

Ab initio SCF study of the barrier to internal rotation in N,N-dimethylcinnamamides

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Dedicated to Academician Ivan Juchnovski on the occasion of his 70th birthday

Received January 28, 2008; Revised January 30, 2008

The barrier to internal rotation around the amide C–N bond in R–C₆H₄–CH=CH–C(O)N(CH₃)₂ (R = *p*-NO₂, *m*-NO₂, *m*-Cl, *p*-Cl, *m*-OCH₃, H, *p*-CH₃, *p*-OCH₃) was studied at the MP2(fc)/6-31+G**/6-31G* level of theory. The solvent effect was estimated using polarizable continuum model (PCM) and the free energies of activation were compared with the NMR data in CHCl₃. For all studied compounds the *anti* transition state (*anti* TS) is more stable and determines the rotational barrier. A linear relationship is established linking the barrier heights and the shift of C–N bond order difference between *anti* TS and ground state (GS) upon substitution in the aromatic ring.

Key words: N,N-dimethylcinnamamides, barrier to internal rotation, *ab initio* SCF study.

INTRODUCTION

The great interest for the amide functional group in chemistry is mainly related to its occurrence as a building block in peptides and proteins. The internal rotation about the amide C–N bond in amides and thioamides has been intensively studied experimentally by NMR spectroscopy in gas [1–7] and in the liquid phase [8]. The experimental results were used to judge theoretical methods of calculating barrier heights [9]. The origin of the C–N rotational barrier, its relation to amide resonance and its response to the medium have received much attention in the last years [10–25].

Recently, the electronic effect of polar substituents on the barrier of internal rotation around the amide carbon-nitrogen bond in *p*-substituted acetanilides [26, 27] and thioacetanilides [28] were studied at the B3LYP/6-31G(d,p) level. Several linear relationships were established linking the barrier heights with structural and electronic parameters that characterize the amide and thioamide grouping. The results obtained are consistent with the views for a classical amide resonance as being the origin of higher rotational barriers in thioamides than in amides.

Here we present our *ab initio* calculation of barrier to internal rotation about C–N bond in N,N-dimethylcinnamamides, which were studied by dynamic NMR spectroscopy [29, 30]. The aim of this study is

to analyze the influence of phenyl substituents remote effects on the barrier of internal rotation around the amide C–N bond in these compounds. On the other hand, the interest to cinnamamides, namely coumaric amides, increases in the last years because of potential antioxidant activity of these compounds [31, 32].

METHODS

The *ab initio* SCF calculations were performed using the package GAMESS [33]. The complete geometry optimization was carried out using the 6-31G* basis sets. The molecules were assumed to have C₁ symmetry in the ground state (GS) and C_S symmetry in the transition states (TS). The bond order analysis was done at the HF/6-31G* level of theory as it is implemented in program GAMESS for closed shells by Giambiagi [34] and Mayer [35]. For recent review about bond orders see ref. [36]. The energies were then calculated at the MP2(fc)/6-31+G**/6-31G* level of theory. In calculating the vibrational energies, the vibrational frequencies were scaled by 0.89 [37]. In each case 7 (TS) or 8 (GS) scaled frequencies below 500 cm⁻¹ were treated as rotations ($E = RT/2$) [37]. The imaginary frequency for the transition states is ignored in all thermodynamics calculations. The effect of solvent on the relative stabilities of the GS and TS was studied using the polarized continuum model (PCM) proposed by Tomasi *et al.* [38]. In our investigations only the electrostatic contributions were taken into account utilizing single point PCM calculations at HF/6-31G* level of theory.

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RESULTS AND DISCUSSION

Geometry optimization

The heavy-atom framework of the studied molecules in GS was found to be essentially planar and close to C_s symmetry. The transition state geometries of the studied amides (Fig. 1) were optimized in C_s symmetry. This approach usually yields transition states, but for some of our structures additional refining of saddle point was necessary in order to locate TS structure with only one imaginary frequency. The calculated energies for GS, *anti* and *syn* TS, are presented in Table 1. The *anti* TS is much more stable in all cases. Therefore, *anti* TS of the studied compounds give the main contribution to the rotational barrier.

The most significant structural changes in the process of rotation towards the transition states are

that the nitrogen is pyramidalized and the C–N bond lengthens from 1.357–1.361 to 1.427–1.431 Å (Table 2). The C=O bond length shortens by 0.01–0.02 Å only, which indicates that the carbonyl group is relatively unaffected by this rotation. The C–C bond between carbonyl group and double bond decreases also slightly in the process of rotation from GS to *anti* TS. This can be explained by the decrease of conjugation. The C=C double bond is almost not affected by the rotation.

