Rotational Barriers of 1,1'-Binaphthyls: A Computational Study

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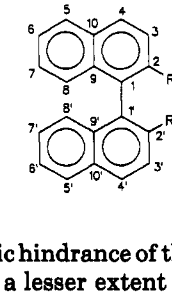
Received January 4, 1993

The activation energies for rotation about the σ-bonds of 1,1'-binaphthyl (1) and 2,2'-dibromo-1,1'-binaphthyl (2) have been computed with MNDO, AM1, and PM3 and of 2,2'-dilithio-1,1'-binaphthyl (3)·2EDA (ethylenediamine) (3a) with MNDO. All methods find that 1 should racemize preferably through the *anti* path, in agreement with previous force field calculations. The PM3 rotational barrier for 1 (23.1 kcal/mol) matches the experimental value (22.5 kcal/mol) best; the ground-state bond lengths correspond well with the X-ray data. We developed a procedure which evaluates the distortion and the steric repulsion effects in the transition structures roughly. In 1, distortion effects (e.g., ring deformation) account for about 2/3 of the activation energy. On the basis of the rotational behavior of 1, previous authors have only considered the *anti* racemization mechanism to be viable for 2,2'-dimethyl-1,1'-binaphthyl (4). In contrast, we found that in 2 (methyl is about the same size as bromine) the *syn* pathway is favored substantially over the *anti* route by 15.1 (MNDO), 20.6 (AM1), and 26.3 (PM3) kcal/mol. For 2, PM3 again yields the lowest rotational barrier (30.3 kcal/mol) but the AM1 value (38.4 kcal/mol) is in better agreement with an earlier estimate for 4 (37-40 kcal/mol). The transition structures (TS) related to 2 are even more strongly dominated (75-93%) by distortion effects than those for 1. Two energetically almost degenerate energy minima are computed with MNDO for 3a: one with the lithiums symmetrically doubly bridging the markedly twisted naphthyl rings (twist angle: 42.5°) and the other with each lithium closely coordinated to the contiguous π-system (twist angle: 122.0°). Despite the size of the Li·ethylenediamine 2,2'-substituents in 3a, the *anti* racemization pathway is preferred by 6.4 kcal/mol with an unusually close Li···H contact (1.79 Å). However, the *syn*-TS is 6.3 kcal/mol lower in energy with Li·EDA (3a) instead of hydrogens (1) in the 2,2'-positions. Thus, the *syn*-TS of 3a profits from electrostatic stabilization through lithium double bridging. Upon further rotation, the lithium atoms swap their counterions. To correct for the known overestimation of the Li-C bond strength by MNDO, we compared its performance on a model system (1,4-dilithio-1,3-butadiene (6)) with the MP2/6-31G*//6-31G* results. Deviations between the semiempirical and the ab initio geometries of four isomers of 6 suggest that the magnitude of the MNDO overestimation are 8 kcal/mol for Li-C and 4 kcal/mol for Li-H interactions. When these corrections are applied, the activation energy of 3a (*anti*-TS: 22.1 kcal/mol) should be close to the experimental estimate for 2,2'-dilithio-1,1'-binaphthyl (3) in solution (18.4 kcal/mol).

Introduction

The rotation about the σ-bond of 1,1'-binaphthyl (1) and its derivatives is so hindered[1,2] that optical isomers may be isolated.[3,4] This "atropisomerism"[5] has been exploited for chiral induction.[6,7] The barriers to rotation of 1,1'-binaphthyl derivatives have been estimated,[8,9] determined experimentally,[1,2,9,10] and investigated computationally.[11-15] However, the calculations only employed molecular mechanics methods. Our interest in the conformational behavior of 2,2'-dilithio-1,1'-binaphthyl[16] (3) triggered the present semiempirical molecular orbital study of the barriers to racemization of the parent system (1), 2,2'-dibromo-1,1'-binaphthyl (2), and 2,2'-dilithio-1,1'-binaphthyl (with the metals complexed with ethylenediamine EDA) (3a).



R = H		(1)
R = Br		(2)
R = Li		(3)
R = Li	EDA	(3a)

Steric hindrance of the substituents in the 8,8'-positions and to a lesser extent in the 2,2'-positions is responsible for the atropisomerism in binaphthyls. Racemization may occur through a *syn* inversion path with close contacts of

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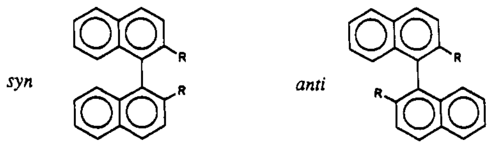
the groupings at 2,2′ and at 8,8′ or an *anti* process in which positions 2,8′ and 2′,8 must pass by each other.



If rigid models are considered, the *anti* route appears to be less hindered than the *syn* pathway. Two alternative pathways for *anti* passage for a symmetrically substituted 1 have been suggested by Harris and Cooke:[1] a one-step mechanism in which the 2,8′- and 2′,8-positions pass each other simultaneously and a multistage process in which the obstacles are overcome stepwise. The stepwise pathway involves an intermediate, an energy minimum between two identical energy barriers. Qualitative analysis[1] of the steric interactions in 1,1′-binaphthyl-2,2′-dicarboxylic acid and in 1,1′-binaphthyl-8,8′-dicarboxylic acid favored a simultaneous racemization process for the 2,2′-derivative but a two-step inversion path for the 8,8′-diacid. The experimental barrier to racemization for 1 by kinetic measurements (22.5 kcal/mol)[1] has been confirmed by others.[2] On the basis of experimentally derived increments, Harris et al.[9] predicted a racemization energy for 2,2′-dimethyl-1,1′-binaphthyl (4) on the order of 37–40 kcal/mol. This rather high value is corroborated by the observation that 4 fails to racemize after 40 h at 240 °C.[17] In contrast, racemization of the parent binaphthyl system (1) can be followed with a polarimeter at room temperature.[2]

Conformations of 1[12,14,15] and its 2,2′-dimethyl derivative 4[13,14] have been computed with different extensions (MMPI,[12,13] MOMM,[14] and MM2′[15]) of Allinger's force field methods.[18] Carter et al.[12] and Kao et al.[14] both favor a two-step *anti* mechanism for 1; the barrier heights are computed to be 20.4 and 18.3 kcal/mol, respectively. Both authors describe a local energy minimum, only 0.2 kcal/mol below the two identical transition structures (TS). For the 2,2′-dimethyl derivative 4, Liljefors et al.[13] and Kao et al.[14] both excluded the *syn* inversion route from consideration. Their intuitive reasoning was that in 1 this process is substantially higher in energy than the *anti* pathway. In contrast, we will show that the *syn* mechanism is drastically favored for 2. In the most recent paper on 1, Tsuzuki et al.[15] do not even mention the *syn* mechanistic alternative and find a one-step *anti* mechanism by MM2′. Their computed barrier is 24.8 kcal/mol.

