



# Ab Initio Study of Atropisomers of Derivatives of N-Benzyl-2-phenylpyridinium Ions

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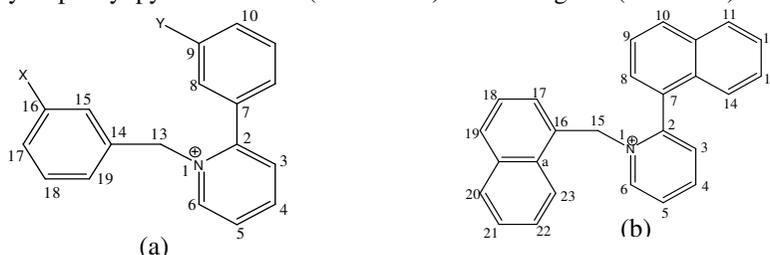
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**Abstract:** *Ab initio* calculation at RHF/6-31G<sup>\*</sup> level of theory for geometry optimization of conformers of *N*-benzyl-2-phenylpyridinium ions are reported. The series of electron-withdrawing and electron-donating groups have been replaced by 3-H phenyl and benzyl of *N*-benzyl-2-phenylpyridinium ions and the energy difference between the *syn*- and *anti*- forms discussed in terms of  $\pi$ - $\pi$  stacking.

**Keywords:** *Ab initio* calculations, Atropisomers, *N*-benzyl-2-phenyl pyridinium ions, Stacked conformer, Splayed conformer

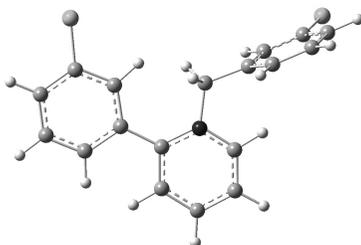
## Introduction

Atropisomers are stereoisomers resulting from hindered rotation about single bonds where the barrier to rotation is high enough to allow the isolation of the conformational isomers<sup>1</sup>. Among the non-covalent weak interactions,  $\pi$ - $\pi$  interactions between aromatic rings have attracted much attention due to their importance in many fields of science such as chemistry, biology and material science<sup>2</sup>. This interaction holds molecules together in natural and artificial supra molecules including DNA<sup>3</sup> and other biological systems<sup>4-10</sup>. In continuation of our work on  $\pi$ - $\pi$  interaction in atropisomers<sup>11,12</sup>, in the current work, the structural optimization of conformers of *N*-benzyl-2-phenyl pyridinium ions (models 1-7) are investigated (Scheme 1).



**Scheme 1.** The selected models: (a) Model 1: X, Y=H; Model 2: X, Y= Cl; Model 3: X, Y= OMe; Model 4: X, Y= CN; Model 5: X, Y= CF<sub>3</sub>; Model 6: X=CN, Y= OMe; (b) Model 7

It was found in solution and solid phases that these compounds preferred the conformation in which the benzyl groups would stack center to edge to the phenyl rings. This preference was relatively insensitive to electronic substituent effects on the benzyl groups<sup>13</sup>. The models exist as a mixture of *syn*- and *anti*- isomers. Interconversion of the isomers requires the phenyl ring rotate about the C<sub>2</sub>-C<sub>7</sub> (sp<sup>2</sup>-sp<sup>2</sup>) bond. Thus the phenyl ring will be resting as the same plane as pyridine in transition state (Figure 1).



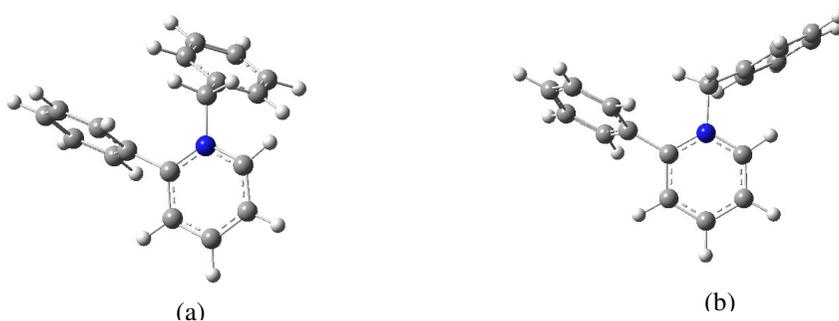
**Figure 1.** The transition state

## Experimental

*Ab initio* molecular orbital calculations were carried out using the Gaussian 1998 program<sup>14</sup>. The restricted Hartree-Fock calculations with the split-valence 6-31G\* basis set, which include a set of *d*-type polarization functions on all non-hydrogen atoms, were used<sup>15</sup>. The frequencies were scaled by a factor of 0.9135<sup>16</sup> and were used to compute zero-point vibrational energies.