In the case of *m*-NO₂, *m*-Cl, *m*-OCH₃ derivatives, they are two conformations depending on the orientation of aryl substituent against C=C double bond. The more stable conformation of *m*-NO₂ and *m*-Cl is the *synclinal* conformation, while in case of *m*-OCH₃ derivative the *antiperiplanar* conformation is more stable.

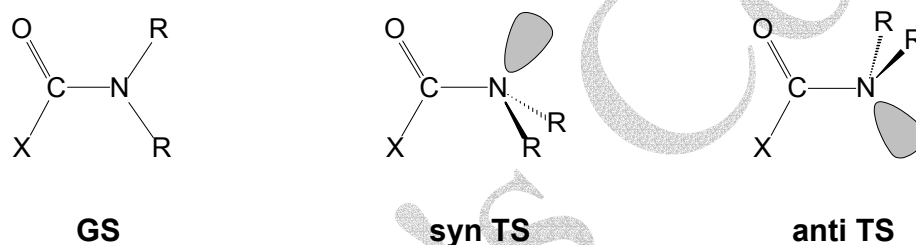


Fig. 1. Conformations of the studied amides $X = R-C_6H_4-CH=CH$
($R = p-NO_2, m-NO_2, m-Cl, p-Cl, m-OCH_3, H, p-CH_3, p-OCH_3$)

Table 1. Calculated Electronic energies E_e^o for the studied amides $RC_6H_4-CH=CH-CON(CH_3)_2$ in Hartrees.

R	State	ZPE ^b	HF/6-31G*	MP2(fc)/6-31+G**/6-31G*	PCM/6-31G* ($\epsilon = 4.9$) ^c
<i>p</i> -NO ₂	GS	132.54	-756.898270	-759.204688	-9.025
<i>p</i> -NO ₂	<i>anti</i> TS	132.28	-756.879231 ^a	-759.183975 ^a	-7.799
<i>p</i> -NO ₂	<i>syn</i> TS	132.10	-756.872329	-759.178001	-9.312
<i>m</i> -NO ₂	GS	132.54	-756.898605	-759.203737	-8.943
<i>m</i> -NO ₂	<i>anti</i> TS	132.30	-756.879322 ^a	-759.183409 ^a	-7.887
<i>m</i> -NO ₂	<i>syn</i> TS	132.12	-756.872720	-759.177756	-9.186
<i>m</i> -Cl	GS	124.75	-1012.326958	-1014.222284	-6.525
<i>m</i> -Cl	<i>anti</i> TS	124.52	-1012.308192 ^a	-1014.202267 ^a	-5.340
<i>m</i> -Cl	<i>syn</i> TS	124.33	-1012.301472	-1014.196209	-6.735
<i>p</i> -Cl	GS	124.74	-1012.327078	-1014.221772	-6.566
<i>p</i> -Cl	<i>anti</i> TS	124.53	-1012.308572 ^a	-1014.202103 ^a	-5.329
<i>p</i> -Cl	<i>syn</i> TS	124.33	-1012.301713	-1014.195886	-6.748
<i>m</i> -OCH ₃	GS	150.12	-667.307444	-669.382656	-7.290
<i>m</i> -OCH ₃	<i>anti</i> TS	149.89	-667.288887 ^a	-669.362644 ^a	-6.183
<i>m</i> -OCH ₃	<i>syn</i> TS	149.71	-667.282214	-669.357077	-7.443
H	GS	130.38	-553.427464	-555.187857	-7.121
H	<i>anti</i> TS	130.18	-553.409162 ^a	-555.168490 ^a	-5.711
H	<i>syn</i> TS	129.99	-553.402390	-555.162334	-7.390
<i>p</i> -CH ₃	GS	146.68	-592.465061	-594.359397	-6.362
<i>p</i> -CH ₃	<i>anti</i> TS	146.50	-592.446874 ^a	-594.340710 ^a	-5.197
<i>p</i> -CH ₃	<i>syn</i> TS	146.31	-592.440104	-594.334565	-6.570
<i>p</i> -OCH ₃	GS	150.15	-667.308843	-669.381867	-7.454
<i>p</i> -OCH ₃	<i>anti</i> TS	149.96	-667.290747 ^a	-669.363369 ^a	-6.327
<i>p</i> -OCH ₃	<i>syn</i> TS	149.78	-667.283988	-669.357231	-7.687

a - more stable TS; b - ZPE is reported in kcal/mol at the HF/6-31G* level scaled by 0.89; c - Energy change from gas phase to solvent in kcal/mol.

