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Calculation of Rotational Barriers of 4-Acyloxy-4'-N-N-Butylcarbamyloxy-Biphenyls by Molecular Calculation and Linear Free Energy Relationships

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Abstract

Rotational barriers of ten 4-acyloxy-4'-N-n-butylcarbamyloxy-biphenyls were calculated by density functional theory. Linear free energy relationships between rotational barriers and reduced mass existed in these compounds. Rotational barriers of these compounds from dihedral angle of 45^0 to 90^0 (ΔE_{90} 's) were linearly correlated with the inverse of reduced mass (1/m'). Thus, this rotational mechanism was just a simple physical rotation of an object about its center axis. On the other hand, rotational barriers of these compounds from dihedral angle of 45^0 to 0^0 (ΔE_0's)) were dependent upon both 1/m' and the vibrational energy difference at the C(1)-C(1') bond near dihedral angle of 0^0(σ^*'s). Values of $E_{vib} = (\Delta E_{vib} = (1/2)$ were linearly correlated with the inverse of the root of reduced mass (1/√m'). Thus, the Δ E_0 values calculated from density functional theory combined both physically rotational energy barrier, ΔE_{90}, and vibrational (or stretching) energy barrier, ΔE_{vib}. A two-step mechanism for the rotation of biphenyl from dihedral angle of -45^0 to 45^0 through the intermediate with an increasing C(1)-C(1') pivot bond length of 0.027Å was proposed. Accordingly, values of the bond length incensement of these ten biphenyls were calculated to be from 0.037 to 0.046 Å. Thus, the experimental ΔE_0 values were estimated to be the calculated ΔE_0 values minus the ΔE_{vib} values.

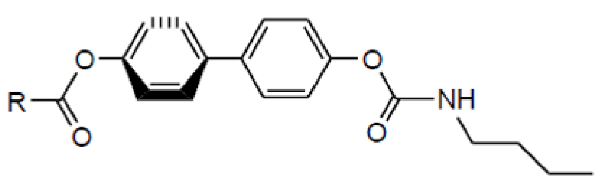
Keywords: Rotational Barriers; Density Functional Theory; Biphenyls; Gaussian; Linear Free Energy Relationship

Introduction

One of the paradoxical results in Chemistry was that the rotational barriers of biphenyls obtained from experiments were significant different to those calculated by quantum mechanism. In the gas-phase experiments, Bastiansen and Samdal estimated the barriers from ground state (dihedral angle, $\phi = 45^0$) to $\phi = 0^0$ and $\phi = 90^o$ to be $\Delta E_0 = 6.0 \pm 2.1$ kJ/mol and $\Delta E_{90} = 6.5 \pm 2.0$ kJ/mol, respectively [1]. Theoretical calculation for rotation barriers of biphenyl by different levels of basis sets of quantum mechanism was always active in this field since the second half of last century. Tsuzuki and Tanabe reported ΔE_0 = 13.93 kJ/mol and ΔE_{90} = 6.32 kJ/mol from HF/6-31G** level of quantum mechanism calculation [2]. Rubio et al. found ΔE_0 = 12.93 kJ/mol and ΔE_{90} = 6.40 kJ/mol from 4s3p1d/2s1p basis set level of quantum mechanism calculation [3]. Karpfen et al. estimated that the ΔE_0 values were 13.8, 16.3, and 8.4 kJ/mol and that the ΔE_{90} values were 6.3, 7.5, and 10.0 kJ/mol by SCF, MP2, and B3LYP methods, respectively [4].

Values of ΔE_0 were 13.0 and 8.4 kJ/mol and ΔE_{90} were 5.0 and 7.3 kJ/mol using the 6-311++G(d,p) basis set for SCF and B3LYP, respectively. By MP2/cc-pVQZ//MP2/6-31G* calculation, Tsuzuki et al. obtained ΔE_0 and ΔE_{90} were 9.54 and 8.91 kJ/mol, respectively [5]. The best calculated values from Johansson and Olsen by coupled cluster including single and double excitations as well as triples correlations (CCSD(T)) from density functional theory (DFT) were $\Delta E_0 =$ 7.96 kJ/mol and $\Delta E_{90} =$ 8.79 kJ/mol, respectively [6]. In general, ΔE_{90} of biphenyl could be calculated to be very close to the experimental result by low level of quantum mechanism calculation. However, high level of quantum mechanism calculation made ΔE_{90} of biphenyl away from the experimental data. Thus, HF/6-31G** level was good enough for calculation of ΔE_{90} of biphenyl.

