

ARTICLE

**Tuning Ring Inversion and Internal Rotation in
10-Substituted-9-Tert-Butylanthracenes: A Theoretical Study****Wissam Helal***Department of Chemistry, Faculty of Science, The University of Jordan, Amman 11942, Jordan**Received on: 17/12/2017;**Accepted on: 20/2/2018*

Abstract: The energy of ring inversion and internal rotation in 10-substituted-9-tert-butylanthracenes have been calculated using B3LYP/cc-PVDZ level of theory for geometry optimizations and MP2/cc-PVTZ level for single-point calculations. A series of 19 derivatives were modeled with the aim of being able to control and tune the energy needed for inversion of anthracene fused rings. The relaxed potential energy surface PES for such butterfly-like ring inversion for a model compound has been also computed. Two factors; the size and electronic interaction of the substituents with the anthracene fused rings, are found to be equally important in determining the energy of ring inversion and internal rotation.

Keywords: DFT, MP2, Ring inversion, Internal rotational, Potential energy surface, 10-substituted-9-tert-butylanthracenes, Anthracene planarity.

Introduction

9-substituted and 9,10-disubstituted anthracenes, the latter known as meso-substituted anthracenes, are important for their interesting chemical, photochemical and photophysical properties^[1]. Among other remarkable applications, meso-substituted anthracenes are candidates for molecular devices, such as organic light-emitting diodes OLEDs^[2-4], photomechanically responsive organic materials^[5-7] and molecular rotors^[8,9].

In fact, when one or both of the substituents are relatively bulk, the anthracene fused rings are no longer coplanar and a considerably "bent" equilibrium geometry within the anthracene skeleton is observed. One model compound of this kind of molecular system is 9-tert-butylanthracene (TBA), characterized by a dihedral angle between the two lateral benzene rings of around 20°^[10]. With an unusual low energy of activation (4.7 kJ/mol), the anthracene skeleton in TBA undergoes a butterfly-like ring inversion and a simultaneous tert-butyl group rotation^[10].

This low-energy molecular motion make this system a good candidate for mechanical

materials and molecular rotors^[9]. Actually, controlling and fine tuning the activation energy associated with such a molecular periodical motion are obviously necessary as a first step for testing its applicability in the field of molecular materials. Moreover, some studies have focused on the size of the bulky group at position 9 in anthracene, replacing the tert-butyl group in TBA with XMe₃ substituents (E = Si, Ge, Sn)^[11].

However, the primary concern, in this and other similar studies, was rather on the synthesis and geometrical distortions; no emphasis was considered to ring inversions and concerted rotations together with the energy associated with these conformational changes. In some other studies, the energy of internal rotation was computed theoretically, as in the rotation of the CF₃ group at position 3 in a phenanthrene unit^[12]. but no correlation was established with the rigidity or planarity of the conjugated polyaromatic hydrocarbon.

In a previous study, we have proposed the existence of a planar geometry for an excited intramolecular charge transfer state in 10-cyano-

9-tert-butyl-anthracene (CTBA), enhanced in rigid media^[13]. It was suggested that the planar geometry is accompanied with a rotation of the tert-butyl group in which one of the three methyls becomes coplanar with the anthracene aromatic plane. It is our aim in this work to investigate the effect of different substituents at position 10 in 9-tert-butyl-anthracene on the energy of ring inversion and internal rotation of the tert-butyl group in the ground electronic state, in order to control; i.e., be able to tune, the energy barrier of the butterfly-like ring inversion of anthracene fused rings. As a matter of fact, *ab-initio* electronic structure computational methods are useful in this context, as they are able to predict accurately the potential energy surface of internal rotations and other conformational and structural changes.

Herein, we report the effect of different substituents at position 10 on the energy of ring inversion and internal rotation of 9-tert-butyl-anthracene (TBA). The substituents proposed in

this investigation were selected in such a way that they have a range of different sizes and electronic properties, See Figure 1. A total of 19 substituents (R) were used in this study at position 10 in 9-tert-butyl-anthracene; namely, R= H (TBA); cyano, CN (CTBA); fluoro, F; chloro, Cl; bromo, Br; hydroxyl, OH; nitro, NO₂; amino, NH₂; nitroso, NO; ethynyl, CCH; vinyl, CHCH₂; methyl, CH₃; methoxy, OCH₃; dimethylamino, N(CH₃)₂; formyl, COH; carboxyl, COOH; methyl ketone, COCH₃; methyl ester COOCH₃ and amido CONH₂ groups. The numbering scheme of the 10-substituted-9-tert-butylanthracene compounds and the different substituents used in this work are shown in Figure 1. To the best of our knowledge, no theoretical modeling have been reported for the effect of substituent nature on ring inversion and internal rotation in 10-substituted-9-tert-butylanthracene.