Table 2. Selected bond lengths, bond orders and imaginary frequencies calculated at HF/6-31G* level of theory for the studied amides R-C₆H₄-CH=CH-CON(CH₃)₂.

R	State	r_{C-N} , Å	$r_{C=O}$, Å	$r_{C=C}$, Å	r_{C-C} , Å	Bond Order C-N	ν , cm ⁻¹
<i>p</i> -NO ₂	GS	1.357	1.206	1.325	1.498	1.054	
<i>p</i> -NO ₂	<i>anti</i> TS	1.431	1.192	1.327	1.487	0.929	104.0i
<i>p</i> -NO ₂	<i>syn</i> TS	1.427	1.188	1.326	1.496	0.990	87.3i
<i>m</i> -NO ₂	GS	1.357	1.207	1.325	1.497	1.054	
<i>m</i> -NO ₂	<i>anti</i> TS	1.431	1.192	1.327	1.486	0.930	103.3i
<i>m</i> -NO ₂	<i>syn</i> TS	1.427	1.188	1.327	1.495	0.944	88.0i
<i>m</i> -Cl	GS	1.358	1.207	1.326	1.495	1.048	
<i>m</i> -Cl	<i>anti</i> TS	1.432	1.193	1.328	1.484	0.926	101.8i
<i>m</i> -Cl	<i>syn</i> TS	1.429	1.189	1.327	1.493	0.943	87.4i
<i>p</i> -Cl	GS	1.359	1.207	1.326	1.495	1.046	
<i>p</i> -Cl	<i>anti</i> TS	1.433	1.193	1.329	1.483	0.925	101.0i
<i>p</i> -Cl	<i>syn</i> TS	1.429	1.189	1.328	1.492	0.941	87.3i
<i>m</i> -OCH ₃	GS	1.359	1.207	1.326	1.494	1.044	
<i>m</i> -OCH ₃	<i>anti</i> TS	1.434	1.193	1.329	1.482	0.924	101.2i
<i>m</i> -OCH ₃	<i>syn</i> TS	1.430	1.189	1.328	1.491	0.940	86.4i
H	GS	1.360	1.207	1.327	1.493	1.043	
H	<i>anti</i> TS	1.434	1.193	1.329	1.481	0.923	99.8i
H	<i>syn</i> TS	1.430	1.189	1.329	1.490	1.003	86.7i
<i>p</i> -CH ₃	GS	1.360	1.207	1.328	1.492	1.041	
<i>p</i> -CH ₃	<i>anti</i> TS	1.434	1.194	1.330	1.480	0.922	99.0i
<i>p</i> -CH ₃	<i>syn</i> TS	1.431	1.189	1.329	1.489	0.938	86.6i
<i>p</i> -OCH ₃	GS	1.361	1.208	1.328	1.491	1.039	
<i>p</i> -OCH ₃	<i>anti</i> TS	1.435	1.194	1.331	1.479	0.922	97.6i
<i>p</i> -OCH ₃	<i>syn</i> TS	1.431	1.190	1.330	1.488	0.937	86.4i

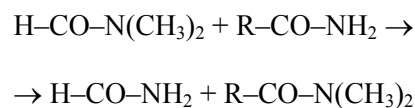
Comparison of calculated activation parameters and experimental data

Calculation of the vibrational frequencies confirmed the assignment of the *anti* and *syn* forms as transition states and allowed computation of the enthalpy, entropy and free energy changes at 298K. The thermodynamic results for the isomerisation of the studied amides are presented in Table 3. In the present case, $\Delta H^\ddagger(0\text{ K})$ is calculated as a sum of the changes in the energies and the zero-point vibrational energy (ZPE) differences while $\Delta H^\ddagger(298\text{ K})$ involves a correction for the difference in heat capacity of GS and TS. The scaled frequencies were used also for the entropy calculation. From the calculated free energies $\Delta G^\ddagger(298\text{ K})$ and using Eyring equation, one obtains the respective rate constants for both *syn* and *anti* TS. The effective rate constant is a sum of the rate constants through the two transition states. In the studied molecules the contribution of *syn* TS is negligible. The effective free energy $\Delta G_{\text{eff}}^\ddagger(298\text{ K})$, which is in turn calculated from the effective rate constant, can be corrected by the energy change from gas phase to solvent (Table 1) and compared with NMR data in CHCl₃. It is seen from Table 3 that the rotational barriers for the studied compounds in chloroform were reproduced very satisfactory at this level of theory. There is also a good relation between

