JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 782–786
Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.540

Short Communication

Enantiomerization of bridged 1,1′-binaphthyls

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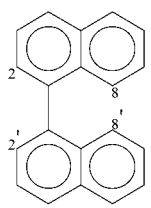
Received 3 March 2002; revised 14 May 2002; accepted 16 May 2002

ABSTRACT: The activation energy for the isomerization of 1,1′-binaphthyl in which positions 2 and 2′ are bridged at by an —O—CH_2—O— unit was calculated at various computational levels. AM1 gave good agreement with the experimental results. The transition-state structure was found to be entirely different from that calculated for the non-bridged parent compound: whereas the latter has C_2 symmetry, the former has C_s symmetry. The C_s symmetry transition state for the non-bridged parent compound was also located and found to be ca 6 kcal mol^{-1} higher than the C_2 one. However, in the bridged compound, the inclusion of the bridge counterbalanced this by raising the energy of the ground state, leaving the activation energy essentially unchanged. The isomerization of optically active bridged 1,1′-binaphthyls bearing linear polyphenyl rods of varying length, at positions 6 and 6′, was recently employed as a probe to gain information on the effect of rubber and glassy polymers on reaction rates. The model showed that the rod segments of these molecules traverse long distances in order to reach the transition state, which was consistent with a strong rod length dependence on racemization of the bridged binaphthyls in the glassy state. However, the present results demonstrate an unexpected twisting motion in the racemization process, suggesting that the appended oligophenyl rods are displaced to about half the distance previously expected. This may contribute in part to the experimental observation in the rubbery state where the microviscosity affects the racemization as a function of the appended rods far less than expected. AM1 results also gave reasonable agreement with the experimental ponderal effect consistent with the prior conclusion of force constant independence of rod length for twisting about the 1,1′ bonds. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: 1,1′-binaphthyls; enantiomerization

INTRODUCTION

Owing to a high barrier to rotation about the 1,1′ bond, 1,1′-binaphthyl (**1**), exists as two separable enantiomers.



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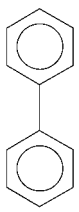

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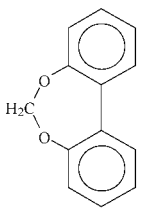

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The isomerization process converting one enantiomer into the other has been thoroughly studied both experimentally and theoretically.[1–14] Two possible paths for enantiomer interconversion are to be considered. One proceeds via a transition state which apposes the hydrogens at positions 8 and 8′ and those at positions 2 and 2′ (the *syn*-TS), whereas the other involves a transition state apposing the hydrogens at positions 2 and 8′ and those at positions 8 and 2′ (the *anti*-TS). In the case of **1** the energy of the anti transition state is slightly lower than that of the *syn*-TS. Bridging positions 2 and 2′ leave the *syn*-TS as the sole option. Such bridged 1,1′-binaphthyls were recently used[15,16] in order to evaluate medium and viscosity effect on the isomerization rate. Surprisingly, the isomerization rates of **1** to which oligophenyl rods of various lengths were attached at positions 6 and 6′, while causing large differences in the racemization rates in the glassy state of polymers,[15] showed far less dependence on the microviscosity of the rubbery polymers in which the isomerizations were performed. In the rubbery state[15] the apparent activation energies were found to be similar to those measured in decalin, a solvent of low viscosity.

Another important result was that a change in the length of the rods, and therefore also in their mass, affected the isomerization rates: the greater the mass, the lower was the reaction rate. These interesting results stimulated us to explore computationally the isomerization of 1,1′-binaphthyl and its 2,2′-bridged derivatives.