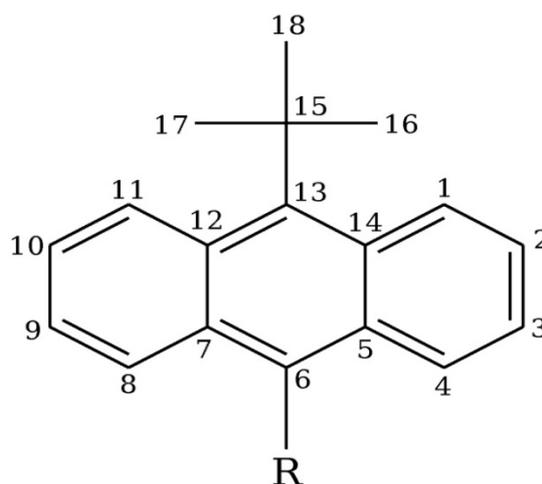


Figure 1. Atom numbering of TBA (9-tert-butyl anthracene) parent compound and its derivatives investigated in this work: R= H (TBA), CN (CTBA), F, Cl, Br, OH, NO₂, NH₂, NO, CCH, CHCH₂, CH₃, OCH₃, N(CH₃)₂, COH, COOH, COCH₃, COOCH₃ and CONH₂.

Computational Details

All calculations in this study have been performed using the ORCA 4.0.1^[14] and GAMESS^[15] codes. The molecular structures of equilibrium (minimum) geometry for all molecules in the gas phase have been optimized without any symmetry restrictions at the density functional theory DFT level using the Becke's three parameters Lee-Yang-Parr hybrid functional (B3LYP)^[16] with correlated-consistent double zeta basis set cc-PVDZ,^[17] denoted as B3LYP/cc-PVDZ. The molecular structures of

the "transition state" (maximum) geometry of all molecules in the gas phase have been obtained by optimizing all geometrical parameters while freezing certain dihedral angles and imposing some symmetry restrictions using B3LYP/cc-PVDZ level of theory (See next section for more detail). Moreover, geometry optimization of the parent compound TBA was performed at the B3LYP/cc-PVTZ and Moller-Plesset second-order perturbation theory^[18] using cc-PVDZ basis, denoted as MP2/cc-PVDZ, in order to test

the validity of the geometry optimizations of the parent and other compounds at B3LYP/cc-PVDZ level. Subsequent frequency calculations were carried out for all optimized geometries at the same level of theory in order to test the nature of the stationary points. Only real frequency values for equilibrium state structures and one imaginary frequency for transition state structures were accepted.

Single-point calculations for the equilibrium and transition state geometries have been performed at the MP2/cc-PVTZ level, starting from the optimized geometries of the equilibrium and transition states at B3LYP/cc-PVDZ level. In addition, relaxed Potential Energy Surface (PES) for one case study, 10-cyano-9-tert-butyl-anthracene (CTBA), for the ring inversion was obtained at the B3LYP/cc-PVDZ level, through scanning the dihedral angle (C1-C14-C13-C12) at 1° interval and optimizing the geometry at each single dihedral angle. Energy barriers were not corrected for zero-point energy (ZPE), since it was found that those corrections are actually negligibly small.

