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THEORETICAL CONFORMATIONAL ANALYSIS OF 8-(P-TOLYL)NAPHTHALEN-1-OL

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ABSTRACT

Theoretical conformational analysis of 8-(p-tolyl)naphthalen-1-ol (8tn) has been performed in terms of semiempirical (AM1, PM3 and PM6), ab-initio Hartree Fock (HF) and density functional theory (DFT: B-LYP, B-P86, B3-PW91, B3-LYP) methods with the 6-31G(d) and 6-31++G(d) basis sets. Regarding all the calculations, C_1 form of 8tn ($C_{17}H_{14}O$) seems energetically more favorable and the lowest energy case for the optimized structures have been obtained with B3LYP/6-31++G(d) level.

Keywords: *8-(p-tolyl)naphthalen-1-ol, Naphthalene derivatives, Molecular structure, DFT.*

8-(P-TOLYL)NAFTALİN-1-OL MOLEKÜLÜNÜN KURAMSAL KONFORMASYON ANALİZİ

ÖZET

8-(P-Tolyl)Naftalin-1-Ol (8tn) molekülünün kuramsal konformasyon analizi 6-31G(d) ve 6-31++G(d) baz setleri kullanılarak yarı deneysel (AM1, PM3 ve PM6), ab-initio Hartree Fock (HF) ve yoğunluk fonksiyonel teori (DFT: B-LYP, B-P86, B3-PW91, B3-LYP) yöntemleri ile incelenmektedir. Tüm hesaplamalara göre 8tn ($C_{17}H_{14}O$) molekülünün enerji olarak en tercih edilebilir formu C_1 olarak görülmekte ve optimize yapı için en düşük enerji B3LYP/6-31++G(d) yöntemi ile elde edilmektedir.

Anahtar Kelimeler: *8-(p-tolyl)naftalin-1-ol, Naftalin türevleri, Moleküler yapı, DFT*

1. INTRODUCTION

Naphthalene is an organic compound and the simplest polycyclic aromatic hydrocarbon. Naphthalene derivatives are of diverse importance as intermediates for agricultural, construction, pharmaceutical, photographic, rubber, tanning, and textile chemicals [1]. For example, naphthalenesulfonic acids are important chemical precursors for dye intermediates, wetting agents and dispersants, naphthols, and air-entrainment agents for concrete while naphthalenols, naphthalenediols, and their sulfonated and amino derivatives are important intermediates for dyes, agricultural chemicals, drugs, perfumes, and surfactants [1]. Several naphthalene containing drugs are available, such as nafacillin, naftifine, tolnaftate, terbinafine, etc.

which play vital role in the control of microbial infection. Several other synthetic derivatives have also been reported which possess significant and satisfactory antimicrobial [2] and antimycobacterial properties [3]The number of naphthalene derivatives is very large, since the number of positional isomers is large. 8tn is a naphthalene derivative and there is no any information present in literature about its molecular structure and spectroscopic properties except for some crystal data [4]. A detailed quantum chemical study will aid in determining the molecular structure of 8tn and in clarifying the obtained experimental data for this molecule. Furthermore, the presented data may be helpful in context of the further studies of 8tn.

In this work, we have theoretically investigated the geometric parameters (bond lengths, bond-dihedral angles) of two conformers (C_1 and C_s) of 8tn using semiempirical (AM1, PM3 and PM6), ab-initio Hartree Fock (HF) and density functional theory (DFT: B-LYP, B-P86, B3-PW91, B3-LYP) methods with the 6-31G(d) and 6-31++G(d) basis sets. Furthermore, the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the title molecule have been predicted.

2. CALCULATIONS

For the theoretical conformational analysis, it was first investigated the internal rotation in 8tn about C8-C9-C12-C15 and C10-C1-O11-H25 (Figure 1) dihedral angles scanning from 0 to 360 degrees in 10 degrees increments, which was calculated at the AM1 level. Figure 2 shows potential energy surface (PES) for internal rotation. Analysis of PES allowed us to determine the conformational composition of 8tn with a high accuracy and showed that 8tn exists as C_1 or C_s conformers which are seen from Figure 1.