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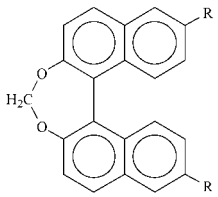
Table 1. AM1-computed energies and kinetic parameters at 423 K



	R
BN	H
BN1	phenyl
BN2	biphenyl

Compound	*E* ground state (a.u.)	*E* transition state (a.u.)	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)	10^3k (s^{-1})
BN	0.042518	0.090425	29.17	−3.67	1.18
BN1	0.123779	0.171495	29.06	−4.22	1.04
BN2	0.204881	0.252488	28.98	−4.65	0.91

RESULTS AND DISCUSSION

Methods

Using Gaussian 98,[17] we calculated the activation energies for the isomerization of 2,2′-O—CH_2—O—bridged 1,1′-binaphthyl (**BN**) at several levels of theory. After correction for zero point energy, the activation energies obtained are 37.86 kcal mol^{-1} (B3LYP/6–31G*),[18] 25.34 kcal mol^{-1} (PM3) and 29.43 kcal mol^{-1} (AM1) (1 kcal = 4.184 kj). The experimentally measured activation energy is 33 kcal mol^{-1}. Thus, both AM1 and B3LYP/6–31G* gave results which were close to the experimentally determined value,[15] with the AM1 method being slightly better. Because of this and because the semi-empirical method was much less time consuming, we employed AM1 in the present study.

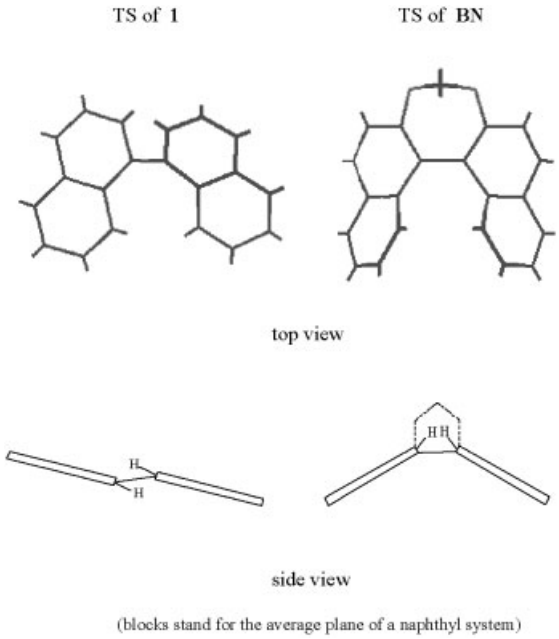
All stationary points were characterized by frequency analysis.

Effect of the bridge

The AM1-computed energies for the BN series are given in Table 1. Surprisingly, the bridge has only a marginal effect on the activation energy when compared with the *syn* isomerization path of 1,1′-binaphthyl. As can be seen from Table 1, the activation energy for BN is 29 kcal mol^{-1}, whereas that reported by Schlegel *et al.* (AM1 calculations)[14] for the *syn* path of the parent binaphthyl is 29.5 kcal mol^{-1}. On the other hand, the bridge induced a drastic effect on the transition-state structure. Whereas the transition state for the isomerization of the parent molecule has C_2 symmetry, that for the bridged molecule has C_s symmetry (Scheme 1).

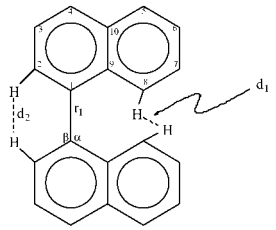
In order to clarify why the effect of the bridge on the isomerization barrier is marginal, we computed the activation energies, at the AM1 level, for the isomerization of several model compounds: biphenyl (**2**), bridged biphenyl (**3**) and 1,1′-binaphthyl itself (**1**). For the latter molecule the findings for the *syn*-TS structure fully reproduced the literature[14] AM1 calculations.

