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LETTERS TO THE EDITOR

The Estimation of the Optical Activity of Polyatomic Molecules by DFT Methods

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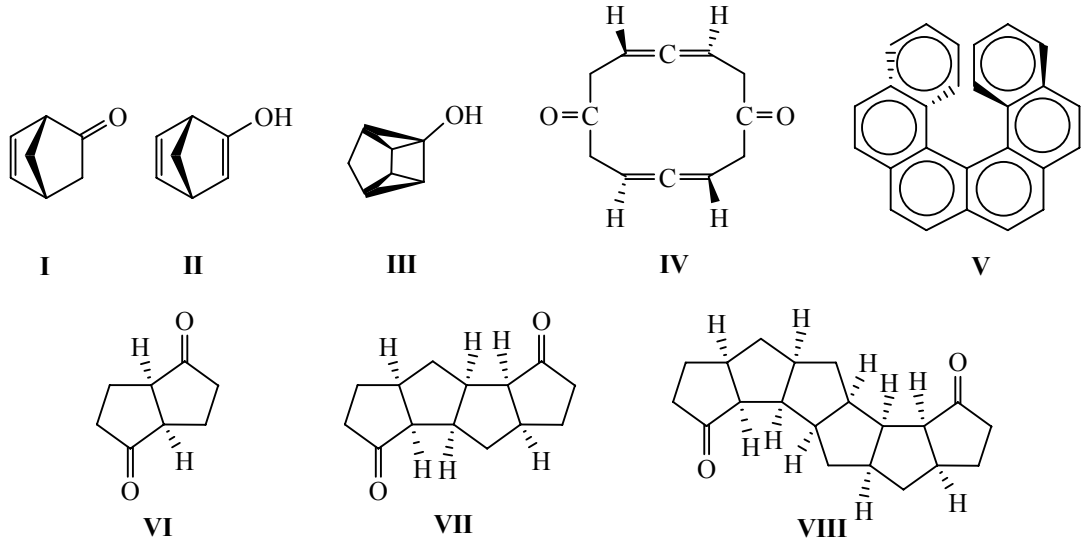
In papers [1, 2] for the differentiation of absolute configurations of enantiomers when discussing the degenerate tautomerism of chiral organic molecules we determined the sign of the specific rotation of the polarized light $[\alpha]_D$ by means of the quantum-chemical calculation. The present work is devoted to the estimation of the accuracy and reliability of the calculations of $[\alpha]_D$ by various DFT methods (B3LYP, PBE0, M06-2X, and ωB97X-D) using Gaussian basis cc-pVTZ and aug-cc-pVTZ sets selecting as examples bicyclo[2.2.1]hept-5-ene-2-one (**I**), the corresponding enol (**II**), hypothetical photoisomer (**III**), cyclododeca-3,4,9,10-tetraene-1,7-dione (**IV**), hexahelicene (**V**), and diketones **VI–VIII** (Scheme 1).

To account for the electrostatic interaction with the solvent the model of the polarizable continuum is applied (PCM [3, 4]). The accordance of the structural parameters to the energy minimum for all molecules is confirmed by the absence of imaginary wave numbers in the vibrational spectra. Values $[\alpha]_D$ are presented in deg $cm^3\ g^{-1}\ dm^{-1}$.

The specific rotation $[\alpha]_D$ of free molecules of optically pure bicyclo[2.2.1]hept-5-ene-2-one (**I**) calculated by B3LYP/cc-pVTZ, PBE0/cc-pVTZ, M06-2X/cc-pVTZ, and ωB97X-D/cc-pVTZ methods +1070, +1067, +891, +856 increases in chloroform to +1194, +1195, +1002, +965 respectively, becoming closer to

Scheme 1.



the experimental value of +1233, which is obtained as the ratio of the measured value $[\alpha]_D$ +592 [5] to the optical purity of the sample of 0.48 (48%). Supplementing the basis cc-pVTZ by diffuse orbitals aug increases the value of $[\alpha]_D$ calculated using the PBE0 for free molecules to +1148, i.e. by 8%. Calculations of solvated molecules by PCM DFT/aug-cc-pVTZ method are technically possible but the using of diffuse orbitals non-localized within the molecular cavity does not agree with the PCM model [3, 4].

Hydroxynorbornadiene **II,** an enol tautomer of bicyclo[2.2.1]hept-5-ene-2-one, is characterized by the value $[\alpha]_D$ +72 out of the polarizable environment and +75 in chloroform, according to the calculation PBE0/cc-pVTZ method. Hydroxyquadricyclane **III,** which is isomeric to compounds **I, II** and hypothetical product of the photoisomerization of enol **II,** is characterized by the calculated value $[\alpha]_D$ +37 out of the polarizable environment and +21 in chloroform. The energies of free molecules **II** and **III** exceed the energy of the free molecule **I** by 25 and 42 kcal/mol, respectively (PBE0/cc-pVTZ). Therefore, the content of high-energy isomers **II** and **III** under conditions of the thermodynamic equilibrium is negligible and cannot be detected by the optical activity of a ketone **I** solution.

In case of symmetric (D_2) cyclododeca-3,4,9,10-tetraene-1,7-dione (**IV**) chiral molecule B3LYP/cc-pVTZ, PBE0/cc-pVTZ, and M06-2X/cc-pVTZ methods give the gas phase values $[\alpha]_D$ +3295, +3121, +2697 that are many times greater than the experimental value ($[\alpha]_D$ +56) obtained in [6, 7] for a sample with an unknown enantiomer excess. Using PBE0/aug-cc-pVTZ//PBE0/cc-pVTZ method for **IV** we have obtained the value of $[\alpha]_D$ of +3278, greater by 1.8% than in the calculation without diffuse orbitals aug. From the ratio of the calculated and experimental values $[\alpha]_D$ one can conclude that the enantiomeric excess of the sample experimentally investigated is close to 2%.

In case of *P*-hexahelicene molecule **V** with the symmetry C_2, the PBE0/cc-pVTZ method gave $[\alpha]_D$ +4384 for the gas phase and +3924 for a solution in chloroform. The latter value is by 6% greater than the experimentally measured value of +3707 [8].

In a series of symmetric (C_2) chiral polycyclic diketones **VI–VIII** B3LYP/cc-pVTZ, PBE0/cc-pVTZ, and M06-2X/cc-pVTZ methods gave positive $[\alpha]_D$ +148, +146, +113 for **VI**, negative –229, –211, –185 for **VII**, as well as negative values –240, –216, –208 for **VIII**. In diketone **VI** the carbonyl groups are almost antiparallel, in diketone **VII** the dihedral angle O=C···C=O is 157.5°–155.3° while in the tris-(bicycloalkane) structure **VIII** it is considerably smaller: 81.8° (B3LYP), 81.2° (PBE0), and 76.5° (M06-2X). Supplementing the basis by diffuse functions aug decreases $[\alpha]_D$ of diketone **VI** to +139, +138, +92 without changing the sign of the optical activity.

The calculations were performed using the computer program GAUSSIAN-09 [9] in the resource center "Computing Center of St. Petersburg State University" (http://cc.spbu.ru).

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