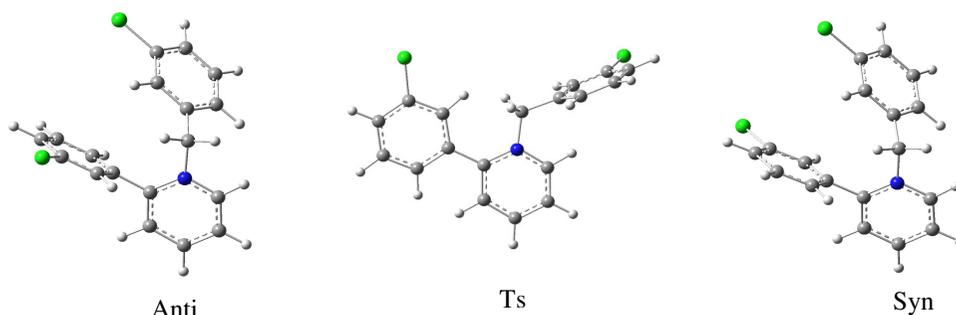
## Results and Discussion

At the first the structure of *N*-benzyl-2-phenyl pyridinium ion (model 1) was studied. For model 1, we have found two minima, one splayed and one stacked conformer (Figure 2)<sup>11</sup>.



**Figure 2.** Conformers of (a) Stacked and (b) Splayed

By replacing the various substitutions as electron-donating (-OMe), electron-withdrawing (-CF<sub>3</sub>, -CN), hindered (naphthyl) and halogen (-Cl), we studied the created models. These different substitutions cause some conflicts in electronic characteristics of the rings. It can be determined whether electrostatic interaction or dispersion forces are merely responsible to the effects on the distributions of the conformers. Rotation of aryl ring around the sp<sup>2</sup>-sp<sup>2</sup> bond connecting the pyridine ring generates the transition states. In the all transition states the substituted benzene ring is placed on with pyridine ring on the same plane and the substituted benzyl rings goes as far as possible (Scheme 2).



**Scheme 2.** Three conformers *N*-(3-chloro benzyl)-2-(3-chloro phenyl) pyridinium salt (model 2)

The values of dihedral angles of stacked and splayed conformers are summarized in Table 1.

**Table 1.** Comparison of dihedral angles in studied models (The angles are in degree)

Model	1	2	3	4	5	6	7
N1-C2-C7-C8 (stacked/ <i>anti</i> )	73.45	285.70	-	286.56	286.00	289.26	270.84
N1-C2-C7-C8 (stacked/ <i>syn</i> )	-	109.38	110.97	108.95	106.08	110.90	100.00
N1-C2-C7-C8 (splayed/ <i>anti</i> )	70.31	286.88	285.52	287.36	287.49	286.89	78.00
N1-C2-C7-C8 (splayed/ <i>syn</i> )	-	109.70	109.46	111.20	111.06	110.22	268.72
C2-N1-C13-C14 (stacked/ <i>anti</i> )	79.33	280.91	-	280.21	281.69	280.30	260.65
C2-N1-C13-C14 (stacked/ <i>syn</i> )	-	282.98	279.37	286.26	284.56	110.89	249.75
C2-N1-C13-C14 (splayed/ <i>anti</i> )	136.7	231.92	230.35	236.08	233.92	241.09	156.61
C2-N1-C13-C14 (splayed/ <i>syn</i> )	-	231.55	230.49	230.97	232.36	239.68	172.42

Our studied showed that in these models, dihedral angles of N1-C2-C7-C8 change between +73 to +289 ° (or -71°) in stacked *anti*-conformers and +100 to 109° in stacked *syn*-conformers to make  $\pi$ - $\pi$  interaction possible between two rings. The values of this angle have been faced between 1 to 5° in splayed conformers. Model 3 (with -OMe as an electron-donating substitution in both rings) does not stack in *anti*-conformer. Phenyl and benzyl ring polarized by electron-donating substituent (-OMe) which caused increasing the  $\pi$ - electron repulsion<sup>2</sup>.

The values of dihedral angles of C2-N1-C13-C14 in stacked *syn*- and *anti*- models are between +287 to +249° (or -73 to -111°). Due to positioning of substituted benzyl rings at splayed models (in both *syn*- and *anti*- conformers) the value of this angle is ranged between +230 to +241, except model 1 (Table 1).