The results are presented in Table 2. In addition, we calculated the C_s symmetric transition state for **1** (which is similar to that of **BN** without the bridge; see Scheme 1). The activation energy for the isomerization of **2** is 1.5 kcal mol^{-1}. Introducing the bridge (**3**), as for the binaphthyl system, did not have much effect on the activation energy (the activation energy is 0.05 kcal mol^{-1}) (the difference between the $\Delta H^{\neq}$ for **2** and **3** is within the reliability range of the computational method) or change much the geometries involved. In the next step, we re-examined the binaphthyl system. The symmetric transition state for the isomerization of **1** where the binaphthyl units adopt C_s symmetry was indeed observed. However, the activation energy going



Scheme 1

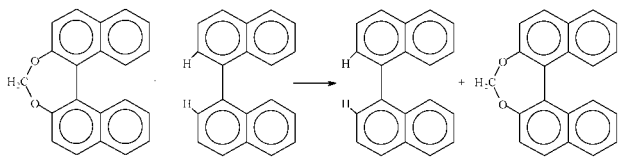
Table 2. AM1-computed geometric parameters and heats of formation



Compound		r_1	α	β	Dihedral angle 9,1, 1′,9′ (°)	Dihedral angle 2,1,1′,2′ (°)	d_1	d_2	Heat of formation (a.u.)[a]	$\Delta H^{\neq}$ (kcal mol^{-1})
1	GS	1.469	120.4	119.8	112.0	110.0	4.150	3.950	0.453741	29.0
	TS	1.482	112.0	131.3	53.0	36.0	1.663	2.291	0.499964	
2	GS	1.462	120.4	120.4	40.6	40.6		2.341	0.280456	1.5
	TS	1.465	121.2	121.2	0.0	0.0		1.889	0.282792	
3	GS	1.462	118.6[b]	125.1[b]	21.4	22.0			0.199672	0.05
	TS	1.466	119.2	125.6	0.0	0.0			0.199751	
BN	GS	1.466	123.5	118.1	52.1	44.8	2.590		0.377528	29.2
	TS	1.464	124.0	121.0	0.0	0.0	1.694		0.424017	

[a] at 150 °C.
[b] Average value of α and α' (differ by 2°).

through this transition state was 35.2 kcal mol^{-1}, ca 6 kcal mol^{-1} higher than that for the C_2 transition state path. Hence it would seem that the symmetry imposed on the binaphthyl unit at the transition state for the isomerization of **BN** is in fact counterproductive. However, in **BN** the bridge whose presence induces a C_s symmetric transition state results in lowering of the activation energy from 35.2 to 29 kcal mol^{-1}. It therefore remains to be determined whether its major role is in destabilizing the ground state or stabilizing the transition state. To determine this, we recalculated the ground- and transition-state structures of **BN**, replacing the bridge with hydrogens at positions 2 and 2′ while keeping all other geometric parameters frozen, optimizing only the position of the two added hydrogens. Depicted in Scheme 2 is the isodesmic reaction in which the core binaphthyl system retains the corresponding geometries of **BN** in the ground and the transition states. This isodesmic reaction is exothermic ($\Delta E = -7.5$ kcal mol^{-1}), clearly indicating that the bridge destabilizes the ground state.



GS	TS	GS	TS
Fully optimized	**BN** transition state with core frozen, bridge removed and the replacement H positions optimized	**BN** ground state with core frozen, bridge removed and the replacement H positions optimized	Fully optimized
0.042518 a.u.	0.204101 a.u.	0.144177 a.u.	0.090425 a.u.

