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Structural stability and analysis of vibrational spectra of 1,2,4,5-tetroxane and 3,6-diphenyl-1,2,4,5-tetroxane

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ABSTRACT

The diperoxide 3,6-diphenyl-1,2,4,5-tetroxane was synthesized and its infrared and Raman spectra were measured. The structural stability and the vibrational spectra of 1,2,4,5-tetroxane and 3,6-diphenyl-1,2,4,5-tetroxane were investigated by the DFT-B3LYP and the ab initio MP2 calculations with the 6-311G** basis set. From the calculations, the *chair* form of 1,2,4,5-tetroxane was predicted to be about 9, 20, and 50 kcal/mol lower in energy than the *twist*, *boat*, and *planar* structures, respectively. The ring inversion in 1,2,4,5-tetroxane is concluded to take place most probably through the *twist* structure of the ring. In the case of 3,6-diphenyl-1,2,4,5-tetroxane, the *planar-equatorial* (P_{eq}) conformation was predicted by both levels of theory to be the lowest energy and predominant form of the molecule. The *planar* $\leftrightharpoons$ *perpendicular* and *axial* $\leftrightharpoons$ *equatorial* interconversion barriers were calculated to be about 2 and 12 kcal/mol, respectively. Reliable vibrational assignments were provided for the spectra of 1,2,4,5-tetroxane and 3,6-diphenyl-1,2,4,5-tetroxane by combining experimental and theoretical data of the two molecules.

1. Introduction

The interesting structure and properties of sulfolene (tetrahydrothiophene) and its unsaturated derivative 3-sulfolene (2,5-dihydrothiophene) have turned the attention to investigate their ring inversion and vibrational spectra [1–6]. The structural stability of the two molecules has been the subject of rotational microwave [3,4], vibrational infrared, Raman spectroscopic techniques [1,2], and electron diffraction [5]. In an electron-diffraction study of sulfolane (tetramethylene sulfone) the authors could not succeed on the basis of experimental data in unambiguously establishing the conformation of the five-membered ring [5].

Another more recent microwave study of sulfolane reported that two situations may be compatible with the available data: pseudorotation with the bent form lowest in energy or a near planar structure with a small barrier at the planar configuration [3]. Furthermore, the analysis of the microwave spectra of the ground and five excited states of the ring-puckering vibration of 3-sulfolene has shown this vibration to have a double-minimum potential function with a barrier of about 100 cm^{-1} (286 cal/mol) to planarity of the ring [4].

In a recent study, sulfolane was predicted by both DFT-B3LYP and MP2 levels of theory to exist predominantly in the *twist* structure [6]. From this study too the calculated symmetric ring-puckering potential function of 3-sulfolene at the B3LYP level is consistent with a flat minimum that corresponds to a *planar* ring but at the MP2 level with a double minimum with a barrier of about 193 cal/mol to ring planarity in reasonable agreement with experimental findings [6].

As a continuation of our interest in the structural stability of heterocyclic compounds we investigated 3,6-diphenyl-1,2,4,5-tetraoxane and its central and fundamental building block 1,2,4,5-tetroxane (Fig. 1) for the purpose of comparison. We carried out DFT-B3LYP and ab initio MP2 calculations of the energies for all possible configurations using the 6–311G** basis set. From the data the relative conformational stability and the magnitude of the ring-inversion barriers were estimated. Additionally, we calculated the vibrational wavenumbers and made detailed assignments of the normal modes of the two tetroxane molecules in their low energy structures. The results of this work are presented herein.

2. Experimental

2.1. Synthesis of 3,6-diphenyl-1,2,4,5-teroxane

The diperoxide, 3,6-diphenyl-1,2,4,5-tetraoxane, was prepared using procedure as described [7,8]; mp 201–202 °C (Ref. [9] mp 201–202 °C) with a modification of the isolation procedure.

Thus to a stirred solution of sulfuric acid (98%) (46 cm^3), absolute ethanol (35 cm^3), water (4 cm^3) and hydrogen peroxide (30%) (4.0 cm^3, 35.3 mmol) at −20 °C was added dropwise a solution of