According to calculations performed, splayed conformers have a little lower energy comparing to stacked conformers. The achieved result shows a clear indication of the presence

of  $\pi$ - $\pi$  interaction in stacked conformers. Otherwise, there must be much more difference between the energy of splayed and stacked conformers. The difference in stability in studied models with electron-withdrawing (Models 4 and 5) is less than models with electron-donating (Models 2 and 3) and non-substituted models (Models 1 and 7). The lowest difference in energy is in *syn*-conformer model 6; which proves there is greater  $\pi$ - $\pi$  interaction at this model than the others. The energies are given in Table 2.

**Table 2.** Energies of stacked and splayed conformers

Model	<i>Anti</i> , Stacked	<i>Anti</i> , Splayed	$E_{rel}$	<i>Syn</i> , Stacked	<i>Syn</i> , Splayed	$E_{rel}$
1 <sup>b</sup>	-745.2102	-745.2126	-1.5	-	-	-
2	-1662.9995	-1663.0017	-1.35	-1662.9993	-1663.0015	-1.39
3 <sup>c</sup>	-	-972.9769	0	-972.9739	-972.9769	-1.9
4	-928.6595	-928.6613	-1.0	-928.6591	-928.6606	-0.9
5	-1416.4415	-1416.4431	-0.9	-1416.4415	-1416.4428	-0.8
6	-950.8194	-950.8209	-0.93	-950.8199	-950.8208	-0.54
7	-1050.5118	-1050.5152	-2.1	-1050.5091	-1050.5147	-3.48

<sup>a</sup>Absolute values are in hartree and relative values are in kcal mol<sup>-1</sup>, <sup>b</sup>There is no *anti* or *syn* conformer. <sup>c</sup>There is no *anti* stacked conformer

In Table 3 absolute and relative energies between splayed and stacked conformers are given. According to gained data, in model 7 with naphthyl groups, the relative energy of stacked conformers is greater than splayed. Naphthyl has an area larger than benzyl and phenyl. So it showed the much stronger interaction than the other models. Moreover, in all models, except model 6, the *anti*-isomers are more stable than *syn*-isomers. In model 6, the *syn*-stacked isomer (+0.33 kcal mol<sup>-1</sup>) is more stable than the *anti*-isomer.

**Table 3.** Relative energies of stacked and splayed conformers

Model	<i>Anti</i> , Stacked	<i>Syn</i> , Stacked	$E_{rel}$	<i>Anti</i> , Splayed	<i>Syn</i> , Splayed	$E_{rel}$
1 <sup>b</sup>	-745.2102	-	-	-745.2126	-	-
2	-1662.9995	-1662.9993	-0.15	-1663.0017	-1663.0015	-0.1
3 <sup>c</sup>	-	-972.9739	-	-972.9769	-972.9769	-0.005
4	-928.6595	-928.6591	-0.28	-928.6613	-928.6606	-0.42
5	-1416.4415	-1416.4415	-0.01	-1416.4431	-1416.4428	-0.18
6	-950.81945	-950.8199	+0.33	-950.8209	-950.8208	-0.05
7	-1050.5118	-1050.5091	-1.69	-1050.5152	-1050.5147	-0.32

<sup>a</sup>Absolute values are in hartree and relative values are in kcal mol<sup>-1</sup>, <sup>b</sup>There is no *anti*- or *syn*-conformer. <sup>c</sup>There is no *anti*-stacked conformer

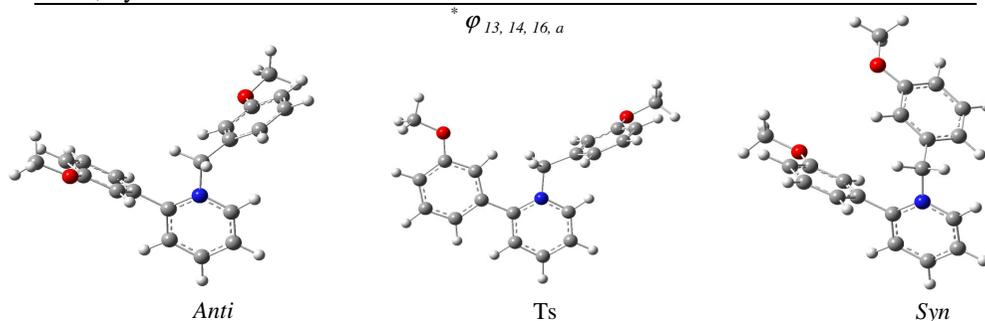
The rotational energy barriers for stacked isomers show that rapid interconversion of *syn*- and *anti*-atropisomers<sup>17</sup> can take place at room temperature (Table 4). Model 7 is the most hindered of the isomers studied and it is reasonable to assume that the bulk of the groups cause enough  $\pi$ - $\pi$  interaction to increase the rotational energy barrier and hence make the isomer separation possible at room temperature.