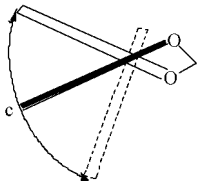
Scheme 2

Path to the transition state

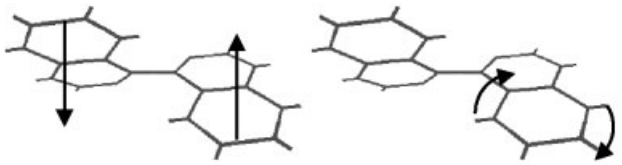
It has been suggested[15,16] that in the isomerization of bridged 1,1′-binaphthyls to which polyphenyl rods were attached, the longer rods have to sweep across longer distances in the medium and, since this motion will be hindered by the solvent, a dependence on the transition from rubbery to the glassy state[15] and on the microviscosity of the rubbery state[16] might be observed. Table 3 shows the distance traversed, according to Ref. 15, by a terminal hydrogen of one of the polyphenyl rods relative to the other in order to reach the transition state. Thus, for example, for **BN2**, the total travel distance of the terminal H is 23.1 Å, implying that on its way to the transition state, this hydrogen will have to cover a distance (c/2) of 11.55 Å. Table 3 also presents our AM1-computed distances between the two terminal hydrogens in the ground states and in the transition states of the different **BN**s, and the distances that these hydrogens are displaced in reaching the transition state (the data for **BN5**, a rod of five *p*-phenyl groups, are obtained by simple geometric extrapolation from the other derivatives). The data show that these distances, which should be considered as the lower essential limit, are about half of those estimated previously.[15]

Table 3. The distances (r) between the terminal hydrogen atoms of the polyphenyl rods of the various **BN** systems and the distance by which one of them is displaced relative to the other in order to reach the transition state according to the two models

Compound	r at the ground state (Å)	r at the transition state (Å)	Difference (Å)	$c/2$[a] (Å)
BN	8.44	7.03	1.41	4.4
BN1	14.09	10.81	3.28	8.0
BN2	19.74	14.60	5.14	11.5
BN5	36.67	25.95	10.72	22.3



[a] Ref. 15.



Scheme 3

The differences in the results between the present study and the previous study[15] stem from the differences in the visualization of the path leading from the ground state to the transition state. The motion envisioned by Green *et al.*[15] is associated with a scissoring vibration [see the sketch in Table 3 and Scheme 3(a); the O—CH_2—O bridge at the rear has been omitted for clarity]. However, on the basis of the present results we suggest that the transition-state structure for **BNX** (see Scheme 1) is reached by a rotation of one naphthyl unit around an axis roughly going through C-2 and C-6 (Scheme 3). This rotation is coupled with a distortion which distances the hydrogens in positions 8 and 8′ from each other. The latter motion is responsible for the displacement of the polyphenyl rods that we observed (Table 3) and which is about half the distance suggested previously.[15]

Finally, it is worthwhile mentioning that our calculations of the rate constants of the various **BN**s at 423 K (Table 1) reproduce the ponderal effect found experimentally, namely, the ratio of the rate constants is proportional to the square root of the mass ratios. A comparison of the theoretical and experimental results is given in Table 4.

Table 4. Summary of computational and experimental results for the ponderal effect

Compound	$(m_{BN}/m_{BNX})^{1/2}$	k_{BNX}/k_{BN} computational	k_{BNX}/k_{BN} experimental
BN	1	1	1
BN1	0.89	0.88	0.81
BN2	0.81	0.77	0.59

CONCLUSIONS

The observations in this study can be summarized as follows. (a) The structures of the transition states for the isomerization of the parent and the bridge compounds are not identical (Scheme 1). (b) The transition state for the **BNX** series can be attained by a twisting vibration which necessitates a much smaller motion amplitude than formerly assumed for the proposed scissoring vibration (Scheme 3). (c) Imposing the transition-state structure of the bridge compound on the parent molecule yielded a transition state higher in energy by ca 6 kcal mol^{-1}. (c) In the bridged compound this increase in energy is counterbalanced by a ground-state destabilization caused by the bridge. (d) The experimentally observed ponderal effect was computationally reproduced with reasonable agreement.

Acknowledgements

We thank Professors Abraham Nitzan and Milon Sprecher for helpful discussions. We also thank Professor M. Green for his comments and for critical reading of the manuscript. Ren Yi thanks the Barbara and Fred Kort Sino-Israel Post-Doctoral Fellowship Program at Bar-Ilan University.

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