Results and Discussion

Actually, the tert-butyl group in TBA is hindered by two adjacent carbon-hydrogen bonds, both of which point directly at the tert-butyl group. The geometry of anthracene fused ring is not planar in the solid state as measured by x-ray^[10], nor in solution or gas phase as predicted by computational *ab-initio* quantum chemical methods^[10]. In addition, the tertiary butyl group is displaced in a direction opposite to the ring bending (see Figure 2). Furthermore, upon rotation of the tert-butyl group relative to the anthracene fused rings plane; i.e., internal rotation, the anthracene fused rings become planar and a further rotation results in an inversion of the fused rings to yield a mirror image of the original structure. This flapping of the anthracene rings resembles a butterfly-like motion. The total energy required for this internal rotation, or inversion, process was found to be only 4.7 kJ/mol^[10]. For the sake of comparison, the calculated phenyl rotation energy in 9-phenylanthracene is around 88 kJ/mol^[19]. It is also important to notice that in the solid state, the dihedral angle C14-C13-C15-C16, in TBA is 30.5° , while in solution and gas phase, this angle becomes around 20° due to relaxed geometry from the crystal packing forces.

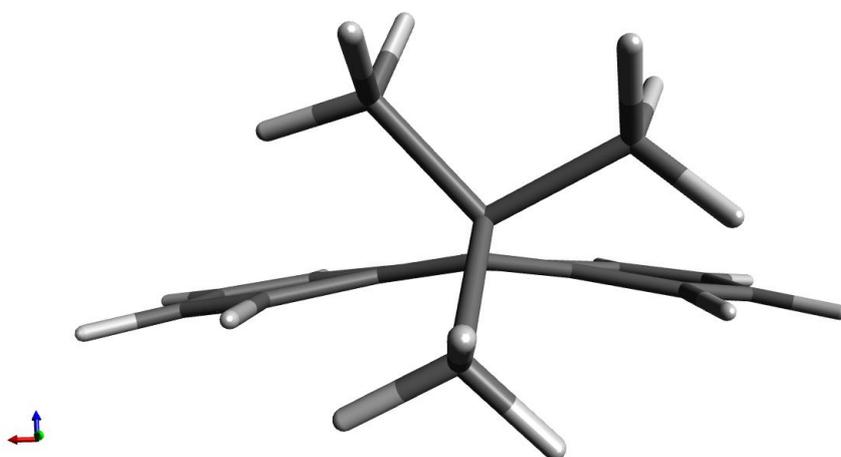


Figure 2. A view of the molecular structure of 9-tert-butyl-anthracene (TBA), showing its non-planar geometry. Atoms C13 and C6 are made in the axis perpendicular to the page plane.

Some of the calculated geometrical parameters; namely, dihedral angles, of the optimized geometry at the B3LYP/cc-PVDZ, B3LYP/cc-PVTZ and MP2/cc-PVDZ for TBA, are reported in Table 1. It is found that different dihedral angles calculated of TBA using B3LYP/cc-PVDZ level are in very good agreement with the corresponding experimental

x-ray results, which are also reported in Table 1. For instance, most of the calculated dihedral angles are in general 1° close to the experimental values, with the exception of C14-C13-C15-C16, C14-C13-C15-C17 and C14-C13-C15-C18 dihedral angles which are found to be 11.9° , 10.1° and -9.4° , respectively, different from that of the reported x-ray data, which is attributed to

the relaxation of the orientation of tert-butyl group in the liquid and gas phase as indicated above. Moreover, B3LYP/cc-PVTZ and MP2/cc-PVDZ geometries are both in very good agreement with that of B3LYP/cc-PVDZ geometry, see Table 1. Therefore, we are

comfortable with the validity of the structures obtained using B3LYP/cc-PVDZ level for other derivatives in terms of both basis set (double zeta *versus* triple zeta) and method (DFT *versus* MP2).

Table 1. Selected dihedral angles, in ($^{\circ}$), for 9-tert-butyl-anthracene (TBA) calculated at different levels of theory: B3LYP/cc-PVDZ, B3LYP /cc-PVTZ and MP2/cc-PVDZ in the gas phase; the corresponding geometrical parameters (dihedral angles) taken from reference [10] are also included for comparison.

