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LETTERS TO THE EDITOR

Quantum Chemical Study of Polycyclic Derivatives of Cyclohexa-1,3,5-triene

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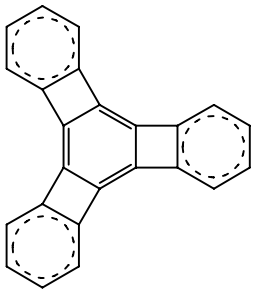
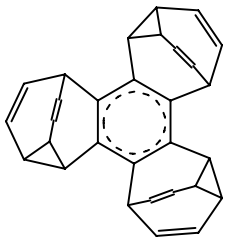
A possibility of the existence of cyclohexa-1,3,5-triene derivatives has been proved by the synthesis of compound **I** [1]. In this work, the quantum chemical calculations of the structural parameters, relative energies, and vibration spectra of similar compounds were performed by PBE0/cc-pVTZ and RHF/3-21G methods using a GAUSSIAN-03 software [2]. The following values were obtained by the PBE0 method.



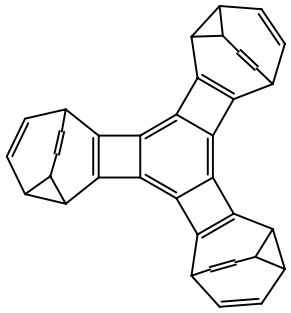
I



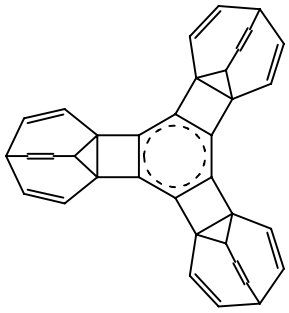
II

The calculated equilibrium bond length of C=C (1.34 Å) and C–C (1.48 Å) in the symmetric (D_{3h}) central ring of **I** are close to the XRD data obtained for the structure of hexakis(trimethylsilyl) derivative of this compound (1.34 and 1.49±0.01 Å, respectively [1]), while in an almost planar benzenoid cycle of tris (dedihydrobullvalene) **II** the calculated alternation of bond length is very little (1.410±0.001 and 1.405± 0.001 Å). The equilibrium lengths of the cyclohexa-1,3,5-triene bonds (C=C 1.33 Å and C–C 1.51 Å) are alternated in the hypothetical compound **IIIa** to a greater extent than in compound **I**.

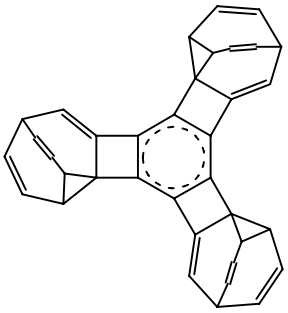
According to the NMR, the unsubstituted isotopically homogeneous bullvalene $C_{10}H_{10}$ undergoes degenerate Cope rearrangements [3,4]. The degenerate Cope rearrangements in the hypothetical isomers **III** of dedihydrobullvalene $C_{10}H_8$ fragments must be accompanied by oscillations of the bond lengths in the central rings. The relative energy (kcal mol^{-1}) of the isomers decreases as the alternation of these bond lengths reduces: 33.7 (**IIIa**) > 22.6 (**IIIb**) > 7.6 (**IIIc**) > 0.0 (**IIId**). Isomer **IIId** has the smallest bonds alternation in the central ring (1.38 and 1.41 Å). For isomer **IIIb** the obtained bonds lengths are 1.36 and 1.43 Å, and for **IIIc**, 1.37 and 1.42 Å.



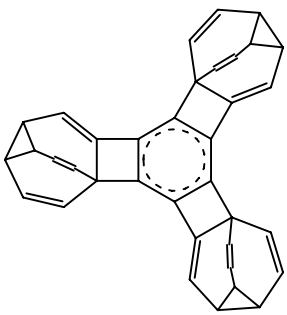
IIIa



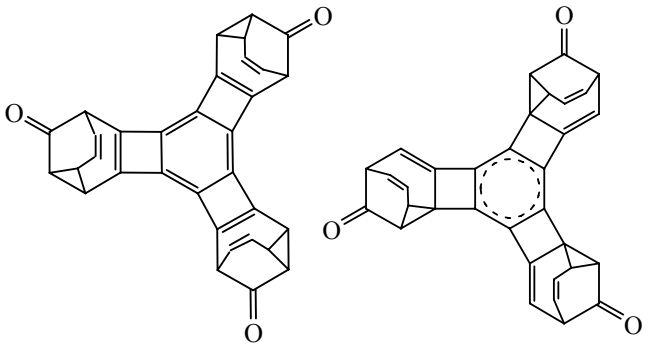
IIIb



IIIc



IIId



IVa **IVb**

Chiral triketones **IV** are of great interest since the replacement of one ethylene group with the keto group in each dedihydrobullvalene fragment of compound **IIIa** excludes the benzoid keto tautomers like isomer **IIId**.

The calculated energies of the hypothetical carbonyl stereoisomers **IVa** with the bond lengths of 1.33 and 1.51 Å are higher by 27.2 kcal mol^{-1} than that of the stereoisomers **IVb** with the bond lengths of 1.37 and 1.43 Å.

REFERENCES

1. Diercks, R. and Vollhardt, K.P.C., *J. Am. Chem. Soc*., 1986, vol. 108, no. 11, p. 3150.
2. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A., *GAUSSIAN-03*, Rev. B.05, Pittsburgh PA: Gaussian, 2003.
3. Doering W.v.E., *Zh. Vseross., Khim. Obshch.,* 1962, vol. 7, no. 3, p. 30; Doering, W.v.E. and Roth, W.R., *Tetrahedron*, 1963, vol. 19, no. 5, p. 715; *Angew. Chem*., 1963, vol. 75, no. 1, p. 27.
4. Schröder, G., *Chem. Ber*., 1964, vol. 97, no. 11, p. 3140; Merenyi, R., Oth, J.F.M., and Schröder, G., *Chem. Ber*., 1964, vol. 97, no. 11, p. 3150; Schröder, G., Merenyi, R., and Oth, J.F.M., *Tetrahedron Lett*., 1964, vol. 5, no. 14, p. 773; Schröder, G., Oth, J.F.M., and Merenyi, R., *Angew. Chem*., 1965, vol. 77, no. 17, p. 774; Schröder, G. and Oth, J.F.M., *Angew. Chem*., 1967, vol. 79, no. 10, p. 774.