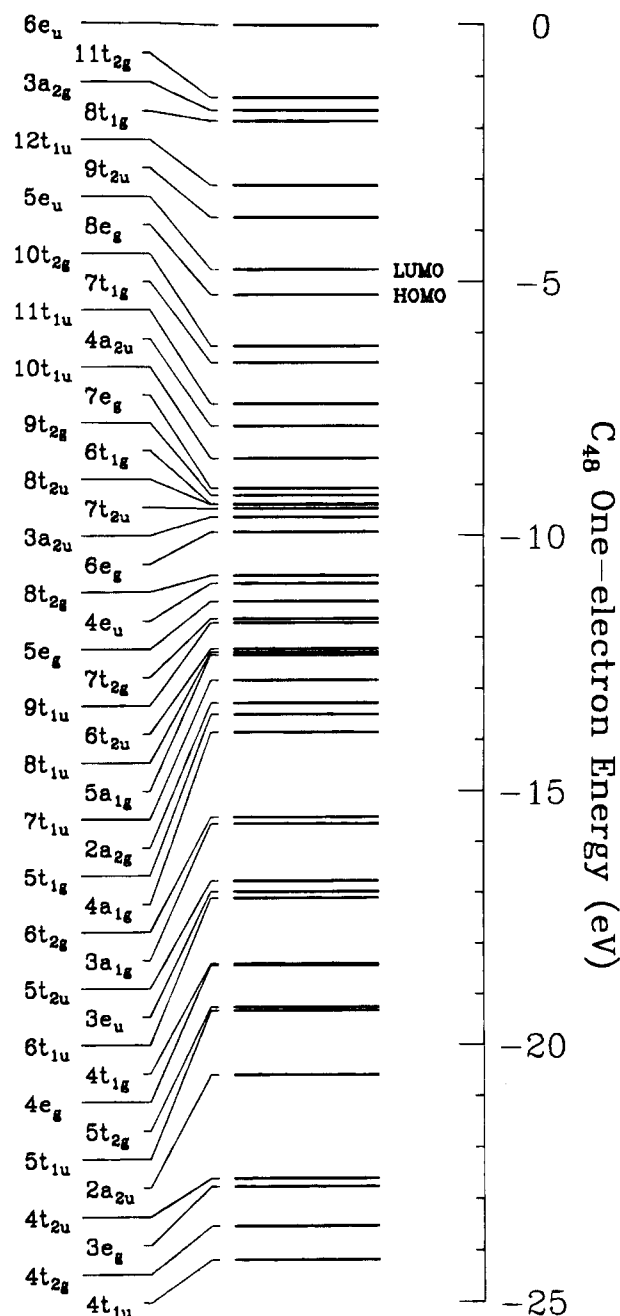*J. Phys. Chem.*, Vol. 98, No. 43, 1994 **11019**

Figure 3. LDF one-electron energy eigenvalues of C_{48}.

TABLE 2: Optimized Bond Distances (Å) in C_{48}

method	6–8 bond	4–8 bond	4–6 bond
LDF	1.384	1.447	1.466
MNDO[10]	1.346	1.485	1.501

and octagons; the squares contain "single" bonds of different length. The MNDO bond alternation is bigger than the LDF bond alternation for both C_{48} and C_{60}. For C_{60} the LDF distances are in excellent agreement with experiment.

Table 4 gives the full electronic structure of C_{48}, *i.e.*, the total number of electrons of each orbital symmetry. Each one-electron symmetry is ordered by the relative energy of its HOMO. The first HOMO is the $8e_g$ orbital. The second

TABLE 3: Comparison of Experimental and Theoretical Bond Distances (Å) in C_{60}

method	6–6 bond	6–5 bond
expt[11]	1.391	1.455
LDF[12]	1.387	1.445
MNDO[13]	1.400	1.474

TABLE 4: Electronic Structure of C_{48}

$32e_g, 60t_{2g}, 42t_{1g}, 66t_{1u}, 8a_{2u}, 48t_{2u}, 16e_u, 10a_{1g}, 4a_{2g}, 2a_{1u}$

TABLE 5: Comparison of the LDF Radii, Vertical Ionization Potentials, and Electron Affinities of C_{48} and C_{60}

molecule	radius, Å	scaled radius, Å	IP, eV	EA, eV	HOMO–LUMO gap, eV
C_{48}	3.303	3.158	6.93	3.18	0.49
C_{60}	3.531		7.60	2.82	1.68

through fifth HOMOs are $10t_{2g}$, $7t_{1g}$, $11t_{1u}$, and $4a_{2u}$, respectively. The valence one-electron levels are drawn in Figure 3. The LUMO is the $5e_u$ orbital. Thus, the HOMO–LUMO excitation is dipole-forbidden, just as it is in C_{60}.

Table 5 compares HOMO–LUMO gap of C_{48} to the gap C_{60}. The HOMO–LUMO gap of C_{48} is less then one-third that of C_{60}. Other physical properties also suggest that C_{48} is considerably less stable. If each atom on the surface of the two spheres occupied the same area, then the radii of the two molecules would scale as the square root of the number of atoms. The radius of C_{60} is scaled by $\sqrt{48/60}$ and compared to the actual radius of C_{48} in Table 5. The scaled radius is 5% smaller. The binding energy per atom is 6% smaller. The ionization potential (IP) and electron affinity (EA) differences between the two molecules also indicate the relative stability of C_{60}.

The ability to share the strain of curvature equally among all of its atoms is not the entire explanation for the fact that C_{60} is special among hollow 3-fold-coordinated carbon molecules.

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