2,2′-Dilithio-1,1′-binaphthyl (3) reacts stereospecifically,[4,7] but no X-ray structure is available. The barrier to racemization (18.4 kcal/mol)[8] has been estimated by kinetic measurements in dimethyl ether. The stabilization energy due to symmetrical double lithium bridging[19] in *o,o′*-dilithiobiphenyl (5) has been calculated (without coligands for the metal atoms) to be 16.8 kcal/mol,[20] with a perfectly planar diphenyl moiety. Brown and Murdoch[8] excluded a symmetrical doubly lithium bridged structure for 3, due to its reluctance to racemize below −45 °C, tacitly assuming coplanar naphthyl rings for this arrangement. On this basis, they inferred that the stabilization effect of 16.8 kcal/mol computed for the double bridging in 5 is much too high and that "the lithium bridging observed in dilithiobiphenyl·2TMEDA (tetramethylethylenediamine)[21] is not necessarily a significant factor in the ground-state structures of other dilithiobiaryls in which the parent hydrocarbon has an appreciable barrier to internal rotation".[8] In answering this criticism, two factors must be taken into account. First, when coligands (EDA) on lithium are present the energy advantage for double bridging in 5 is lowered significantly from 16.8 to 8.8 kcal/mol.[16] Hence, the driving force is less. Second, twisted geometries, as can be presumed in 3, do not necessarily prevent symmetrical doubly lithium bridging[16] although it may be less favorable energetically than in untwisted 5. This work focusses on the computation of the barrier to rotation around the σ-bond in 3.

Table I. Experimental and Calculated C–C Bond Lengths (Å) of 1,1′-Binaphthyl (1)

bonds	X-ray I[a]	X-ray II[b]	MNDO	AM1	PM3
1–1′	1.475	1.486	1.492	1.469	1.475
1–2	1.364	1.377	1.392	1.381	1.375
2–3	1.404	1.409	1.427	1.413	1.413
3–4	1.360	1.358	1.380	1.372	1.368
4–10	1.413	1.421	1.438	1.421	1.421
5–10	1.413	1.421	1.440	1.423	1.422
5–6	1.346	1.370	1.381	1.372	1.368
6–7	1.404	1.391	1.428	1.416	1.414
7–8	1.359	1.361	1.382	1.373	1.368
8–9	1.413	1.426	1.442	1.423	1.422
9–10	1.416	1.412	1.437	1.420	1.411
1–9	1.433	1.435	1.452	1.430	1.428

[a] Reference 32. [b] Reference 33.

No optimized semiempirical transition structures of such extended π-systems are known to us. Recently, several semiempirical geometries (MNDO and AM1) of the 1,2′- and 2,2′-biindenide dianions[22] with fixed rotational σ-bond angles were used to estimate barriers to rotation by extrapolation (vide infra). Lithium parameters are only available for MNDO. However, in order to assess the performance of MNDO, 1 and 2 were computed by AM1 and PM3 as well, which are recognized for their improved treatment of π-systems. The known overestimation of the Li–C bond strength in MNDO[23] was taken into account by considering a simple model system: four isomers of 1,4-dilithio-1,3-butadiene (6) were calculated with MP2/6-31G*//6-31G* and with MNDO; the differences were used to correct the semiempirical results for **3a**.

Methods

Three semiempirical methods, MNDO,[24] AM1,[25] and PM3,[26] as implemented in the VAMP program,[27] have been used. Full transition structure optimizations have been done using NS01A[28] or the eigenvector following routine (EF).[29] GAUSSIAN 90[30] has been employed for the 6-31G* geometry optimizations and

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Table II. Heats of Formation and Geometrical Parameters of Stationary Points of 1, 2, and 3a

	NIMAG		heat of formn (kcal/mol)	rel energy (kcal/mol)	twist angle C_2–C_1–$C_{1'}$–$C_{2'}$	shortest dist (Å)		
				1,1'-Binaphthyl (1)				
						H_2–$H_{2'}$	H_8–$H_{8'}$	H_2–$H_{8'}$
GS	0	MNDO	+84.6	0.0	+89.2	3.52	3.74	3.47
	0	AM1	+88.4	0.0	+109.9	3.95	4.15	2.75
	0	PM3	+85.6	0.0	+92.2	3.55	3.68	3.28
						H_2–$H_{2'}$	H_8–$H_{8'}$	
syn-TS	1	MNDO	+119.4	+34.8	−31.7	2.38	1.98	
	1	AM1	+118.2	+29.8	−36.0	2.29	1.66	
	1	PM3	+112.8	+27.2	−29.6	2.09	1.66	
						H_2–$H_{8'}$	$H_{2'}$–H_8	
anti-TS	1	MNDO	+118.4	+33.8	−171.9	1.79	1.79	
	1	AM1	+117.9	+29.5	−170.8	1.64	1.64	
	1	PM3	+108.7	+23.1	−171.0	1.59	1.59	
				2,2'-Dibromo-1,1'-binaphthyl (2)				
						Br–Br'	H_8–$H_{8'}$	Br–$H_{8'}$
GS	0	MNDO	+93.9	0.0	+89.6	4.21	3.71	3.87
	0	AM1	+101.4	0.0	+88.6	4.18	3.56	3.84
	0	PM3	+101.8	0.0	+59.8	2.75	2.82	4.60
TS (GS)	1	PM3	+105.3	+3.5	+69.9	3.21	3.07	4.38
	0	PM3	+104.1	+2.3	+88.1	4.03	3.54	3.86
						Br–Br'	H_8–$H_{8'}$	
syn-TS	1	MNDO	+136.4	+42.5	−4.8	3.05	2.98	
	1	AM1	+139.8	+38.4	+10.2	3.01	3.02	
GS (TS)	0	AM1	+139.1	+37.7	−15.0	3.14	2.46	
syn-TS	1	AM1	+139.6	+38.2	−33.7	3.38	1.97	
	1	PM3	+132.1	+30.3	−3.4	2.69	2.74	
						Br–$H_{8'}$	Br'–H_8	
anti-TS	1	MNDO	+151.5	+57.6	−171.3	2.51	2.51	
	1	AM1	+160.4	+59.0	−167.0	2.34	2.34	
	1	PM3	+158.4	+56.6	−178.3	2.37	2.37	
				2,2'-Dilithio-1,1'-binaphthyl·2 EDA (3a)				
						Li–Li'	H_8–$H_{8'}$	Li–$H_{8'}$
GS 1	0	MNDO	−5.8	0.0	+122.0	4.85	4.34	2.44
TS (GS)	1		+1.1	+6.9	+89.7	3.70	3.87	2.50
GS 2	0		−5.1	+0.7	+42.5	2.57	3.08	4.29
						Li–Li'	H_8–$H_{8'}$	
"*syn*-TS"	2	MNDO	+22.7	+28.5	−36.8	2.84	1.63	
						Li–$H_{8'}$	Li'–H_8	
anti-TS	1	MNDO	+16.3	+22.1	+137.4	2.66	1.79	
GS (TS)	0		+10.0	+15.8	+179.9	2.35	2.35	
anti-TS	1		+16.3	+22.1	−137.4	1.79	2.66	

the MP2/6-31G* single point calculations. Second derivative[31] (frequency) calculations establish the nature of stationary points. Calculations were run on a Convex C-220/256 (Erlangen) and a Cray YMP-432 (Munich).