experimental activation entropies, $\Delta S^\ddagger(298\text{ K})$ and calculated ones for *m*-Cl, *m*-OCH₃ and nonsubstituted cinnamamide. Recently, the barriers of rotation around C-N bond in gas phase of simple amides and tioamides were well reproduced at MP2(fc)/6-31+G**/6-31G* level of theory, as well [20, 21, 25].

Effect of substituents on the rotational barrier

In order to study the effect of nonbonded interactions on the barrier heights we examined the following reaction both in ground state and in the two possible transition states:



This approach was explored before to estimate the difference in repulsion between R and the CH₃ group, the difference in repulsion between R and the amide lone pair and the difference in repulsion between oxygen and amide lone pair [20, 21, 25]. The calculated electronic energies of the studied amides RC₆H₄-CH=CH-CONH₂, ZPE and ΔH° of the above model reaction are presented in Table 4. All values for ΔH° are small enough to conclude that there is not significant difference in nonbonded interactions in GS and TS's and these results are not able to explain the difference in barrier heights.

Table 3. Thermodynamic results for the isomerization of the studied amides $R-C_6H_4-CH=CH-CON(CH_3)_2$ in the gas phase and in $CHCl_3$.

R	Parameter	anti TS	syn TS	Experimental
<i>p</i> -NO ₂	$\Delta H^\ddagger(0K)$	12.74	16.31	
	$\Delta H^\ddagger(298K)$	11.76	15.18	$16.9 \pm 0.4^a (18.13 \pm 0.1)^b$
	$\Delta S^\ddagger(298K)$	-7.42	-8.39	$0.4 \pm 1.3^a (3.99 \pm 0.5)^b$
	$\Delta G^\ddagger(298K)$	13.97	17.68	
	$\Delta G_{eff}^\ddagger(298K)$	13.96 (15.35) ^c		$16.80 \pm 0.06^a (16.94 \pm 0.01)$
<i>m</i> -NO ₂	$\Delta H^\ddagger(0K)$	12.52	15.88	
	$\Delta H^\ddagger(298K)$	11.55	14.77	16.5 ± 0.8^a
	$\Delta S^\ddagger(298K)$	-8.51	-7.04	-0.1 ± 2.6^a
	$\Delta G^\ddagger(298K)$	14.09	16.87	
	$\Delta G_{eff}^\ddagger(298K)$	14.08 (15.29) ^c		16.58 ± 0.07^a
<i>m</i> -Cl	$\Delta H^\ddagger(0K)$	12.33	15.94	
	$\Delta H^\ddagger(298K)$	11.36	14.24	14.0 ± 0.3^a
	$\Delta S^\ddagger(298K)$	-8.90	-16.63	-7.7 ± 1.1^a
	$\Delta G^\ddagger(298K)$	14.01	21.59	
	$\Delta G_{eff}^\ddagger(298K)$	14.01 (15.34) ^c		16.33 ± 0.02^a
<i>p</i> -Cl	$\Delta H^\ddagger(0K)$	12.13	15.83	
	$\Delta H^\ddagger(298K)$	11.15	14.72	$17.9 \pm 1.4^a (17.15 \pm 0.1)^b$
	$\Delta S^\ddagger(298K)$	-10.02	-8.44	$5.6 \pm 4.6^a (2.16 \pm 0.4)^b$
	$\Delta G^\ddagger(298K)$	14.14	17.24	
	$\Delta G_{eff}^\ddagger(298K)$	14.13 (15.58) ^c		$16.25 \pm 0.07^a (16.51 \pm 0.01)^b$
<i>m</i> -OCH ₃	$\Delta H^\ddagger(0K)$	12.33	15.64	
	$\Delta H^\ddagger(298K)$	11.36	14.53	14.4 ± 0.7^a
	$\Delta S^\ddagger(298K)$	-7.67	-8.29	-5.9 ± 2.2^a
	$\Delta G^\ddagger(298K)$	13.65	17.00	
	$\Delta G_{eff}^\ddagger(298K)$	13.64 (15.02) ^c		16.19 ± 0.06^a
H	$\Delta H^\ddagger(0K)$	11.95	15.63	
	$\Delta H^\ddagger(298K)$	10.99	14.52	$14.1 \pm 0.6^a (17.22 \pm 0.1)^b$
	$\Delta S^\ddagger(298K)$	-10.77	-9.35	$-6.8 \pm 1.9^a (2.76 \pm 0.2)^b$
	$\Delta G^\ddagger(298K)$	14.20	17.31	
	$\Delta G_{eff}^\ddagger(298K)$	14.19 (15.60) ^c		$16.16 \pm 0.04^a (16.39 \pm 0.01)$
<i>p</i> -CH ₃	$\Delta H^\ddagger(0K)$	11.55	15.21	
	$\Delta H^\ddagger(298K)$	10.57	14.10	$17.1 \pm 2.1^a (18.04 \pm 0.2)^b$
	$\Delta S^\ddagger(298K)$	-11.25	-10.18	$4.8 \pm 7.1^a (5.89 \pm 0.6)^b$
	$\Delta G^\ddagger(298K)$	13.92	17.14	
	$\Delta G_{eff}^\ddagger(298K)$	13.91 (15.33) ^c		$15.72 \pm 0.09^a (16.29 \pm 0.01)^b$
<i>p</i> -OCH ₃	$\Delta H^\ddagger(0K)$	11.42	15.09	
	$\Delta H^\ddagger(298K)$	10.44	13.98	$16.9 \pm 0.2^a (17.8 \pm 0.1)^b$
	$\Delta S^\ddagger(298K)$	-10.53	-9.66	$3.4 \pm 0.9^a (5.84 \pm 0.4)^b$
	$\Delta G^\ddagger(298K)$	13.58	16.86	
	$\Delta G_{eff}^\ddagger(298K)$	13.57 (14.93) ^c		$15.93 \pm 0.04^a (16.06 \pm 0.01)^b$