In models with electron-withdrawing groups, we can see the decrease of energy barrier (Models 2, 4 and 5) (Table 4). In model 3 the presence of electron-donating group (-OMe) caused increasing electron density on benzyl and phenyl rings. It also indicated increased the repulsion of  $\pi$ -electrons of ring. This repulsion causes the substituted benzyl and phenyl ring far away from each other, so the only stable *anti*-conformer of model 2 is splayed (Scheme 3).

**Table 4.** Total and relative energies, ZPVE and  $\phi_{11,12,14,15}$  for conformers of models 2-7. Total energies and ZPVE are in Hartree, relative energies are in kcal/mol and  $\phi_{11,12,14,15}$  is in degree

Models	HF/6-31G*// 6-31G*	E <sub>rel</sub>	ZPVE	$\phi_{11,12,14,15}$
2, Anti	-1662.9995737	0.0	1043716.37668	-13.06
2, Ts	-1662.9767867	14.29	1043702.62217	-95.37
2, Syn	-1662.9993249	0.16	1043716.18758	5.82
3, Anti	-972.9769829	0.0	610772.6342	-93.96
3, Ts	-972.9526296	15.28	610758.00502	-92.05
3, Syn	-972.9739246	1.92	610770.8241	1.19
4, Anti	-928.6595872	0.0	582921.23498	-15.92
4, Ts	-928.6362161	14.84	582904.25965	-96.54
4, Syn	-928.6591255	0.29	582920.87750	9.86
5, Anti	-1416.4415753	0.0	889017.2305	-13.59
5, Ts	-1416.4185631	14.44	889003.0762	-96.09
5, Syn	-1416.4415584	0.01	889017.2249	4.01
6, Anti	-950.81945836	0.33	596847.8124	-17.01
6, Ts	-950.79550995	15.36	596833.2292	-95.08
6, Syn	-950.81998779	0.0	596848.1636	-3.82
7, Anti	-1050.5118803	0.0	659443.98623	-7.79*
7, Ts	-1050.4489989	39.46	659405.06076	78.74*
7, Syn	-1050.509175	1.69	659442.23696	39.86*

\*  $\phi_{13,14,16,a}$



**Scheme 3.** Three conformers of *N*-(3-methoxy benzyl)-2-(3-methoxy phenyl)pyridinium ion

In all studied stacked conformers (except model 6), the *anti*- isomer is more stable than *syn*- isomer. The amount of this energy difference in model 5 is the least (0.01 kcal/mol) and in models 3 and 7 is the most (1.92 and 1.69 kcal/mol). The presence of electron-donating group (-OMe) in model 3 caused the *anti*-conformer be existing as splayed form. Consequently the difference in stability has been increased between *anti*-splayed isomer and *syn*-stacked isomer. The presence of bulky group (naphthyl) in model 7 increased the  $\pi$ - $\pi$  repulsion; therefore, in *syn*- isomer where the contact surface of naphthyl ring is more, the resulted conformer stability is less. Due to decreasing of electron density on benzyl and phenyl rings in models with electron-withdrawing groups, it causes a little difference in energy level. In model 6, the *syn*-isomer (0.0 kcal/mol) is more stable than the *anti*-isomer (0.33 kcal/mol). The *syn*-isomer has more stacked area relative to *anti*-isomer (Figure 3).



**Figure 3.** Stereo view of substituted benzyl and phenyl rings in stacked conformers of model 6

The computed gas phase energies of conformers of models 2-7 are reported in Table 4.

## Conclusion

The obtained results showed that, these models subsist in stacked and splayed conformers. While the splayed conformer has the priority over, the very low difference is indicated between stacked and splayed conformers. Whereas, there is low difference in energy barriers between stacked conformers of studied models, as a result the electrostatic interaction has small contribution on conformer's distribution compared to dispersion interactions. The effective  $\pi$ - $\pi$  interaction was proved by the less difference between energies of two conformers of stacked and splayed.

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