Results and Discussion

1,1'-Binaphthyl (1). Calculated (MNDO, AM1, PM3) bond lengths of the ground state (GS) of 1 are compared to those from X-ray analyses[32,33] in Table I. Experimental values are matched best by PM3 where deviations do not exceed 0.01 Å. Errors in the bond lengths obtained with the force field methods[12,14] are similar to those of MNDO, but are greater than those of AM1 and PM3.

Table II summarizes the heats of formation, relative energies, and some geometrical features of the ground state and transition structures of 1–3. With molecular mechanics, a pronounced shallow potential energy depression in the region around the perpendicular arrangement of the naphthyl rings (65–110°: $\Delta E = 0.3$ kcal/mol[12]) is found for 1 which is confirmed by all the semiempirical methods ($\Delta E < 1$ kcal/mol: MNDO, 70–105°; AM1, 55–130°; PM3, 60–120°). Experimental C(2)–C(1)–C(1')–C(2') twist angles are 68°[32] and 103°[33] for the two distinct crystalline forms of 1. These deviations from 90° probably are due to crystal packing forces because Raman spectroscopy indicates an orthogonal conformation in solution.[34] The AM1 ground-state geometry largely differs in its C(1)–C(1') dihedral angle (109.9°) from the near perpendicular arrangement of the π-systems calculated with MNDO and AM1. No stationary point could be found with AM1 in the vicinity of a twist angle of 90°.

Recently, the energy profile for the rotation around the σ-bond of the 1,2'-biindenide dianion has been approximated with MNDO and AM1.[22] Several geometries with fixed dihedral angles between the aryl rings were optimized. The extrapolated energy maxima and minima appear at directly opposing twist angles of the π-systems for each method. As can be seen from Figure 1, the MNDO, AM1, and PM3 transition structures look very similar in the *syn* as well as in the *anti* inversion state of 1. In both processes, the passage of the crucial hydrogens is facilitated by out-of-plane deformation of the two ring systems. In accord with rigid model considerations (vide supra), the *anti* passage is favored by each method although to different extents (cf. Table II). Unlike AM1 and MNDO, which overestimate the height of the rotational barrier, the PM3 activation energy (23.1 kcal/mol) agrees almost

(30) Gaussian 90. Revision: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M. A.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1990.

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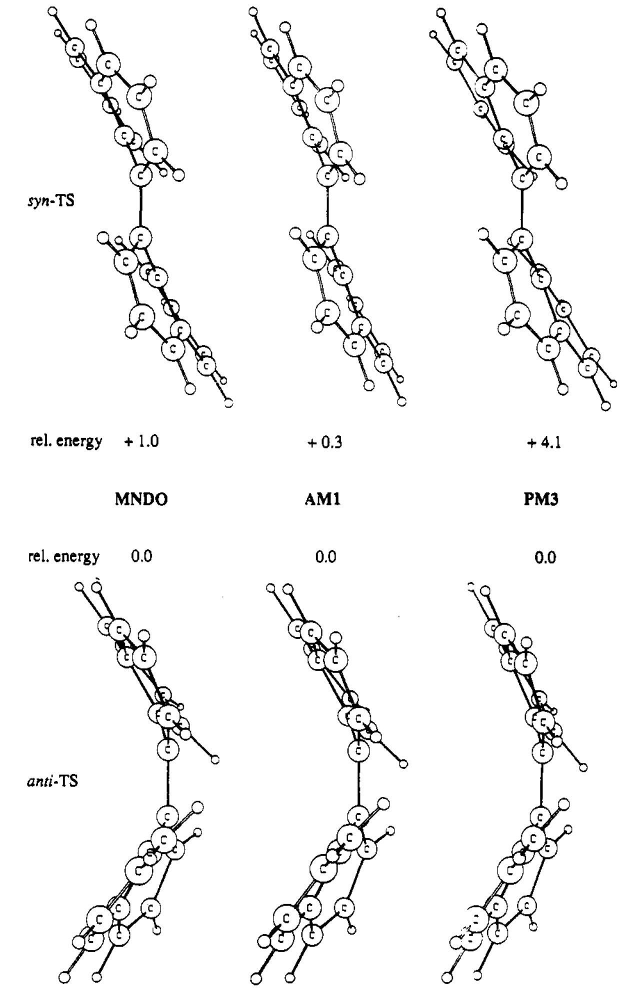

Figure 1. *Syn-* and *anti*-transition structures (TS's) of **1** as calculated with MNDO, AM1, and PM3.

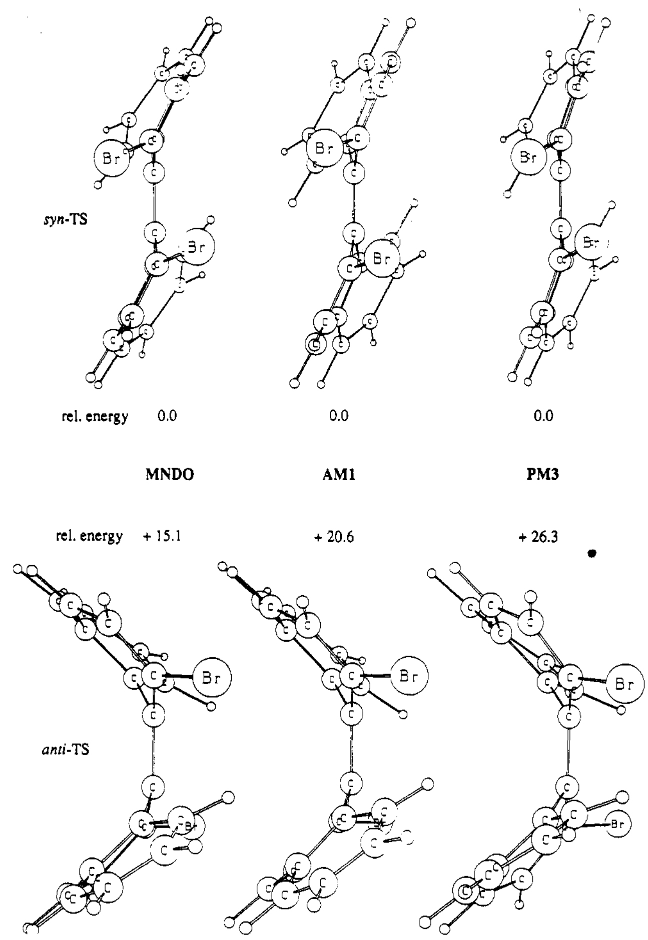

Figure 2. *Syn-* (Br···Br′ closest contacts) and *anti*-TS's of **2** as calculated with MNDO, AM1, and PM3.