Dihedral angle	X-Ray ^a	B3LYP/cc-PVDZ	B3LYP/cc-PVTZ	MP2/cc-PVDZ
C1-C14-C13-C12		160.6	159.9	158.3
C2-C1-C14-C13	178.4	178.5	178.6	177.9
C3-C4-C5-C14	4.8	4.7	5.0	5.0
C1-C2-C3-C4	4.3	3.9	4.1	4.2
C2-C3-C4-C5	0.5	1.1	1.1	1.3
C3-C4-C5-C6	174.8	173.9	173.6	173.5
C5-C6-C7-C8	171.5	172.3	172.0	171.4
C6-C7-C8-C9	173.6	175.7	175.4	175.1
C7-C8-C9-C10	1.3	0.6	0.5	0.8
C8-C9-C10-C11	2.9	2.9	3.1	3.4
C9-C10-C11-C12	1.9	1	1.1	0.9
C15-C13-C12-C11	26.4	20.4	21.0	23.3
C14-C13-C15-C16	30.5	18.6	19.2	22.1
C14-C13-C15-C17	143.3	133.2	133.6	136.1
C14-C13-C15-C18	93.8	103.2	102.8	100.2
C7-C12-C13-C15	158.1	161.9	161.5	159.3
C5-C14-C13-C15	158.4	160.9	160.6	158.4

^a see reference [10].

The energy difference (ΔE) for internal rotation, which is the same as that for ring inversion, can be calculated as the difference between the absolute energies of the equilibrium "bent" geometry and that of the transition state "planar" geometry. The transition state planar geometry could be calculated in many ways. One obvious choice is imposing a plane of symmetry σ_h within the anthracene fused rings, in other words imposing a C_s point group, while optimizing all other parameters. In doing so, one of three methyls in the tert-butyl group becomes coplanar with the anthracene plane and the other two methyls becoming equivalent, one above the ring and the other below the ring with the same angle. While this option is the most "natural" way to compute the energy of the optimized structure of the transition planar state, it can only be applied for the derivatives that form linear extensions at position 10 out of the anthracene middle ring; namely, in cases with R=H, F, Cl, Br, CN and CCH. However, our calculations

indicated that for all other derivatives, in which R is a formyl group (COH) for example, the plane of the R group cannot lie coplanar with the plane of the anthracene ring, for reasons discussed below and thus, imposing a C_s symmetry is not possible. The other option for obtaining the lowest energy of the transition planar state is the optimization of all geometric parameters except one of the dihedral angles associated with internal rotation and ring inversion. Preliminary calculations showed that three independent dihedral angles could be kept frozen at a particular angle in order to obtain the planar geometry of the transition state:

C1-C14-C13-C12=180 $^{\circ}$ C7-C12-C13-C15=180 $^{\circ}$ and C14-C13-C15-C16 = 0 $^{\circ}$. We have computed the energy and the optimized geometry while freezing those three dihedral angles independently. We have also computed the corresponding energy and geometry by imposing a C_s symmetry, for one test compound, 10-cyano-9-tert-butyl-anthracene (CTBA). When

the values of ΔE of internal rotation and ring inversion are compared, it is found that the differences between the four methods are negligibly small (around 0.02 kJ/mol at most) relative to the ΔE value obtained by imposing C_s symmetry, which is around 7.4 kJ/mol for CTBA, see Table 2. Therefore, we decided to compute the minimum energy of the planar transition states for all derivatives by optimizing the geometry while freezing the dihedral angle

C1-C14-C13-C12 at 180°. As an additional test for the validity of the selected regime of calculating the energy of the planar geometry, we have computed the relaxed potential energy surface (PES) as a function of the dihedral angle C1-C14-C13-C12 for CTBA. The PES obtained was found to be smooth through the entire reaction coordinate and symmetric about the angle 180°, as clearly demonstrated in Figure 3.

Table 2. Absolute energies, in hartree, relative energies (ΔE) for ring inversion, in kJ/mol and some characteristic geometrical parameters, dihedral angles in (°), of different equilibrium and planar, or transition state geometries of 9-cyano-10-tert-butyl-anthracene (CTBA) calculated at B3LYP/cc-PVDZ level.

Geometry	E (hartree)	ΔE^a (kJ/mol)	C1-C14- C13-C12	C7-C12- C13-C15	C14-C13- C15-C16
Equilibrium (or minimum)	-789.03339555	0.0000	158.1	158.3	22.5
Planar (C_s)	-789.03056873	7.4218	180.0	180.0	0.0
Planar (C1-C14-C13-C12 = 180)	-789.03057626	7.4020	180.0	180.0	0.0
Planar (C14-C13-C15-C16 = 0)	-789.03057558	7.4038	179.8	179.8	0.0
Planar (C7-C12-C13-C15 = 180)	-789.03057534	7.4045	179.9	180.0	0.2

^a Relative to the equilibrium most stable geometry.