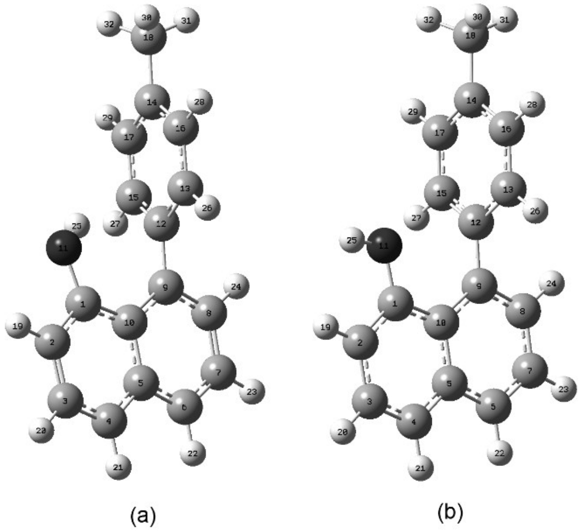

Figure 1. C_1 (a) and C_s (b) conformations and numbering of 8tn.

After the scan process, C1 and Cs conformers were optimized by semiempirical (AM1, PM3 and PM6), ab-initio Hartree Fock (HF) and density functional theory (DFT: B-LYP, B-P86, B3-PW91, B3-LYP) methods with the basis sets 6-31G(d) and 6-31++G(d) in the gas phase. Additionally, in the calculations all frequencies were positive. All the calculations were performed by using Gaussian 09 program [5] on a personal computer and GaussView program [6] was used for visualization of the structure.

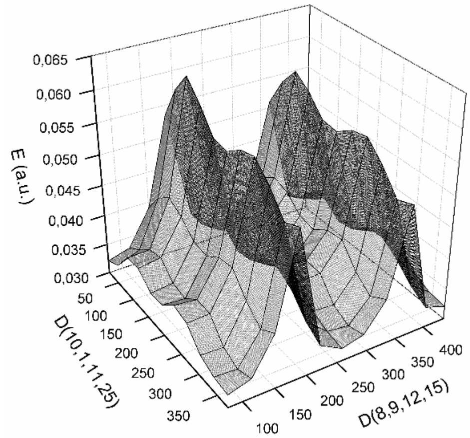

Figure 2. Potential energy surface of 8tn according to the AM1.

3. RESULTS AND DISCUSSION

The results of the calculations on the molecular conformations and geometrical parameters of 8tn are discussed first. A brief discussion of the HOMO and LUMO of the title molecule is then presented. Gibbs free energy and relative stability of the optimized geometries in gas phase of two forms of 8tn are given in Table 1. Regarding the calculated free energies except for HF and PM6 models, C_s form relative to the most stable form C_1 could be neglected for the calculation of equilibrium constant since their energy differences are larger than 2 kcal/mol [7-10]. For AM1, PM3 semiempirical and BP86, BLYP, B3PW91 and B3LYP methods with the 6-31G(d) and 6-31++G(d) basis sets, C_1 form is more stable than the other and molecule prefers C_1 conformer with approximate preference of 100 %. Regarding the HF/6-31G(d), HF/6-31++G(d) and PM6 models, C_1 also is more stable than C_s by 1.86 kcal/mol, 0.33 kcal/mol and 1.61 kcal/mol. Consequently, 8tn in the gas phase prefers C_1 and C_s forms with preference of 96 % and 4 %, 63 % and 37 % and 94 % and 6 %, respectively.

Table 1. Gibbs free energy and relative stability for two forms in gas phase of 8tn.

Method – Conformation	ΔG,Hartree	Relative Stability, kcal/mol	Mole Fractions, %	C8-C9-C12-C15, deg	C10-C1-O11-H25, deg
AM1 – C_1	0.254659	0.00	-	77.51	15.46
AM1 – C_s	0.259012	2.73		88.61	180.00
PM3 – C_1	0.240463	0.00	-	87.75	-0.01
PM3 – C_s	0.244666	2.64		88.66	180.00
PM6 – C_1	0.216416	0.00	93.87	88.63	-0.02
PM6 – C_s	0.218989	1.61	6.13	89.05	180.00
HF/6-31G(d) – C_1	-726.553854	0.00	95.88	83.03	2.84
HF/6-31G(d) – C_s	-726.550887	1.86	4.12	87.85	180.00
HF/6-31++G(d) – C_1	-726.57015	0.00	63.42	88.41	0.18
HF/6-31++G(d) – C_s	-726.569631	0.33	36.58	88.12	180.00
BP86/6-31G(d) – C_1	-731.254281	0.00	-	59.95	-2.60
BP86/6-31G(d) – C_s	-731.245959	5.22		87.55	180.00
BP86/6-31++G(d) – C_1	-731.281121	0.00	-	65.68	-5.16
BP86/6-31++G(d) – C_s	-731.271084	6.30		87.71	180.00
BLYP/6-31G(d) – C_1	-730.947932	0.00	-	61.77	-1.21
BLYP/6-31G(d) – C_s	-730.943804	2.59		87.68	180.00
BLYP/6-31++G(d) – C_1	-730.983194	0.00	-	70.67	-3.93
BLYP/6-31++G(d) – C_s	-730.977215	3.75		87.79	180.00
B3PW91/6-31G(d) – C_1	-730.981801	0.00	-	64.31	-1.54
B3PW91/6-31G(d) – C_s	-730.974116	4.82		87.60	180.00
B3PW91/6-31++G(d) – C_1	-731.004896	0.00	-	70.05	-3.70
B3PW91/6-31++G(d) – C_s	-730.995034	6.19		87.75	180.00
B3LYP/6-31G(d) – C_1	-731.258729	0.00	-	63.66	-0.56
B3LYP/6-31G(d) – C_s	-731.255045	2.31		87.76	180.00
B3LYP/6-31++G(d) – C_1	-731.288695	0.00	-	72.40	-3.38
B3LYP/6-31++G(d) – C_s	-731.282798	3.70		87.93	180.00