exactly with the experimental value (22.5 kcal/mol), better than the force field methods. In agreement with Tsuzuki et al.,[15] the two sets of opposing hydrogens pass by each other simultaneously during the *anti* inversion. One of the claimed advantages of the AM1 and PM3 parametrization is an improved hydrogen representation.[25,26] This is reflected in the shortest H···H distances in both TS's of **1**, which are very similar for both methods. However, twist angles and relative energies are different when computed by the two methods. Carter et al.[12] could not locate the *syn*-TS, whereas the relative energy obtained by Kao et al.[14] (30 kcal/mol) is in the region of the semiempirical results (27–35 kcal/mol).

2,2′-Dibromo-1,1′-binaphthyl (2). This isomer has been chosen in order to test the performance of the semiempirical methods on a 2,2′-disubstituted binaphthyl known to be optically stable at 95 °C for several hours.[35] We know of no experimentally determined barriers of activation for **2**, but bromine is of about the same size as a methyl group,[36] and the experimental estimate for the barrier of the 2,2′-dimethyl derivative (**4**) is 37–40 kcal/mol.[9]

The bulky substituents in **2** demand a perpendicular orientation of the naphthyl rings in the ground state. All three semiempirical methods agree in this respect. To our surprise, at a rather acute twist angle of the naphthyl moieties (59.8°) the PM3 potential energy surface reveals a second energy minimum which is even lower (2.3 kcal/mol) in energy than that with a perpendicular arrangement (88.1°: Table II). A force field twist angle of 60° for the GS of **4** has been calculated.[13]

Again, the three transition structures for each inversion pathway for **2** (Figure 2) look similar but differ in details. Ring deformations are definitely more pronounced than in **1**. The *syn* inversion path, which was not even considered in previous reports on **4**,[13,14] is favored drastically for **2** over the *anti* pathway by 15–26 kcal/mol depending on the computational method (Table II). Like in **1**, PM3 gives the lowest activation barrier (30.3 kcal/mol). The PM3 Br···Br distance in the *syn*-TS (2.69 Å) is shorter by about 0.3 Å than with MNDO and AM1, although of all the methods the bond length in molecular bromine (Br_2) is largest with PM3 (2.44 Å; MNDO, 2.17 Å; AM1, 2.18 Å; expl, 2.28 Å).[26] The experimental guess of 37–40 kcal/mol[9] for the barrier to rotation of the 2,2′-dimethyl derivative **4** is matched best by the AM1 value for **2** (38.4 kcal/mol). The *anti* barriers of **4** calculated previously with molecular mechanics (34.9[13] and 33.6 kcal/mol[14]) differ markedly from the semiempirical results (57–59 kcal/mol).

In contrast to **1**, the lowest energy inversion pathway for **2** proceeds *via* a two-step mechanism. The portions of the potential energy surfaces around the geometries involved in Br···Br′ and H(8)···H(8′) passages are very shallow with all three methods. However, only the stationary point for the Br···Br′ encounter could be located with MNDO and PM3. With AM1, the bromine atoms reach their shortest nonbonded distance at a C(2)–C(1)–

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(36) Reference 9, footnote 8.

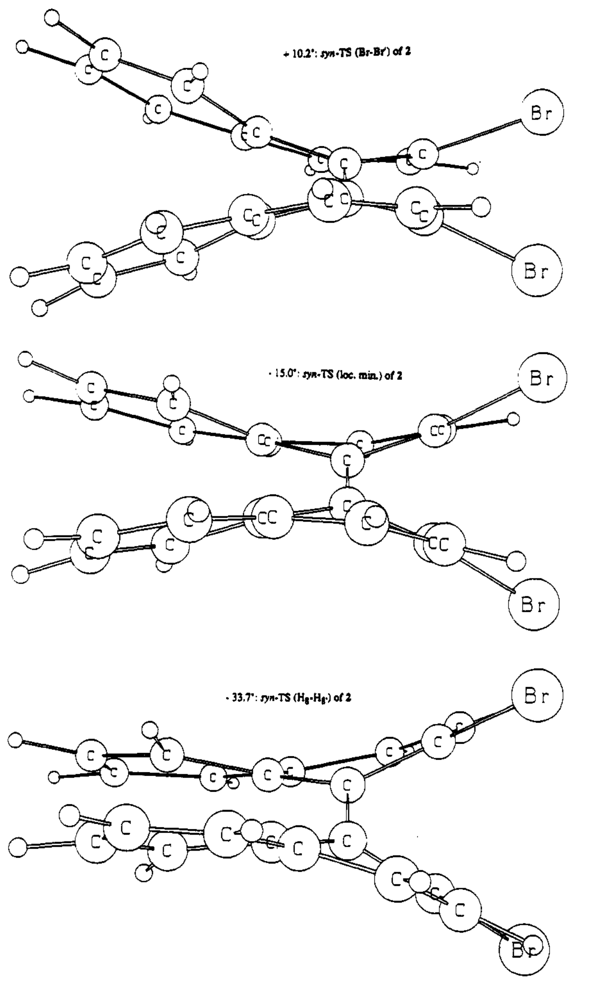


Figure 3. "Top view" of both AM1 *syn*-TS's and the intermediate local minimum of 2.