On the other hand, the calculated ΔE_{90} of biphenyl was difficult to match with the experimental data. Complicated levels of calculations not only lowered ΔE_0 of biphenyl yet increased ΔE_{90} of biphenyl. Therefore, ΔE_{90} (rotational barrier of biphenyl from $\phi = 45^0$ to $\phi = 90^0$) and ΔE_0 (rotational barrier of biphenyl from $\phi = 45^o$ to $\phi = 0^0$) might be dominated by two different mechanisms. In order to test this ideal, ten 4,4'-disubstituted biphenyls [1-10] (Figure 1) [7-9], which were potent inhibitors of acetylcholinesterase, butyryl cholinesterase's and lipase, were chose to calculated ΔE_0 and ΔE_{90} by HF/6-311G(d,p) method [10]. The reason why we chose 4,4'-disubstituted biphenyls for this study was because steric effects from 4,4'-positions for these compounds were most insignificant while the electronic or polar effect from these positions were important for these conformational (rotational) changes.



1 R = CH_3;
2 R = $CH_2CH_2CH_2CH_3$;
3 R = $(CH_2)_5CH_3$;
4 R = $(CH_2)_7CH_3$;
5 R = $CH_2C_6H_5$;
6 R = $CH(C_6H_5)_2$
7 R = $C(C_6H_5)_3$
8 R = C_6H_5;
9 R = CCl_3;
10 R = $C(CH_3)_3$;

Figure 1: Chemical structures of compounds 1-10.

Materials and Methods

4-Acyloxy-4'-N-n-butylcarbamyloxy-biphenyls (1-10) were synthesized from biphenyl [7-9]. All DFT calculations were preformed from B3LYP method and basis function of 6-311G(d,p) by Gaussian 03 [10]. MM-2 energy minimization was performed by CS Chem 3D (version 6.0). Origin (version 6.0) was used for linear and nonlinear least-squares curve fittings ΔE_{90}.

Results and Discussion

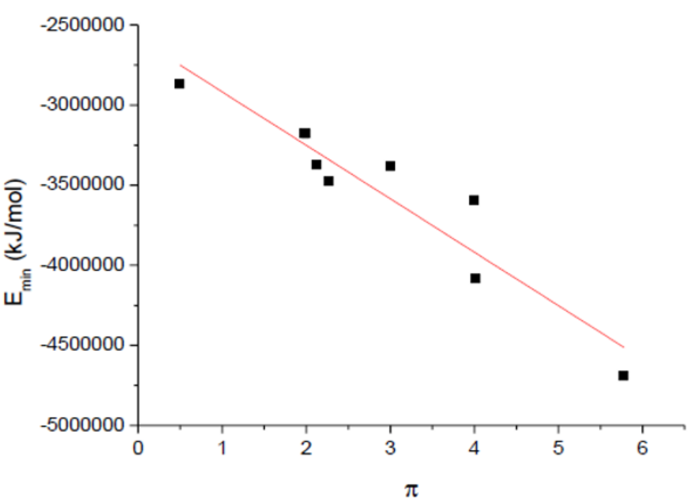


Figure 2: A linear correlation between Emin and Emin = -(2.6±0.1)x106-(3.3±0.4)x105 (kJ/mol); R=0.93777.

The minimized energies (Emin's) of compounds 1-10 (except 9) calculated by HF/6-311G(d,p) method (Table 1) were linearly correlated with Hansch electronic values [11] (Figure 2). Thus, all electronic effects of all substituents were taken into consideration in HF/6-311G(d,p) calculation. Similar to the rotational spectroscopy for end-over-end rotation, rotational energy (EJ) was quantized as Eq. (1), where J and I were rotation quantum number (J= 0, 1, 2, 3,...) and moment of inertia, respectively [12].

$$E_J = J(J+1)\hbar^2 / 2I \qquad (1)$$

Table 1: Dihedral angles (ϕ 's) and minimized energies ($E_{min's}$) for the ground states of biphenyls and energy barriers for rotations of biphenyls from ϕ = -45^0 to 45^0 through 0^0(ΔE_0) and from ϕ = 45^0 to 135^0 through 900 (ΔE_{90}) about the center axis.

Compounds	ϕ (in degree) in ground state	Emin (kJ/mol)	$\Delta x\ at = 0^0$ (kJ/mol)	ΔE_{90} (kJ/mol)
Biphenyl	44.6	-1208627	13.95	6.42
1	46	-2868465	14.36	6.05
2	45.9	-3178168	14.33	6.03
3	45.9	-3384598	14.33	5.95
4	45.5	-3591065	14.25	6.05
5	45.9	-3475192	14.27	5.96
6	45.2	-4082913	14.17	5.85
7	46	-4689459	14.14	5.79
8	46	-3371927	14.24	5.93
9	45.4	-6490148	14.2	5.96
10	46	-3178168	14.24	5.92

The moment of inertia (I) might be written as Eq. (2), where R and m' were rotated distance and reduced mass, respectively.

$$I = m_1 m_2 R^2 / (m_1 + m_2) = m' R^2 \qquad (2)$$

was linearly correlated with the inverse of reduced mass (1/m') (Figure 3). Therefore, rotation of biphenyl from dihedral angle of 45∘to 90∘was just a simple physical rotation of an object about its center axis. Hence, both electronic and steric effects were insignificant in this mode of rotation.

