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Theoretical Study Of 3,6-Difluoro-1,2,4,5-Tetroxane Isomers

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ABSTRACT

This article is devoted to the presentation of the results of a theoretical study of the chair conformer at the *axial-axial, axial-equatorial, and equatorial-equatorial* isomers of the 3,6-difluoro-1,2,4,5-tetroxane. Besides, we resort to an analysis of the vibrational frequencies in order to verify that stationary points are or are not absolute minima. The relative stability of the different conformers are analyzed on the basis of several geometrical and electronic factors in order to get a better understanding of the main features determining the molecular stability. The factors analyzed here are the *syn-axial* effect, the steric effect, the anomeric effect, the anomeric effect and the free-electron pairs repulsions.   © 2006 Trade Science Inc. -INDIA

INTRODUCTION

At present, peroxide compounds have attracted a wide consideration since they play an important role as intermediate species in the ozone chemistry reaction with ethylene like compounds in the high atmosphere[1,2-5]. Several experimental X-ray and nuclear magnetic resonance (NMR) spectroscopic studies of substituted tetroxane derivatives have shown that they adopt a distorted chair conformation at the equilibrium position[6,7], which seem to suggest that the *trans* isomer has less energy than the *cis* one.

Some recent research on 1,2,4,5-tetroxane[8] show that the chair structure is the energetically preferred one and theoretical calculations on the basis of the Restricted Hartree Fock (RHF) method with a 3-21+G basis set of atomic orbitals yields geometrical

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results in quite agreement with available experimental data. Jorge et al. have performed several theoretical studies on di- and tetra substituted tetroxane compounds resorting to the semiempirical molecular orbital (MO) AM1 and PM3 methods[9]. They found that AM1 method underestimates the O-O peroxidic bond length by nearly 12%, while PM3 method describes this bond in a better manner.

This article is devoted to the presentation of the results of a theoretical study of the chair conformer at the *axial-axial, axial-equatorial, and equatorial-equatorial* isomers of the 3,6-difluoro-1,2,4,5-tetroxane. Besides, we resort to an analysis of the vibrational frequencies in order to verify that stationary points are or are not absolute minima. The relative stability of the different conformers are analyzed on the basis of several geometrical and electronic factors in order to get a better understanding of the main features determining the molecular stability.

CALCULATIONS

Geometries corresponding to the chair structure of the *axial-axial, axial-equatorial* and *equatorial-equatorial* isomers of 3,6-difluoro-1,2,4,5-tetroxane were optimized by means of the *ab initio* RHF method with a 3-21+G basis set and the Density Functional Theory (DFT) B3LYP method with identical basis set. The optimal calculated geometrical parameters are referred to the experimental data for substituted compounds.

The absolute minimum energy value on the po-

tential energy surface (PES) for each optimal geometry was verified through the calculation of the vibrational frequencies at the stationary points on such surface. All calculations were performed with the GAUSSIAN 94 package[10].

RESULTS AND DISCUSIÓN

We display in figure 1 the structure of the different isomers studied in this work.

TABLE 1 contains the electronic energy values of the conformers obtained via the theoretical methods mentioned before. The examination of the energetic results demonstrate that the more stable conformer is the *chair axial-axial* according to all the methods employed here, which is in agreement with those previous findings for substituted tetroxane derivatives via semiempirical MO methods[9].

In TABLE 2 we present the geometrical parameters which were obtained through the different MO methods: bond lengths, bond angles and dihedral angles. The geometry corresponding the most stable conformer (i.e. *chair axial-axial*), which is in concordance with the experimental data, is that computed

TABLE 1: Total energy (in Hartree) of the 3,6-difluoro-1,2,4,5-tetroxane calculated by two different theoretical methods

Isomer		RHF 3-21+G	B3LYP 3-21+G
trans	a-a	-571.9791869	-574.7788764
cis	a-e	-571.972148	-574.7725853
trans	e-e	-571.9668705	-574.7669859

trans aa 3,6-difluoro-1,2,4, 5-tetroxane	*cis* ae 3,6-difluoro-1,2,4, 5-tetroxane	*trans* ee 3,6-difluoro-1,2,4, 5-tetroxane