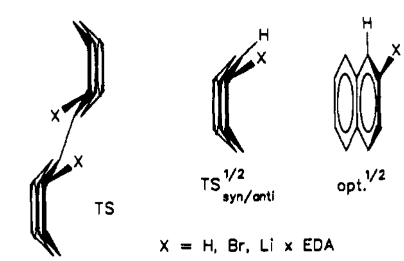
C(1′)–C(2′) twist angle of +10.2° but the hydrogens H(8) and H(8′) are closest together at a −33.7° twist (Figure 3). Between these twist angles, a local energy minimum at −15.0° is found; this is about 0.5 kcal/mol below the energy of the two transition structures. Surprisingly, the two AM1 transition structures have almost the same energy. Hence, the major contribution to the racemization barrier is not the direct steric clash of the "obstacle" atoms (e.g., the bromines in 2), but is rather due to the deformation of the whole system. We tested this conclusion by calculating the heat of formation of a single 2-bromonaphthalene ring deformed to the geometry from the TS; a hydrogen was simply substituted for the second ring system. Only the parameters of the newly introduced hydrogen atom were optimized. The difference between the heats of formation calculated for this deformed and for the fully optimized 2-bromonaphthalene should give a rough estimate for the deformation energy of a single naphthyl moiety in the TS. By doubling the single-distortion energy and then subtracting it from the respective activation energy, the nondistortion effects of the binaphthyls can be assigned (Scheme I). In this way, steric repulsions between atoms in the two different naphthalene moieties are eliminated. The same procedure was applied to the TS's of 1 (Table III). Despite the artificiality in this treatment, the results should be a rough measure of the interatomic contributions to the inversion barriers. Removing a molecular fragment (LiH) from the TS of the LiH addition to a ketone and recalculating the energy of the remaining distorted ketone has been used

Table III. Heats of Formation of Optimized and *syn*- and *anti*-Distorted (See Text) Naphthalene, 2-Bromonaphthalene, and 2-Lithionaphthalene·EDA and the Amount of Nondistortion Effects in the TS of 1, 2, and 3a, Respectively[a]

	MNDO		AM1		PM3	
	heat of formn (kcal/mol)	rel energy (kcal/mol)	heat of formn (kcal/mol)	rel energy (kcal/mol)	heat of formn (kcal/mol)	rel energy (kcal/mol)
			Naphthalene			
opt.	+38.3	0.0	+40.6	0.0	+40.7	0.0
syn-dist.	+49.5	+11.2	+49.6	+9.0	+49.2	+8.5
anti-dist.	+49.1	+10.8	+50.2	+9.6	+49.4	+8.7
	C	D	C	D	C	D
syn-dist.	+22.4	+12.4 (35)	+18.0	+11.8 (40)	+17.0	+10.2 (38)
anti-dist.	+21.6	+12.2 (36)	+19.2	+10.3 (35)	+17.4	+5.7 (25)
			2-Bromonaphthalene			
opt.	+41.0	0.0	+45.4	0.0	+48.2	0.0
syn-dist.	+58.9	+17.9	+61.7[b]	+16.3[b]	+62.3	+14.1
			+59.7[c]	+14.3[c]		
anti-dist.	+62.3	+21.3	+65.5	+20.1	+66.8	+18.6
	C	D	C	D	C	D
syn-dist.	+35.8	+6.7 (16)	+32.6[b]	+5.8 (15)[b]	+28.2	+2.1 (7)
			+28.6[c]	+9.6 (25)[c]		
anti-dist.	+42.6	+15.0 (26)	+40.2	+18.8 (32)	+37.2	+19.4 (34)
			2-Lithionaphthalene			
opt.	+0.0	0.0				
syn-dist.	+36.5	+36.5				
anti-dist.	+10.6	+10.6				
	C	D				
syn-dist.	+73.0	−44.5				
anti-dist.	+21.2	+0.9				

[a] C: Relative energy doubled (kcal/mol). D: Difference between C and the activation energy of 1-TS, 2-TS, and 3a-TS, respectively (kcal/mol). In parentheses: percentage of activation energy attributed to nondistortion effects. [b] Br–Br′ closest contacts (cf. Table II). [c] H_8–$H_{8'}$ closest contacts (cf. Table II).

Scheme I



$$\Delta H_f(TS^{1/2}) - \Delta H_f(opt.^{1/2}) = \Delta H_f^{1/2}(dist.)$$

$$\Delta H_f(TS) - 2 \cdot [\Delta H_f^{1/2}(dist.)] = E(nondist.)$$

before[37] in order to assess qualitatively the contribution of distortion effects.

With all methods, roughly two thirds of the barrier heights of 1 can be attributed to distortion effects (Table III); these dominate even more in the TS's of 2 (PM3 *syn*-TS: 93%; cf. Figures 1 and 2). Considerable distortion of aromatic rings can be tolerated without much expenditure of energy.[38] Recently, molecular mechanics and ab initio calculations have been used to investigate several deformation modes of benzene.[39] In order to check the

(37) Wu, Y.-D.; Houk, K. N.; Paddon-Row, M. N. *Angew. Chem.* **1992,** *104*, 1087; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1019.
(38) Wynberg, H.; Nieuwpoort, W. C.; Jonkman, H. T. *Tetrahedron Lett.* **1973**, 4623.
(39) Tsuzuki, S.; Tanabe, K. *J. Chem. Soc., Perkin Trans. 2* **1990**, 1687.