The calculated single-point energy values of ring inversions ($\otimes E$) for all derivatives at MP2/cc-PVTZ level of theory are reported in Table 3, in an ascending order according to their $\otimes E$ values. Some of the characteristic geometrical parameters of the optimized equilibrium geometries are also reported in Table 3. First, it is noted that the energy of ring inversion is greatly dependent on the nature of substituent. For instance, the difference between the lowest (3.9 kJ/mol for R = F) and the highest (18.0 kJ/mol for R = NH₂) values is more than 4 fold, with a wide “spectrum” of ΔE values in between for the other compounds, which implies

a great flexible tuning ability of the molecular ring inversion and internal rotation in substituted TBA derivatives. Second, it is also noted that while there is a general correlation between ΔE values and the degree of anthracene skeleton bending—the higher the bending or deviation from planarity the higher the $\otimes E$ value—we find exceptions in many cases. This could be explained considering the fact that geometry and steric factors are not the only variables controlling the energy needed to activate such internal rotation and ring flipping. Electronic structure factors are, indeed, important as well.

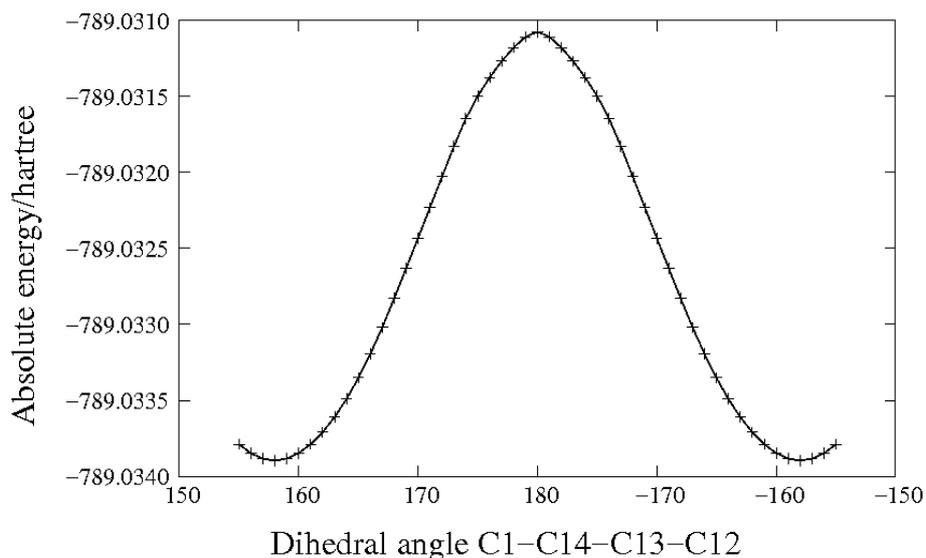


Figure 3. Relaxed Potential Energy Surface (PES) of ring inversion and simultaneous internal rotation of t-butyl group in 9-cyano-10-tert-butyl-anthracene (CTBA), as a function of the dihedral angle C1-C14-C13-C12, computed at B3LYP/cc-PVDZ level of theory, through scanning the dihedral angle (C1-C14-C13-C12) at 1° interval.

Table 3. Relative energies (ΔE), in kJ/mol, of ring inversion for all compounds using single-point calculations at MP2/cc-PVTZ level starting with the optimized geometries at B3LYP/cc-PVDZ level. Some characteristic geometrical parameters, dihedral angles in ($^{\circ}$), are also included for the optimized equilibrium geometries at B3LYP/cc-PVDZ in the gas phase.

R	ΔE (MP2/cc-PVTZ)	C1-C14-C13-C12	C7-C12-C13-C15	C14-C13-C15-C16
-F	3.9	161.2	162.5	17.8
-H	4.5	160.6	161.9	18.6
-NO ₂	5.2	156.3	158.6	22.8
-CONH ₂	5.5	158.2	159.4	21.6
-OCH ₃	5.9	159.2	160.2	20.7
-OH	6.2	159.3	161.2	19.5
-COCH ₃	6.6	157.4	157.4	25
-CN	7.0	158.1	158.3	22.5
-COOCH ₃	7.5	154.4	156.4	26.3
-CCH	7.6	158.0	158.3	22.7
-CHCH ₂	7.7	158.0	159.9	21.7
-N(CH ₃) ₂	7.8	158.4	158.5	23.0
-COOH	7.8	154.1	155.8	27.8
-Cl	8.3	158.0	158.5	22.8
-Br	9.5	157.3	157.9	23.7
-CH ₃	12.0	156.7	157.7	24.3
-COH	15.3	154.5	154.0	30.3
-NO	16.8	153.8	154.4	30.4
-NH ₂	18.0	158.8	157.9	23.7