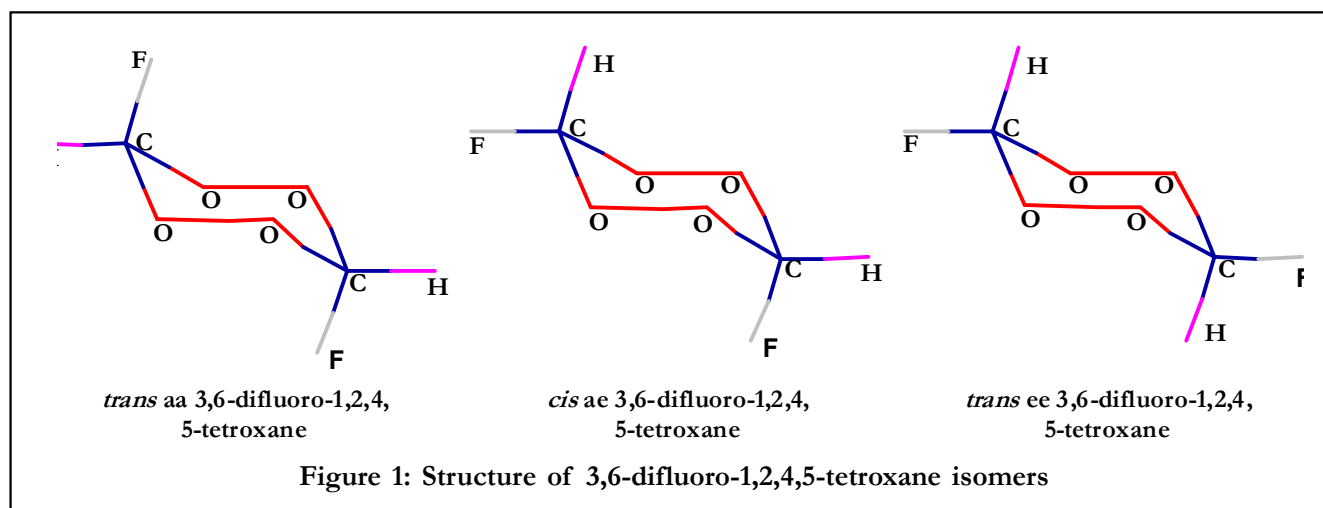**Figure 1: Structure of 3,6-difluoro-1,2,4,5-tetroxane isomers**

TABLE 2: Geometrical parameters

Geometrical parameters	trans aa 3,6-difluoro-1,2,4,5-tetroxane		cis ae 3,6-difluoro-1,2,4,5-tetroxane		trans ee 3,6-difluoro-1,2,4,5-tetroxane	
	RHF 3-21+G	B3LYP 3-21+G	RHF 3-21+G	B3LYP 3-21+G	RHF 3-21+G	B3LYP 3-21+G
Bond length (A)						
O_1O_2	1.4659	1.5383	1.4694	1.5412	1.4702	1.5387
O_4O_5	1.4659	1.5383	1.4694	1.5412	1.4702	1.5387
C_6O_5	1.4175	1.4424	1.4337	1.4637	1.4348	1.4665
C_6O_1	1.4175	1.4424	1.4334	1.4638	1.4349	1.4667
C_3O_2	1.4176	1.4424	1.4184	1.4427	1.4348	1.4665
C_3O_4	1.4175	1.4424	1.4178	1.4429	1.4348	1.4667
C_3X_8	1.3775	1.4129	1.3733	1.4071	1.0698	1.0868
C_3X_7	1.0710	1.0909	1.0715	1.0918	1.3622	1.3923
C_6X_9	1.0710	1.0909	1.3616	1.3922	1.3622	1.3924
C_6X_{10}	1.3776	1.4130	1.0705	1.0878	1.0698	1.0868
Bond angle(°)						
$C_6O_1O_2$	109.17	107.84	105.52	103.53	105.47	103.41
$C_6O_5O_4$	109.17	107.85	105.45	103.53	105.47	103.42
$C_3O_4O_5$	109.18	107.85	109.11	107.65	105.47	103.41
$C_3O_2O_1$	109.17	107.85	109.10	107.65	105.47	103.41
$O_2C_3O_4$	110.11	112.05	109.57	111.63	107.53	108.73
$O_1C_6O_5$	110.12	112.04	107.95	109.07	107.52	108.72
$X_7C_3X_8$	111.23	111.02	111.28	111.10	112.59	113.17
$O_2C_3X_8$	110.06	110.56	110.45	111.03	112.32	112.59
$O_2C_3X_7$	107.65	106.24	107.47	105.92	105.80	104.58
$X_{10}C_6X_9$	111.23	111.00	112.32	112.85	112.59	113.17
Torsión angle (°)						
$C_6O_5O_4C_3$	-59.57	-58.79	-63.12	-62.86	-66.37	-66.66
$C_6O_1O_2C_3$	59.58	58.82	63.08	62.85	66.37	66.66
$O_1O_2C_3O_4$	-60.15	-61.45	-60.66	-61.96	-67.82	-70.57
$O_5O_4C_3O_2$	60.15	61.44	60.70	61.96	67.82	70.57
$O_5C_6O_1O_2$	-60.16	-61.48	-67.51	-70.35	-67.82	-70.57
$O_4O_5C_6O_1$	60.15	61.47	67.52	70.35	67.82	70.57