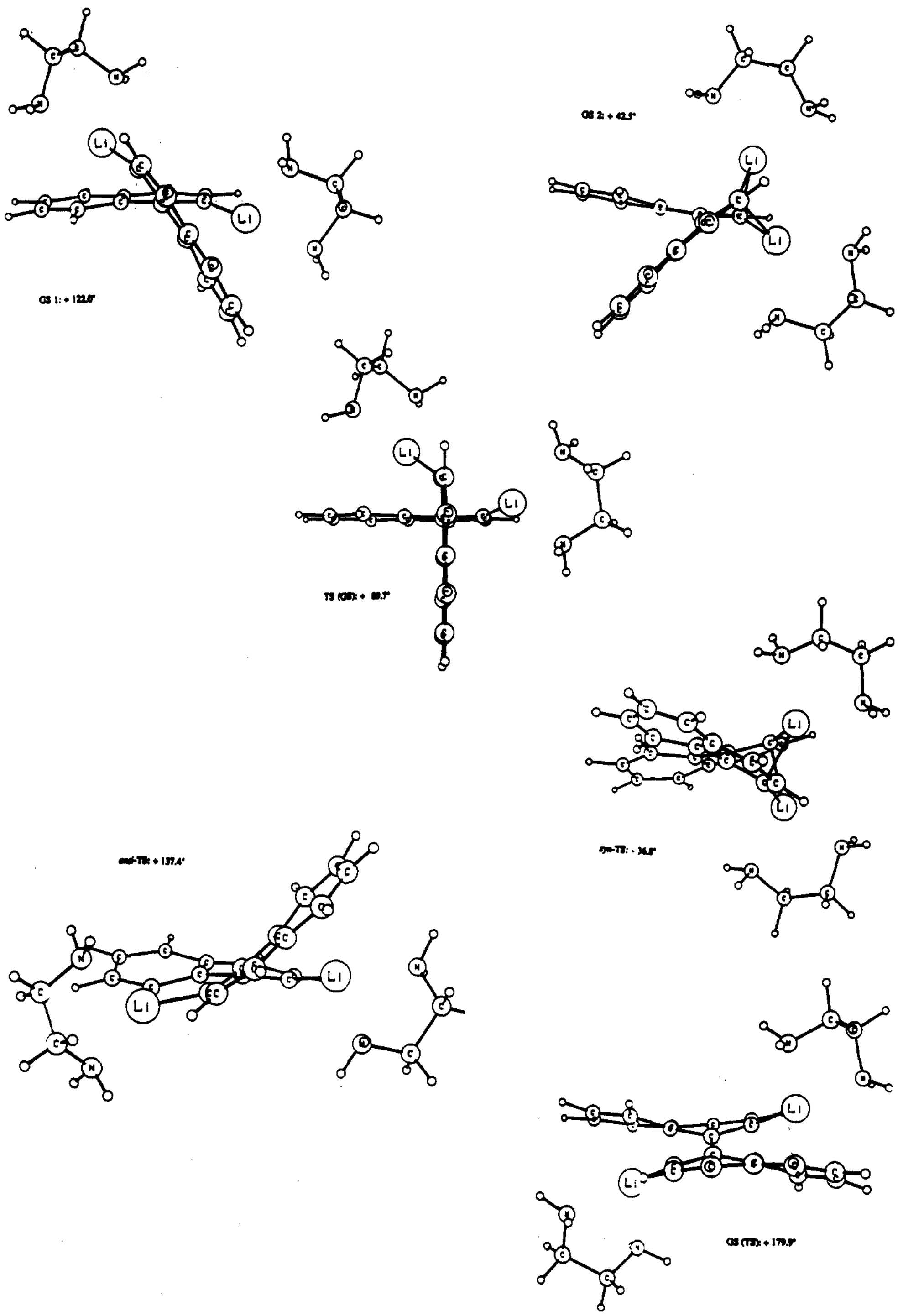


Figure 4. "Top view" of the MNDO structures of the stationary points of **3a**.

performance of the semiempirical methods, we compared the reported ab initio results with MNDO, AM1, and PM3. All three methods gave good results. The maximum deviations from the ab initio deformation energies given in ref 39 are 21%, 15%, and 4% for MNDO, AM1, and PM3, respectively. However, steric effects contribute to a greater extent when the activation barrier is larger (Table III). The racemization of binaphthyls can be rationalized as follows: upon rotation around the σ-bond, the first steric contact causes the aromatic systems to deform. The transition structure is governed by distortional effects if the sterically restricted groups can pass by each other relatively easily. If more energy is needed for further rotation, the distortion increases but less adjustment is possible. Hence, the steric repulsion contribution to rotation rises.

2,2′-Dilithio-1,1′-binaphthyl·2EDA (3a). The barrier to racemization of **3** is estimated to be 18.4 kcal/mol.[8] The structures of the energy minima of **3a** have been discussed before.[16] No fewer than seven stationary points could be located with MNDO for rotation around the σ-bond of **3a** (Table II). The perpendicular arrangement of the two naphthyl rings is not an energy mininum, as in **1** and **2**, but it is the TS between the two lowest energy geometries of **3a**. The global minimum twist angle (122°) allows each lithium atom to coordinate to the contiguous naphthyl ring (Figure 4). In the symmetrical lithium doubly bridged structure, the rings of **3a** are not coplanar as in the corresponding *o*,*o*′-dilithiobiphenyl **5**.[20,21] Steric hindrance in **3a** results in a twist angle of 43°.

Like **1**, the lowest inversion pathway for **3a** proceeds via the *anti* conformation and, like **2**, by a two-step mechanism.

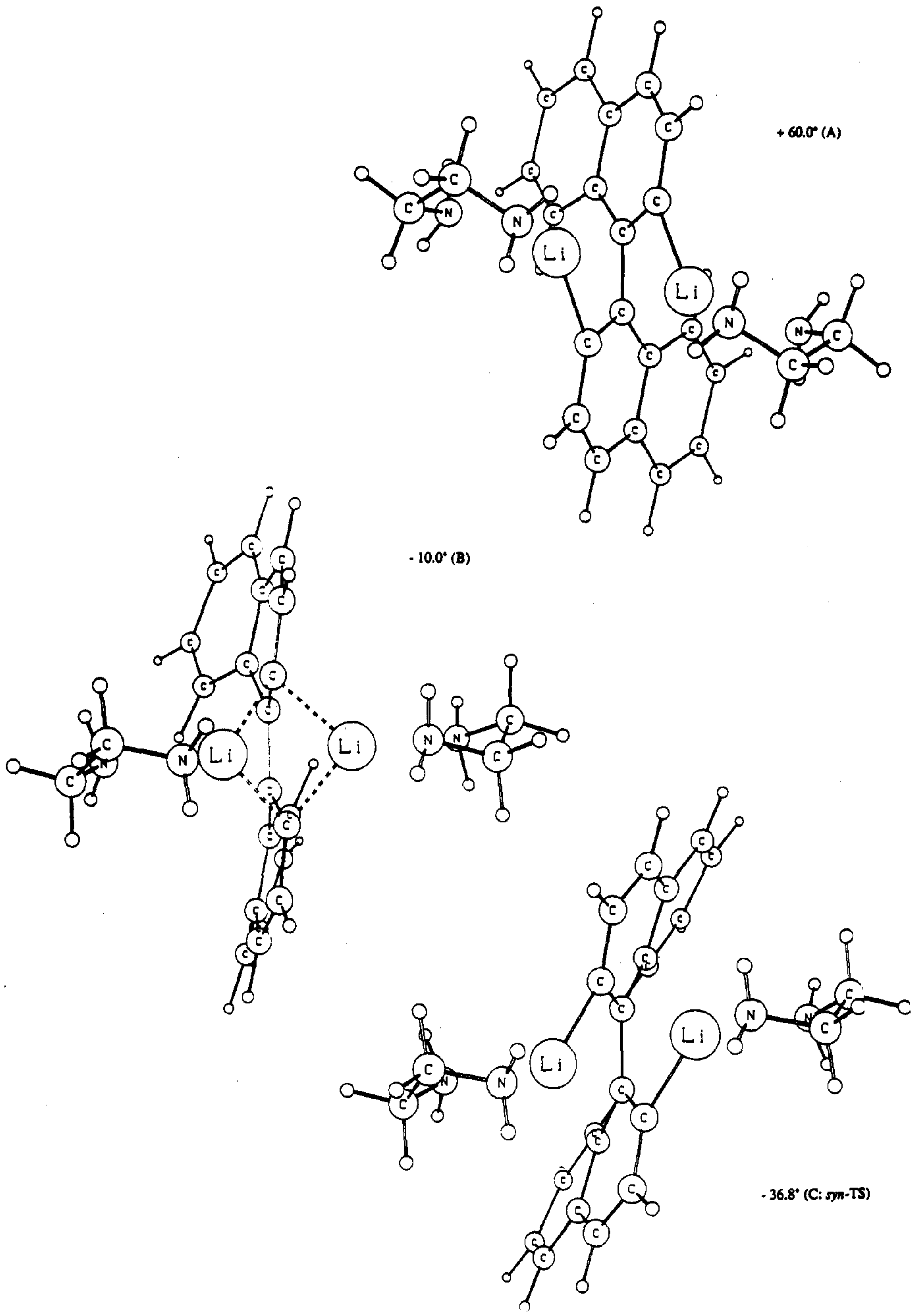


Figure 5. Three geometries of **3a** with twist angles of +60° (A), −10° (B), and −36.8°, the *syn*-TS (C).