The optimized geometric parameters (bond lengths, bond and dihedral angles) calculated by B3LYP/6-31++G(d) are listed in Tables 1-2 along with their some experimental data. Generally, it is expected that the bond distances calculated by electron correlated methods are longer than the experimental distance. This situation is clearly observed in Table 2 as expected, especially where hydrogen is present. Overall, the calculated bond lengths are in good agreement with experimental results. The largest value for root mean square (RMS) error of bond lengths in C_1 form is about 0.094 for AM1. The RMS values for the HF, B3LYP and B3PW91 methods with both basis sets are about 0.077, 0.085, 0.085, respectively. For all calculations, the biggest difference between the experimental and calculated bond distances belong to CH or OH bond distances. The observed differences in bond distances are not due to the theoretical shortcomings since experimental results are also subject to variations owing to insufficient data to calculate the equilibrium structure and which are sometimes averaged over zero point vibrational motion. In X-ray structure the error in the position of the hydrogen atoms is such that their bonding parameters greatly vary compared to the non-hydrogen atoms. Intra- or intermolecular hydrogen bonding is also an important factor in the crystalline state of compound which usually leads to shortening of these bond.

Table 2. Optimized geometric parameters for C_1 form of 8tn.

Bond Length, Angstroms	Exp.[4]	B3LYP 6-31++G(d) – C_1	Bond Angle, deg	Exp.[4]	B3LYP 6-31++G(d) – C_1
C1-C2	1.371	1.385	C3-C4-H21	119.80	120.89
C1-C10	1.443	1.434	C5-C4-H21	119.80	118.74
C1-O11	1.362	1.366	C4-C5-C6	119.79	119.80
C2-C3	1.400	1.408	C4-C5-H10	120.95	120.66
C2-H19	0.950	1.086	C6-C5-H10	119.26	119.54
C3-C4	1.364	1.378	C5-C6-C7	120.92	121.16
C3-H20	0.950	1.087	C5-C6-H22	119.50	118.27
C4-C5	1.415	1.420	C7-C6-H22	119.50	120.57
C4-H21	0.950	1.087	C6-C7-C8	119.77	119.59
C5-C6	1.423	1.422	C6-C7-H23	120.10	120.67
C5-C10	1.432	1.444	C8-C7-H23	120.10	119.74
C6-C7	1.361	1.374	C7-C8-C9	121.87	121.93
C6-H22	0.950	1.087	C7-C8-H24	119.10	119.45
C7-C8	1.414	1.413	C9-C8-H24	119.10	118.60
C7-H23	0.950	1.087	C8-C9-C10	119.41	119.63
C8-C9	1.376	1.386	C8-C9-C12	116.79	116.18
C8-H24	0.950	1.087	C10-C9-C12	123.79	124.17
C9-C10	1.429	1.441	C1-C10-C5	116.07	116.65
C9-C12	1.498	1.501	C1-C10-C9	125.15	125.22
O11-H25	0.840	0.972	C5-C10-C9	118.75	118.11
C12-C13	1.402	1.407	C1-O11-H25	109.50	111.06
C12-C15	1.396	1.406	C9-C12-C13	122.07	121.08
C13-C16	1.386	1.396	C9-C12-C15	120.24	120.91
C13-H26	0.950	1.087	C13-C12-C15	117.60	117.87
C14-C16	1.393	1.403	C12-C13-C16	121.23	120.89
C14-C17	1.396	1.402	C12-C13-H26	119.40	119.34
C14-C18	1.503	1.511	C16-C13-H26	119.40	119.77
C15-C17	1.385	1.396	C16-C14-C17	117.88	117.80
C15-H27	0.950	1.087	C16-C14-C18	121.80	121.07
C16-H28	0.950	1.088	C17-C14-C18	120.32	121.12
C17-H29	0.950	1.088	C12-C15-C17	120.98	120.92
C18-H30	0.980	1.096	C12-C15-H27	119.50	119.23
C18-H31	0.980	1.099	C17-C15-H27	119.50	119.85
C18-H32	0.980	1.095	C13-C16-C14	120.96	121.25
Bond Angle, deg	Exp.[4]	B3LYP 6-31++G(d) – C_1	C13-C16-H28	119.50	119.21
			C14-C16-H28	119.50	119.54
C2-C1-C10	121.10	120.98	C14-C17-C15	121.34	121.26
C2-C1-O11	115.46	115.14	C14-C17-H29	119.30	119.49
C10-C1-O11	123.42	123.87	C15-C17-H29	119.30	119.25
C1-C2-C3	121.31	121.11	C14-C18-H30	109.50	111.48
C1-C2-H19	119.30	117.87	C14-C18-H31	109.50	111.01
C3-C2-H19	119.30	121.01	C14-C18-H32	109.50	111.47
C2-C3-C4	120.06	120.18	H30-C18-H31	109.50	107.31
C2-C3-H20	120.00	119.37	H30-C18-H32	109.50	108.04
C4-C3-H20	120.00	120.45	H31-C18-H32	109.50	107.32
C3-C4-C5	120.49	120.38			