with RHF/3-21+G and it is shown in figure 1, in close agreement with those results obtained for the 1,2,4,5-tetroxane[8].

The stability order of these conformers is discussed taking into account the following main features:

a) The *syn-axial* effect, which arises from the non-bonding repulsions between the free electron pairs located on the non-adjacent oxygen atoms. Assuming the existence of a tetrahedrical hybridization for the oxygen atom in the organic ring, repulsions between the 1,5 *syn-axial* free electron pairs are weaker for the *twist* structure than those for the *chair* form due to the fact that electric moment corresponding to the free electron pairs are at a less parallel arrangement in the first than the corresponding to the second structure. This effect is revealed by the decreasing of the OCO bond angle and the increasing of the XCX' bond angle (X = fluorine and X' = hydrogen)

b) The steric effect, according to the location of the fluorine atom at the *equatorial* or *axial* position.

c) The anomeric effect the oxygen free electron pairs

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exert on the C-O_{endo} bond and on the

d) C-X_{exo} bonds, when the fluorine atom is at the *axial* position.

d) The exoanomeric effect that free electron pairs corresponding to the substituent fluorine atom exert on the C-O_{endo} bond in the synclinal and antiperiplanar conformations..

e) The interactions between the free electron pairs located on non-adjacent atoms. This effect is noticed in di-substituted molecules. They are the same as the *syn axial* effect, which is a 1,5-interaction, and it is convenient to consider a 1,7 interaction between free-electron pairs of non-adjacent atoms.

The particular stability of the *chair axial-axial* conformer is supported by the anomeric effect and the free-electron pairs located on the fluorine atom with those free-electron pairs on localized on the oxygen atom of the organic molecular ring. The *equatorial-equatorial* structure is the most stable one due to the *syn axial* interaction and the electronic influence between the free-electron pairs belonging to the fluorine atom and the oxygen atom located at the molecular ring. This particular effect is revealed by a shortening of the C-F bond length and the increasing of the OCF bond angle. Results derived from both methods for the *equatorial-equatorial* conformer show an enlargement of the O-O and C-O bond lengths, which suggest a tendency to the breaking of these chemical bonds.

CONCLUSIONS

We have verified that all theoretical methods employed to analize the stability of the chosen 3,6-difluoro-1,2,4,5-tetroxane isomers predict the chair *axial-axial* structure as the most stable one. The RHF method with a 3-21+G basis set yields the best geometrical results when they are compared with available experimental data. The stability order of the possible conformers was discussed taking into account several main electronic and geometrical features and they allowed us to get a microscopic picture of the factors governing the molecular stability.

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