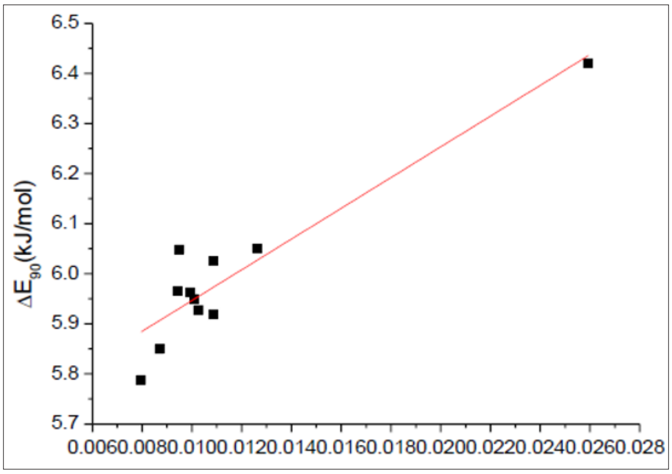


Figure 3: A linear correlation between ΔE_{90} and 1/m′ of biphenyl and compounds 1-10 ΔE_{90} = (5.63±0.05)+(31±4)/m′ (kJ/mol) ; R=0.92355; residual sum of squares=0.03515.

On the other hand, DE0 of biphenyl was not a simple physical rotation of an object about its center axis. A chemical reaction namely atropisomerization was occurred since the symmetry of the molecule is changed during this rotation as the conversion of R- to S-1,1'-bi-2-naphthyl-2,2'-diol. ΔE_0 was fairly correlated with Hammett substituent constant (σ^*) [13] (Figure 4). Therefore, the electronic effect played a role in this mode of rotation as those in six molecules with one ratable dihedral angle: ethane, methylamine, methanol, hydrazine, hydroxylamine, and hydrogen peroxide [14]. Negative ρ^*value (-0.13) for this correlation indicated that the transition states (ϕ = 0°) were more positive charges than ground states (ϕ = 45^0) for these rotations. Electron-withdrawing substituents at the 4 or 4' position of biphenyls would facilitate these rotations. Small absolute value of ρ^* implied that the electronic effect occurred far away from the pivot bond of the rotation (C(1)-C(1')).

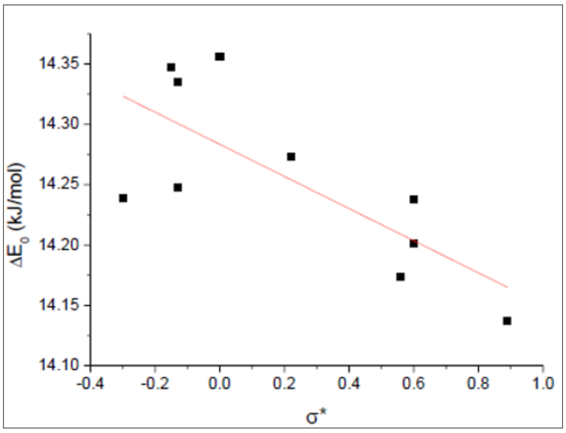


Figure 4: A linear correlation between ΔE_0 and σ^* ΔE_0= (14.28±0.02)-(0.13±0.04) Δ* (kJ/mol); R=0.70694; residual sum of squares=0.0220.

DFT calculated this activation energy by calculation of the energy difference between ground (dihedral angle, ϕ = 45^0) and transitional (dihedral angle, ϕ = 0^0) states. In other words, this method calculated the reaction as a concerted one-step reaction through a single transition state without a dramatic change in bond length of the C(1)-C(1′) pivot bond (Table 2) and (Figure 5). Therefore, ΔE_0 was equal to ΔE_{90} (rotation energy from physical properties) plus Δ Evib, where Δ Evib was the vibrational energy at the mass center near $\phi = 0^0$.