In generally, the biggest differences for all calculations are observed in the calculated H30-C18-H31 and H31-C18-H32 bond angles compared to experimental values. All the other bond angles are reasonably close to the experimental data. The largest value for RMS error of bond angles in C_1 is about 0.391 for PM6. The RMS values for the HF, B3LYP and B3PW91 methods with both basis sets are about 0.288, 0.301, 0.297, respectively.

The HOMO and LUMO are the main orbitals taking part in chemical stability. The transitions can be described from HOMO to LUMO. The HOMO is located over naphthalene group in 8tn whereas the LUMO is dominated for O11 atom together with all structure. The atomic compositions of frontier molecular orbital and their orbital energies are shown in Figure 3.

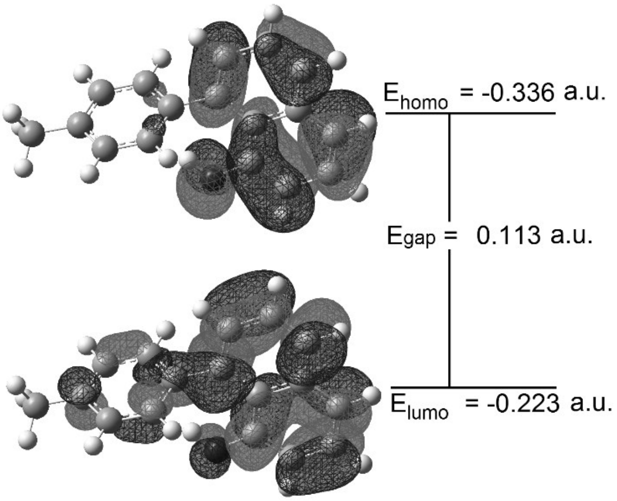

Figure 3. Atomic orbital compositions of the frontier molecular orbital for 8tn at the B3LYP/6-31++G(d).

4. CONCLUSION

According to the completed theoretical conformational analysis of 8tn, following results can be summarized:
1. Results of energy calculations for gas phase indicate that C_1 form is the most stable conformer of 8tn. Furthermore, relative energies of other form except for PM6 and HF are larger than 2.0 kcal/mol. Therefore, relative mole fractions of the other form could be neglected and these results suggest that conformational energy barrier is independent of the methods or basis sets.

2. The lowest energy case for the optimized structures have been obtained with B3LYP/6-31++G(d) level.

3. Theoretical results are successfully compared to available experimental data. Any differences observed between the experimental and calculated values could be due to the fact that the calculations have been performed for single molecule in the gas state contrary to the experimental values in the solid phase have been recorded in the presence of intermolecular interactions.

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