a - Solution data ref. [29]; b - Solution data ref. [30]; c - Values in parenthesis includes $CHCl_3$ solvation correction of energy from Table 1.

The calculated free energy of activation $\Delta G^\ddagger(298K)$ for *anti* TS increases with increasing electron withdrawal of the phenyl substituent and follows almost the same trend as the experimental free energies of activation (Table 3).

The remote substituent effect in the studied compound has a pure electronic origin and therefore can be estimated by the influence on the bond order of the C–N bond. The calculated bond orders for both ground and transition states are presented in Table 2. Figure 2 presents the relationship between C–N bond order difference and calculated energy

barrier ΔE of the studied amides, $\Delta E = E(\text{anti TS}) - E(\text{GS})$. The correlation coefficient is not perfect ($\rho = 0.924$), but we have to take into account the shortness of the basis set and the relative low level of theoretical calculations. The experimental free energies didn't correlate better with the C–N bond order differences. This fact can be explained with the experimental errors and relative low remote substituent effects. The attempt to correlate the $\Delta G_{eff}^\ddagger(298 K)$ values with three sets of empirical reactivity parameter leads to correlation coefficients between 0.902 and 0.953 [29].

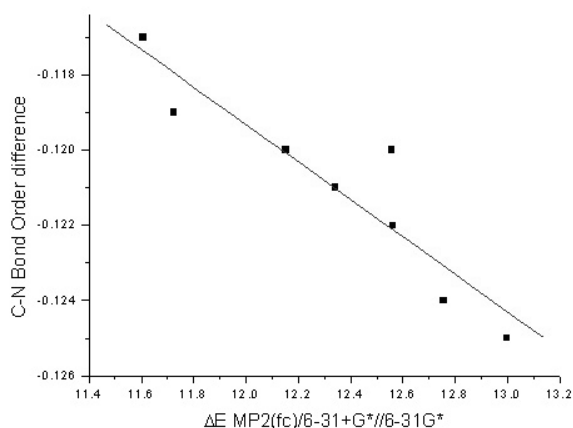


Fig. 2. Relationship between C–N bond order difference (*anti*-TS – GS) and calculated ΔE of the studied amides, $\Delta E = E(\textit{anti}\text{-TS}) - E(\textit{GS})$, $y = -0.0595x - 0.00499$

Table 4. Calculated electronic energies E_e^0 for the studied amides $R-C_6H_4-CH=CH-CONH_2$ in Hartrees and ΔH^0 of following reaction: $H-CO-N(CH_3)_2 + X-CO-NH_2 \rightarrow H-CO-NH_2 + X-CO-N(CH_3)_2$