$$\Delta E_0 = \Delta E_{90} + E_{vib} \tag{3}$$

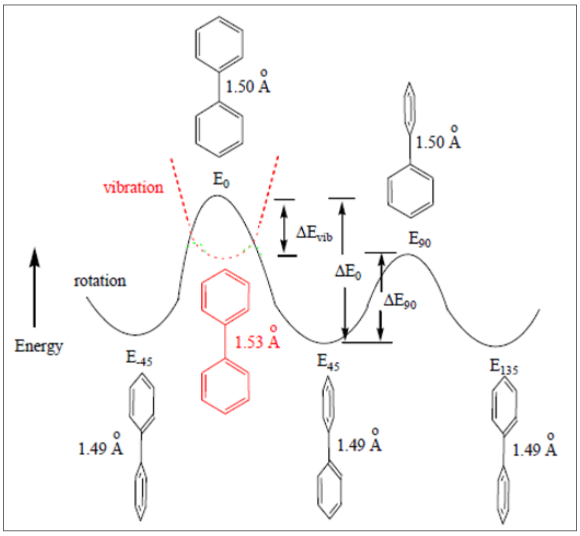


Figure 5: Relative energies and the C(1)-C(1′) pivot bond lengths for different conformations of biphenyl.

Table 2: Calculated the C(1)-C(1′) bond lengths of biphenyls for dihedral angles ϕ = 00, 450, and 900and the maximum bond length difference (Δx) for the C(1)-C(1′) bond stretching at ϕ = 00 (in Å).

Compound	C(1)-C(1′)	bond	Length	s
	ϕ =45⁰	ϕ =90⁰	ϕ =0⁰	
biphenyl	1.491	1.498	1.499	0.027
1	1.49	1.498	1.499	0.037
2	1.49	1.498	1.5	0.04
3	1.49	1.498	1.499	0.041
4	1.49	1.498	1.499	0.043
5	1.487	1.495	1.496	0.041

However, the transition state of any reaction could not be actually detective by any method because the life time of the transition state was too short. Thus, ΔE_0 of biphenyl from experiment was not the activation energy for a single step atropisomerization reaction (Figure 5). Instead, a two-step (two transition states and one intermediate) reaction was proposed for the rotation of biphenyl about its center axis from ϕ = -45^{0}to 45^0 through 0^0. At dihedral angle near 0∘, the principle of least motion [13] predicted that vibration (or stretching) of the pivot axis, the C(1)-C(1') bond would be more favorable than twisting of the bond. Vibrational energy (E_{vib}) could be expressed as Eq. (4), where Δ and k were the vibrational quantum number (Δ = 0, 1, 2, 3, ...) and force constant, respectively [12].

$$E_{vib} = (\Delta + 0.5)\ \hbar\ \left(k / m'\right)^{1/2} \tag{4}$$

Thus, vibrational energy was inversely proportional to the root of reduced mass. A linear correlation between $\Delta E_0 - \Delta E_{90}$ and (1/m')1/2 of biphenyl and compounds 1-10 was observed (Figure 6). Hence, both physical rotation and vibration (or stretching) of the C(1)-C(1') bond played important roles for rotation of biphenyl about the C(1)-C(1') pivot bond from ϕ = -45^0 to 45^0 near ϕ = 0^0. The differences in the C(1)-C(1') bond lengths for the stretching of biphenyl and compounds 1-10 near ϕ = 0^0(x's) were calculated to be 0.027-0.046 Å according to Hooke's law, $\Delta E_{vib} = (1/2)$ k Δ x^2 (Table 2). Hence, the equilibrium C(1)-C(1') bond length of the intermediate for rotation from ϕ = -45^0 to 45^0 near 0∘was about 1.53 Å (Figure 5). Thus, experimental ΔE_0 value of biphenyl (6.0 kJ/mol)1 was the about the calculated ΔE_{90} value (6.4 kJ/mol).

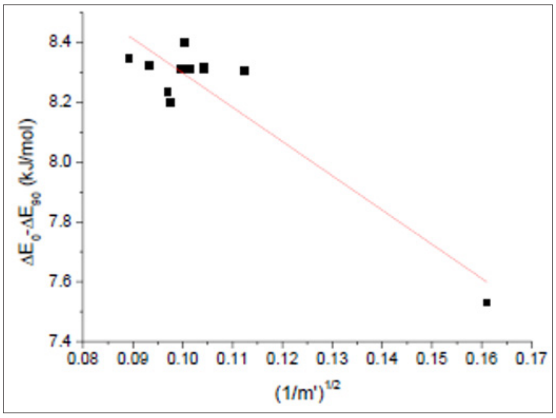


Figure 6: A linear correlation between $\Delta E_0 - \Delta E_{90}$ and $(1/m')^{1/2}$ of biphenyl and compounds 1-10. $\Delta E_0 - \Delta E_{90} = (9.4 \pm 0.2) - (11.5 \pm 1.5)(1/m')^{1/2}$ (kJ/mol); R=0.9187; residual sum of squares=0.08063.

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