The *anti*-TS mirror images (Figure 4, Table II) are separated by a local minimum which is 6.3 kcal/mol below the energy of the *anti*-TS. Notably, the shortest Li···H distance (1.79 Å) in this *anti*-TS is of the same magnitude as the shortest H···H distance in the MNDO *anti*-TS of **1** (Table II) although the bonding radii differ considerably (cf. Li–H, 1.38 Å; H–H, 0.66 Å). Nonbonding agostic[40] Li···H contacts[41] of 2.04 Å have been calculated with MNDO[42] for minimum structures without any TS constraints. The putatively short Li···H distance in the *anti*-TS of **3a** can thus be regarded as normal.

Computation of the *syn* inversion pathway of **3a** posed technical problems. No proper transition structure could be found with just one negative eigenvalue. Instead, several very similar geometries were obtained (all with two negative eigenvalues), even though different optimizing techniques were tried. As this is the less favorable inversion process, it suffices to discuss the *syn*-TS of **3a** with the smallest second negative eigenvalue, $-13.9\ cm^{-1}$ (as well as $-88.3\ cm^{-1}$). Both these imaginary frequencies correspond to the H(8)···H(8′) passage. We have also optimized structures of **3a** with fixed C(2)–C(1)–C(1′)–C(2′) dihedral angles, starting from the perpendicular energy minimum (122.0°) and rotating toward the *syn*-

(40) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.
(41) X-ray data: 2.09 Å (ethyllithium) (Dietrich, H. *Acta Crystallogr.* **1963**, *16*, 681); 2.00 Å (cyclohexyllithium) (Zerger, R.; Rhine, W.; Stucky, G. *J. Am. Chem. Soc.* **1974**, *96*, 6048).
(42) Krug, K. Diplomarbeit, Universität Erlangen-Nürnberg, 1988.

TS (−36.8°). Figure 5 shows three geometries with twist angles of +60° (A), −10° (B), and −36.8°, the *syn*-TS (C). The carbons swap their lithium gegenions during the *syn* inversion process. However, there is no separate stationary point for this process, as these ion triplet[43] arrangements are rather flexible.[16] Instead, the barrier to rotation in **3a** arises from the passage of H(8) and H(8′). The structural arrangement of the ion triplet in the GS 2 of **3a** (C–Li, 2.02; 2.21 Å; Li–Li, 2.57 Å; C(2)–C(2′), 2.93 Å) is basically retained in the *syn*-TS (C–Li, 1.98; 2.21 Å; Li–Li, 2.84 Å; C(2)–C(2′), 2.73 Å). Stabilization through lithium double bridging is thus present in the GS 2 as well as in the *syn*-TS of **3a**.

The H(8)···H(8′) distance is much shorter (1.63 Å) than in the *syn*-TS of 1,1′-binaphthyl (**1**) (1.98 Å) (Figure 6). However, the activation barrier corresponding to the *syn*-TS of **1** (34.8 kcal/mol) is significantly larger than that of **3a** (28.5 kcal/mol). While the ground-state structure of **1** (MNDO) has nearly perpendicular naphthyl moieties (89.9°), the rings in the GS 2 of **3a** (Figure 4) are twisted much less (42.5°). Thus, substituting Li·EDA for hydrogen in the 2,2′-positions of 1,1′-binaphthyl results in a more favorable starting point for the *syn* inversion, due to lithium double bridging. In contrast, Brown and Murdoch argued against symmetrical lithium bridging as a "significant factor in dilithiobiaryls..."[8] (vide supra). They questioned if rotation was facilitated through lithium substituents.[44] Our calculations show that lithium substitution lowers the activation energy for the *syn*-TS by 6.3 kcal/mol (Table II). Keep in mind that the lower energy TS's for both **1** and **3a** are on the *anti* side. Lithium substitution for hydrogen decreases the *anti* barrier by 11.7 kcal/mol.

The electrostatic nature of lithium bonding in **3a** precludes the separation of distortional from nondistortional effects as described for **1** and **2** (Table III).

1,4-Dilithio-1,3-butadiene (6). As a reliability check, the performance of MNDO for the rotation of a model system was compared with ab initio results. 1,4-Dilithio-1,3-butadiene (**6**), the smallest doubly lithiated π-conjugated system, has already been examined by ab initio calculations at low levels of theory.[19] Some conformers also have been investigated with MNDO.[20] Four isomers (**6a–d**: Table IV) were optimized at 6-31G* and their relative energies computed at MP2/6-31G*//6-31G*, i.e., with correction for electron correlation. Doubly bridged **6a** is a local minimum and the most stable form on both potential energy surfaces. The cis,cis *syn* isomer (**6d**), a second-order stationary point, is highest in energy. The cis,cis *anti* conformer (**6c**) is a local minimum (ab initio), but it is a transition structure for the rotation around the C–C σ bond according to MNDO. (For the perpendicular double bond arrangement **6b**, where the C–C–C–C dihedral angle was fixed at 90°, frequency analysis is inappropriate.) Structural details are given in Table V.

Both MNDO and MP2/6-31G*//6-31G* agree on the stability order of the four isomers. The increase in the relative energies from **6a** to **6d** is due to the loss of a second Li···C interaction (Table V). Destabilization of **6b–d** relative to **6a** is more pronounced with MNDO than with ab initio calculations. The lithiums in isomers **6a** and **6d** experience the least stabilization through secondary interactions with neighboring atoms. In this model system, a spurious MNDO stabilization of 8 kcal/mol can be deduced for lithium double bridging from the ΔE (MNDO-MP2) values of Table IV (**6a versus 6b and 6d**). In **6c**, the MNDO C(2)–C(1)–Li bond angle (95.3°) deviates significantly from the 6-31G* value (104.3°). This smaller MNDO angle results in a rather short nonbonded Li···H_3 distance (1.92 Å; ab initio, 2.16 Å), in the range[41,42] for agostic[40] Li···H interactions. Thus, although isomer **6c** has no second Li···C contact, it anticipates an extra stabilization through the Li···H_3 interaction, which decreases the (MNDO-MP2) energy difference, relative to **6a** (4 kcal/mol), by half.

