

**THE VIBRATIONAL SPECTROSCOPIC STUDY
AND *AB INITIO* CALCULATIONS OF A
BROMOFULLERENE $C_{60}Br_{24}$.**

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The molecule of $C_{60}Br_{24}$ (Fig.1), firstly synthesized by the direct bromination of C_{60} (1), is one of the highest-symmetry fullerene derivative obtained up to date. Belonging to the T_h point symmetry group it possess rather simple and tractable IR and Raman spectra, providing thus a convenient base for the model calculations of the bromofullerenes series.

We have performed the quantum-chemical calculations of the geometry parameters and vibrational spectra of $C_{60}Br_{24}$ molecule at the Hartree-Fock level of theory using a PC GAMESS package (2, 3). Conventional full-electron as well as valence only double-zeta quality basis sets accompanied by effective core potentials (HW (4), SBKJC (5, 6)) were employed.

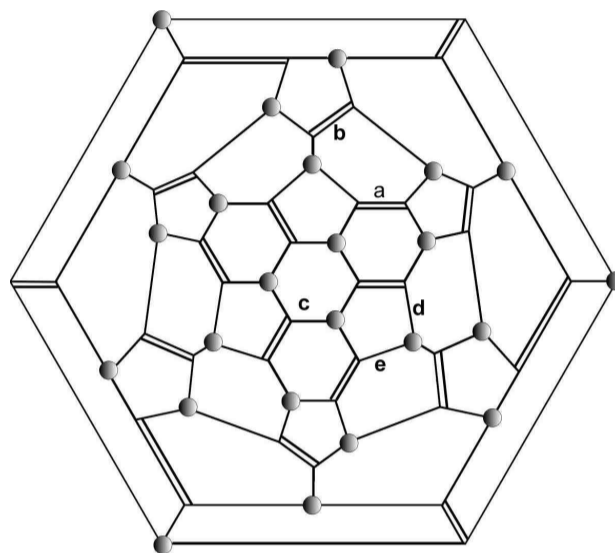
The values of calculated bond lengths are given in table 1 (in the case when two basis sets are spaced by the slash, the first was applied for the carbon atoms and the second one – for the bromine atoms). The comparison with the averaged experimental X-ray values (1) reveals the importance of the polarization functions inclusion for an adequate estimation of the C-Br bond length. In contrast, the geometry of the fullerene carcass does not depend significantly upon the basis set quality and demonstrates the systematic underestimation of double bonds lengths, the only exception being the use of SBKJC basis for the both sets of the atoms. For though the parameters obtained in the latter case are close to experimental ones, this is, probably, a fortuitous cancellation of the errors, since the shortening of C=C bonds is characteristic to the Hartree-Fock approach.

Vibrational spectra were calculated employing 6-31G/SBKJC, 6-31G*/SBKJC* and 6-31G* basis sets, with the subsequent Pulay's scaling procedure. The results obtained, both within full-electron and time-consuming ECP techniques, demonstrated an excellent correspondence to the experimental data. Complete assignment of IR and Raman spectra was proposed. To follow the effect of symmetry reduction on the transformation of parent modes the displacements of the carbon skeleton in $C_{60}Br_{24}$ molecule were described in terms of C_{60} vibrational eigenvectors.

Table 1. Calculated at different levels of theory and averaged experimental bond lengths in $C_{60}Br_{24}$, Å.

	C=C a	C=C b	C-C c	C-C d	C-C e	C-Br
PM3	1.342	1.357	1.475	1.501	1.505	1.918
3-21G	1.309	1.316	1.492	1.516	1.518	1.956
3-21G/ HW	1.309	1.321	1.490	1.515	1.514	2.036
SBKJC	1.338	1.348	1.509	1.526	1.526	2.027
6-31G/ SBKJC	1.318	1.329	1.492	1.512	1.511	2.032
6-31G*	1.314	1.320	1.497	1.511	1.511	1.961
6-31G*/ SBKJC*	1.314	1.323	1.500	1.514	1.512	1.979
exp. (1)	1.338	1.339	1.489	1.512	1.500	1.993

Figure 1. Schlegel diagram and bond labeling in $C_{60}Br_{24}$.



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