R	State	ZPE ^b	HF/6-31G*	ΔH^0 , kcal/mol
<i>p</i> -NO ₂	GS	98.61	-678.846099	-0.18
<i>p</i> -NO ₂	<i>anti</i> TS	98.39	-678.823888 ^a	-0.06
<i>p</i> -NO ₂	<i>syn</i> TS	98.22	-678.816434	-0.28
<i>m</i> -NO ₂	GS	98.51	-678.846494	-0.04
<i>m</i> -NO ₂	<i>anti</i> TS	98.42	-678.823937 ^a	-0.09
<i>m</i> -NO ₂	<i>syn</i> TS	98.24	-678.817022	-0.16
<i>m</i> -Cl	GS	90.84	-934.275021	-0.05
<i>m</i> -Cl	<i>anti</i> TS	90.64	-934.252896 ^a	-0.04
<i>m</i> -Cl	<i>syn</i> TS	90.46	-934.245904	-0.08
<i>p</i> -Cl	GS	90.87	-934.275183	-0.07
<i>p</i> -Cl	<i>anti</i> TS	90.65	-934.253320 ^a	-0.01
<i>p</i> -Cl	<i>syn</i> TS	90.46	-934.246129	-0.09
<i>m</i> -OCH ₃	GS	116.26	-589.255656	-0.01
<i>m</i> -OCH ₃	<i>anti</i> TS	116.01	-589.233639 ^a	-0.01
<i>m</i> -OCH ₃	<i>syn</i> TS	115.85	-589.226786	-0.01
H	GS	96.54	-475.375722	0
H	<i>anti</i> TS	96.31	-475.353943 ^a	0
H	<i>syn</i> TS	96.13	-475.346971	0
<i>p</i> -CH ₃	GS	112.85	-514.413359	0.02
<i>p</i> -CH ₃	<i>anti</i> TS	112.63	-514.391672 ^a	0.01
<i>p</i> -CH ₃	<i>syn</i> TS	112.45	-514.384741	0.04
<i>p</i> -OCH ₃	GS	116.33	-589.257170	0.02
<i>p</i> -OCH ₃	<i>anti</i> TS	116.10	-589.235553 ^a	0.01
<i>p</i> -OCH ₃	<i>syn</i> TS	115.92	-589.228691	0.08

a - more stable TS; b - ZPE is reported in kcal/mol at the HF/6-31G* level scaled by 0.89

CONCLUSION

The free energy of activation of substituted cinnamamides were reproduced very well using MP2(fc)/6-31+G**/6-31G* energies and PCM/6-31G* energy change from gas phase to chloroform. For all studied compounds the *anti* transition state (*anti* TS) is more stable and determines the rotational barrier. The remote effect of phenyl substituents in the studied compound has pure electronic

origin, which was demonstrated by the relationship between C–N bond order difference and calculated energy barrier.

Acknowledgements: Financial support by the Bulgarian National Science Foundation (Grant X-1408) is acknowledged with gratitude. Thanks are due to Dr. Valentin Dimitrov for the inspiration of this study.

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AB INITIO SCF ИЗСЛЕДВАНЕ НА БАРИЕРА НА ВЪТРЕШНА РОТАЦИЯ В
N,N-ДИМЕТИЛКАНЕЛЕНИ АМИДИ

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Посветена на акад. Иван Юхновски по повод на 70-та му годишнина

Постъпила на 28 януари 2008 г.; Преработена на 30 януари 2008 г.

(Резюме)

Барьера на вътрешна ротация около amidната C–N връзка в R–C₆H₄–CH=CH–C(O)N(CH₃)₂ (R = *p*-NO₂, *m*-NO₂, *m*-Cl, *p*-Cl, *m*-OCH₃, H, *p*-CH₃, *p*-OCH₃) е изследвана на MP2(fc)/6-31+G*//6-31G* ниво на теорията. Ефекта на разтворителя е оценен чрез модела на поляризиран континуум (PCM) и свободната енергия на активиране е сравнена с ЯМР данните в CHCl₃. За всички изследвани съединения анти преходното състояние (*anti* TS) е по-стабилно и определя ротационния бариер. Установена е линейна зависимост свързваща височината на бариера и промяната в разликата на C–N порядъка на връзката между *anti* TS и основно състояние (GS) при заместване в ароматното ядро.