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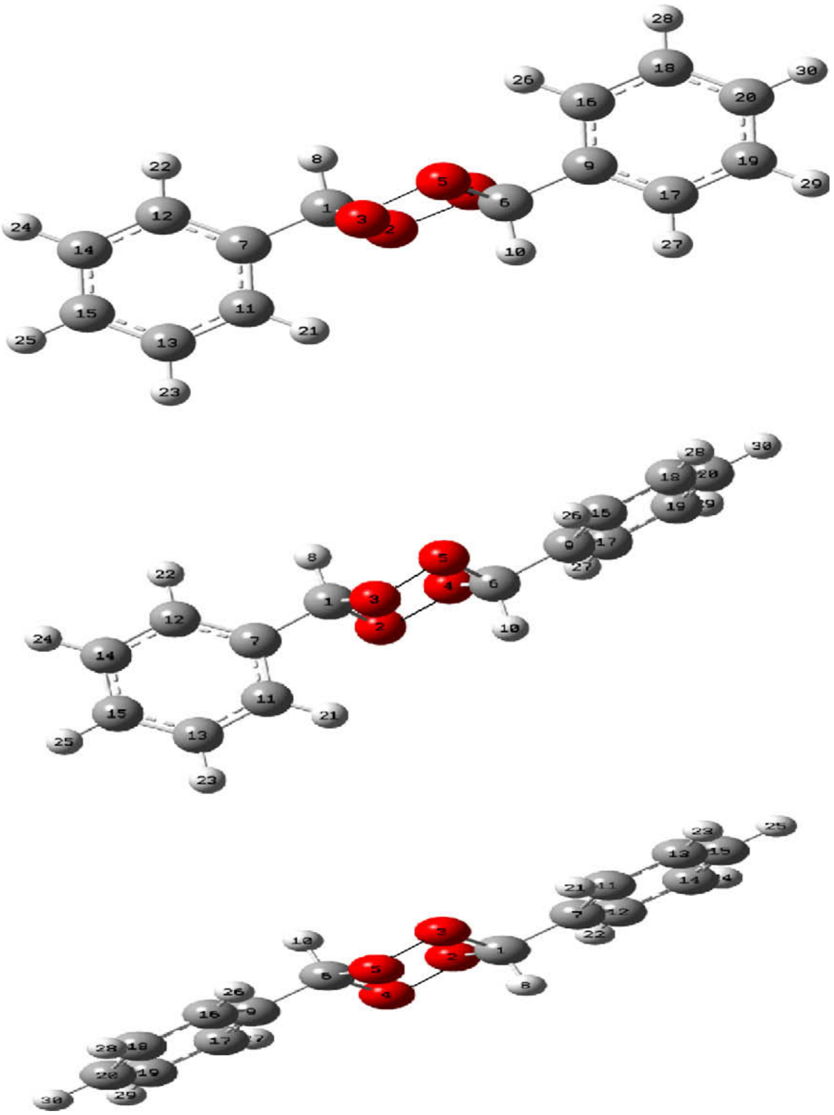

Fig. 1. Atoms numbering of P_{eq}–P_{eq} (upper), P_{eq}–PP_{eq} (middle) and PP_{eq}–PP_{eq} (lower) conformations of 3,6-diphenyl-1,2,4,5-tetroxane.

benzaldehyde 7.2 cm^3, 70.8 mmol) in absolute ethanol (20 cm^3) over a period of 45 min keeping the temperature in the range of −18 to −20 °C. After the addition the reaction mixture was stirred for an additional 1.5 h at −20 °C. The thick reaction mixture was diluted with cold ether (50 cm^3) and the solid compound was recovered by centrifugation. The solid was then dissolved in CH_2Cl_2 (150 cm^3) and washed with a cold $NaHCO_3$ solution. The organic layer was dried ($MgSO_4$) and concentrated to give the diperoxide as a solid (5.5 g, 63.8%, mp 197–199 °C) and crystallized from CH_2Cl_2 to give needle crystals. The IR spectrum of the compound matched with the reported spectrum [10]. δ_H ($CDCl_3$, TMS internal standard) 6.93 (2H, s), 7.43 (4H, t, *J* 7.7 Hz), 7.48 (2H, m), 7.51 (4H, d, *J* 7.0 Hz).

2.2. Infrared and Raman spectra

The infrared spectra of the synthesized 3,6-diphenyl-1,2,4,5-tetraoxane crystals (Fig. 2) were recorded using the Nicolet 6700 FT-IR spectrometer equipped with a globar source, a KBr beamsplitter, and a DTGS KBr detector in the region 4000–400 cm^{-1}. The Nicolet NXR FT-Raman module equipped with a CaF_2 beamsplitter and an InGaAs detector was used to collect the Raman spectra (Fig. 2) of the diphenyl compound. The helium–neon laser source operating at approximately 0.5 W was utilized for sample excitation.

3. Computational details

The GAUSSIAN 03 program [11] running on an IBM RS/6000 model S85 Unix server, was used to carry out the DFT-B3LYP and the ab initio MP2 levels of theory using the 6–311G** basis set to optimize the energies and estimate the ring-inversion barriers in 1,2,4,5-tetroxane and 3,6-diphenyl-1,2,4,5-tetraoxane. Selected calculated structural parameters, total dipole moments and rotational constants of the lowest energy conformations for the two molecules are given in Table 1. The complete structural parameters as calculated at B3LYP/6–311G** and MP2/6–311G** levels of theory can be found in *Tables* 1S and 2S. The structural parameters of the possible structures of both molecules were optimized by minimizing the energy with respect to all the geometrical parameters. The relative stabilities among the different configurations in the two diperoxides are listed in Table 2. Full lists of the total energies and the respective possible conformations are given in *Tables* 3S and 4S.