ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 9, pp. 1790–1791. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © V.V. Kuznetsov, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 9, pp. 1575–1576.

LETTERS
TO THE EDITOR

Conformational Preference of the Hexachloroethane Molecule in Fullerene C_{80}

V. V. Kuznetsov[a,b]

[a] *Ufa State Aviation Technical University, ul. K. Marksa 12, Ufa, 450000 Russia*
e-mail: kuzmaggy@mail.ru

[b] *Ufa State Petroleum Technological University, Ufa, Russia*

Received April 4, 2013

DOI: 10.1134/S1070363213090272

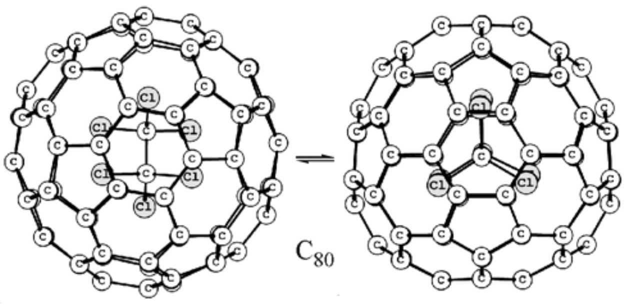
The experimental value of the hindered rotation barrier ($\Delta H^{\neq}$) in hexachloroethane is of 10.8 kcal mol^{-1} in favor of the staggered conformer [1, 2]. On the other hand, nanosized objects may affect physical and chemical characteristics of the encapsulated molecules, and can greatly change the properties of the latter [3–6].

In particular, it has been recently shown that for ethane encapsulated into a nanotube the potential energy minimum of the internal rotation corresponds the eclipsed conformation, but not the staggered form as in a free molecule [7]. In this work, the internal rotation barrier of hexachloroethane molecules encapsulated into fullerene C_{80} sphere was estimated for the first time, using the DFT-PBE/3z method (PRIRODA package [8]).

The results indicated that the applied computational method overestimated the relative stability of the staggered conformer of hexachloroethane by 2 kcal mol^{-1}. However, the calculated geometry parameters of the hexachloroethane molecule, such as C–C and C–Cl bonds lengths (1.590 and 1.792 Å, respectively) and CCCl bond angle (109.9°) were in satisfactory agreement with the experimental data (1.564 Å, 1.759 Å, 110°, respectively [9]).

The internal rotation parameters (kcal mol^{-1}, cal mol^{-1} K^{-1}) are given below.

0.0 $\Delta H^{\neq}_{0}$ 12.9, $\Delta H^{\neq}_{298}$ 12.3, $\Delta G^{\neq}_{298}$ 13.8, $\Delta S^{\neq}_{298}$ –3.8



0.0 $\Delta H^{\neq}_{0}$ 44.4, $\Delta H^{\neq}_{298}$ 44.6, $\Delta G^{\neq}_{298}$ 43.5, $\Delta S^{\neq}_{298}$ –3.8

At the same time, the energy parameters of the internal rotation of hexachloroethane encapsulated into fullerene are significantly changed. The relative stability of the staggered form was increased by 3.2–3.4 times as compared with that of the isolated C_2Cl_6 molecule. The C–C bonds in the staggered and eclipsed forms of the encapsulated hexachloroethane (1.431 and 1.444 Å, respectively) were significantly shorter as compared with the isolated molecule parameters (1.590 and 1.686 Å, respectively). However, the order of the C–C bond changed only slightly: 1.06 and 0.96 for the staggered and eclipsed conformers encapsulated in fullerene and 0.98 and 0.99 for the isolated molecule, respectively. In addition, both forms of the hexachloroethane molecule in the fullerene cavity acquired a small negative (staggered form, –0.2193) or positive (eclipsed conformation, 0.1750) charge, although the whole fullerene – hexachloroethane system was electrically neutral. Noteworthily, unlike the isolated C_2Cl_6 case, the Hessian matrix of the fullerene containing the staggered form of hexachloroethane contained one imaginary frequency corresponding to rotation of the encapsulated molecule as a whole. At the same time, the Hessian matrix of the C_{80} – eclipsed form of C_2Cl_6 system, as in the case of isolated molecule, led to the expected imaginary frequency corresponding to the rotation around the C–C bond of hexachloroethane.

Thus, unlike the ethane molecule in the nanotubes [7], the relative stability of the staggered form of hexachloroethane encapsulated into fullerene increased sufficiently. The results indicated that in the frame of the applied model, a kind of force field was generated inside the fullerene, that drastically changed the conformational properties even in the case of a relatively simple molecules.

REFERENCES

1. Dashevskii, V.G., *Konformatsii organicheskikh molekul* (Conformation of Organic Molecules), Moscow: Khimiya, 1974.
2. *Internal Rotation in Molecules*, Orville-Thomas, W.J., Ed., New York: Willey Interscience, 1974.
3. Tsirel'son, V.G., *Kvantovaya khimiya. Molekuly, molekulyarnye sistemy i tverdye tela* (Quantum Chemistry. Molecules, Molecular Systems and Solids), Moscow: Binom. Laboratoriya Znanii, 2010.
4. D'yachkov, P.N., *Uglerodnye nanotrubki: stroeniye, svoistva, primeneniye* (Carbon Nanotubes: Structure, Properties, and Use), Moscow: BINOM, Laboratoriya Znanii, 2006.
5. Kuznetsov, V.V., *Zh. Obshch. Khim.*, 2012, vol. 82, no. 11, p. 1931.
6. Kuznetsov, V.V., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 1, p. 140.
7. Kuznetsov, V.V., *Russ. J. Org. Chem.*, 2013, vol. 49, no. 2, p. 298.
8. Laikov, D.N. and Ustynyuk, Yu.A., *Russ. Chem. Bull.*, 2005, no. 3, p. 820.
9. Almenningen, A., Andersen, B., and Traetteberg, M., *Acta Chem. Scand.*, 1964, vol. 18, no. 5, p. 603.