It is worth to point out that the higher the rotation of t-butyl group (C14-C13-C15-C16), the higher the anthracene skeleton bending (C1-C14-C13-C12) and the higher the bending of

C13-C15 bond out of plane of the anthracene plane, as indicated by the dihedral angle C7-C12-C13-C15. A close inspection of the values of the dihedral angles C1-C14-C13-C12, C7-

C12-C13-C15 and C14-C13-C15-C16 in Table 3 reveals that the size of the substituent R is, in so many cases, a decisive variable for both geometry bending and thus energy of ring inversion. The larger the size of R at position 10, the higher the deviation from planarity, the higher the rotation of t-butyl group and its deviation away from the anthracene skeleton plane and the higher the value of the energy of ring inversion. For example, ΔE values for the compounds in which R = H (TBA), CN (CTBA), Cl, Br and CH₃, are 4.5 kJ/mol, 7.0 kJ/mol, 8.3 kJ/mol, 9.5 kJ/mol and 12.0 kJ/mol, respectively; and the values of the three dihedral angles for these compounds are all consistent with the fact that a higher strain due to bulky R results in a larger deviation from planarity.

However, there are some cases in which the aforementioned conclusions do not perfectly hold. For instance, it was thought that the energy of activation of the nitro substituent (R = NO₂) is higher than that of the amino substituent (R = NH₂), but it was found that the opposite is true. Our calculations indicate that the plane of the nitro group is tilted 74° out of the anthracene plane about the C-N bond; that is to say, almost perpendicular to the aromatic plane. This actually is in line with the angle obtained by x-ray for 9-nitroanthracene which is reported to be 85°^[20]. On the other hand, the amino group, although not planar by itself, is almost coplanar with the anthracene aromatic plane, with a dihedral angle C5-C6-N-H of 8.9°, resulting in a huge steric effect on the two adjacent hydrogens on C4 and C8, hence causing a significant increase in the energy of ring inversion and concerted rotation. Another similar case is 10-formyl-TBA, in which the dihedral angle C5-C6-C-O (the last two atoms C-O being those of the formyl group COH) is 9.4° and thus a high value of calculated ΔE is found and an extremely bent geometry is observed. The x-ray reported angle of the formyl group in 9-anthracene, in which the anthracene skeleton is completely planar, is 27°^[21]. On the other hand, the calculated dihedral angle C5-C6-C-O for the case in which R is a carboxylic group (R = COOH), is found to be 44°—the corresponding experimental value of anthracene-9-carboxylic acid is 54.9°^[22]; therefore, middle values of energy of inversion and bending geometry are observed, see Table 3. Of course, the steric hindrance that

caused the peri hydrogens attached to carbons C4 and C8 is large relative to the resonance stabilization energy caused by conjugation, the carboxylic group is obliged to go out of the anthracene ring plane.

The electronic structure factor of the substituents in TBA and TBA derivatives system is currently under investigation. We are further interested in the possibility of calculating charge transfer states in cases where the substituents are acceptor groups, using particular theoretical models and methods appropriate to calculate the reaction coordinates for the excited states in addition to excited states structural changes in such molecular arrangements^[23-25], since a charge transfer state in one compound, CTBA, was previously observed^[13].

Conclusions

In this work, we have demonstrated the possibility of tuning the energy barrier of ring inversion of anthracene fused rings and internal rotation of tert-butyl group in 10-substituted-9-tert-butylanthracene, through a careful selection of the substituent attached at meso position with 9-tert-butylanthracene. Two factors are found to be decisive in controlling such energy: The size of the substituent, through steric deformation of the anthracene skeleton; and electronic properties, through the degree of conjugation with the aromatic anthracene fused rings. Future works in this line are directed toward the charge transfer states and the excited states in which the substituent is an acceptor group.

Acknowledgment

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