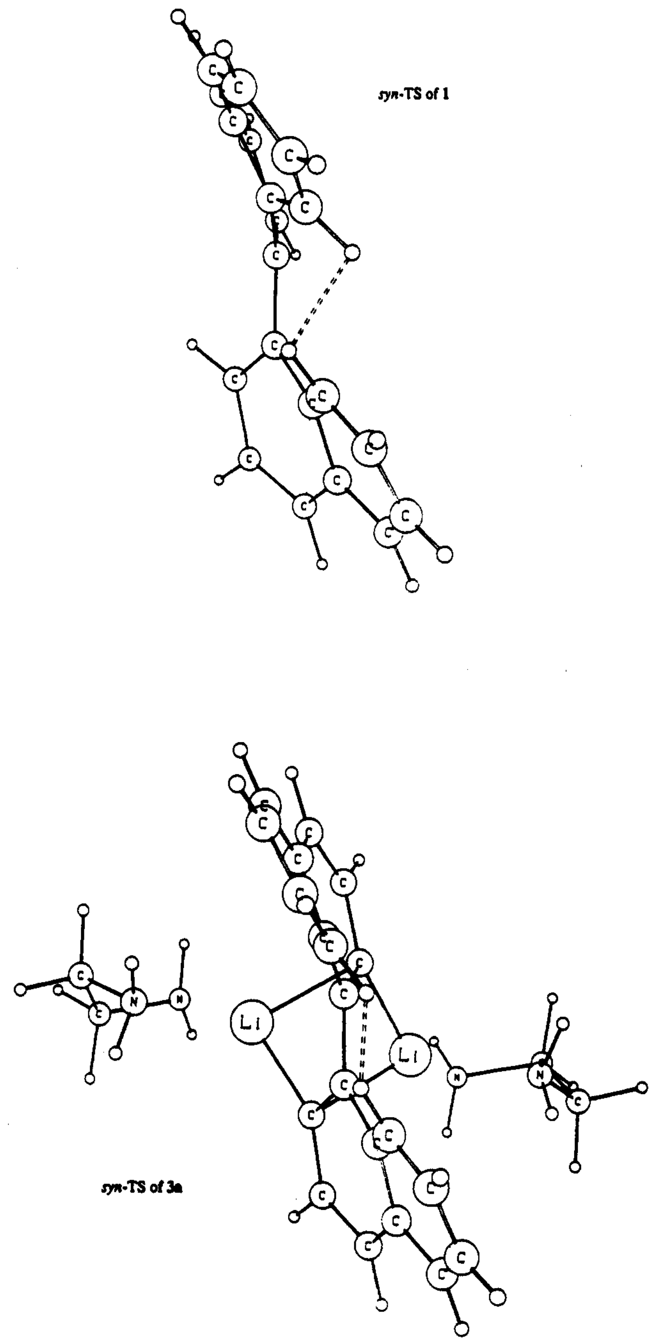
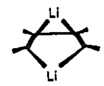
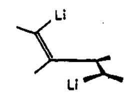
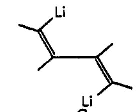
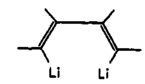


Figure 6. *Syn*-TS of **1** and **3a**.

The above analysis indicates that the estimated barrier to rotation for the most favorable pathway (*anti*-TS: 22.1 kcal/mol) of **3a** should be lowered. There is only one close Li···C contact for each lithium compared to two in the doubly bridged structure (GS 2). If this correction is

(43) (a) Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, *105*, 2502. (b) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355. (c) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353.
(44) Reference 8, footnote 7.

Table IV. MNDO Heats of Formation[a] (kcal/mol), MP2/6-31G*//6-31G* Absolute Energies[a] (Hartrees), and Their Relative Energies (Including Those of 4-31G//STO-3G[b]) (kcal/mol) of 1,4-Dilithio-1,3-butadiene (6) Conformers[c]

	 C_{2v} doubly bridged **6a**	 C_2 cis,cis *gauche* **6b**	 C_{2h} cis,cis *anti* **6c**	 C_{2v} cis,cis *syn* **6d**
MNDO				
ΔH_f	−26.3[d] (0)	−0.2 (−)	+17.0[d] (1)	+41.0 (2)
rel energy	0.0	+26.1	+43.3	+67.3
4-31G//STO-3G[b]				
rel energy	0.0		+34.8	+49.9
MP2/6-31G*//6-31G*				
abs energy	−169.17443 (0)	−169.14550 (−)	−169.11153 (0)	−169.07981 (2)
rel energy	0.0	+18.2	+39.5	+59.4
ΔE (MNDO-MP2)		7.9	3.8	7.9

[a] In parts taken from *The Erlangen Quantum Chemistry Archive System*; Clark, T., Schleyer, P. v. R., Eds.; University of Erlangen: Erlangen, 1991. [b] Reference 19. [c] The number of imaginary frequencies (NIMAG) are given in parentheses. [d] Reference 20.

Table V. Selected Bond Lengths (Å) and Bond Angles (deg) of 6-31G* and MNDO (in Parentheses) Geometries of 1,4-Dilithio-1,3-butadiene (6) Conformers

	doubly bridged **6a**	cis,cis *gauche* **6b**	cis,cis *anti* **6c**	cis,cis *syn* **6d**
C_1–Li	2.07 (2.01)	2.01 (1.89)	1.96 (1.81)	1.95 (1.77)
C_2···Li	2.38 (2.36)	2.39 (2.32)	2.63 (2.36)	3.13 (2.91)
C_3···Li	2.38 (2.36)	2.21 (2.14)	2.79 (2.46)	3.90 (3.59)
C_4···Li	2.07 (2.01)	2.54 (2.61)	4.10 (3.80)	3.97 (3.59)
H_3···Li	3.35 (3.36)	2.90 (2.79)	2.16 (1.92)	4.93 (4.66)
C_2–C_1–Li	85.2 (85.4)	88.2 (88.7)	104.3 (95.3)	142.7 (136.5)
C_1–C_2–C_3	122.8 (121.6)	122.0 (118.3)	126.3 (124.5)	132.2 (130.4)

included, the resulting activation barrier is close to the experimental estimate of 18.4 kcal/mol.[8]

Conclusions

For 1,1′-binaphthyl (**1**) and 2,2′-dibromo-1,1′-binaphthyl (**2**), MNDO, AM1, and PM3 agree that the favorable racemization pathway is different in both cases. The *anti* rotational barrier is slightly lower in **1** (0.3–4.1 kcal/mol) but substituents (bromine) in the 2,2′-positions (**2**) result in a 15–26 kcal/mol preference for the *syn* process. Unlike **1**, the obstacles to rotation in **2** are not overcome simultaneously but stepwise. The aromatic rings distort considerably in the transition structures. This is responsible for roughly 2/3 of the activation barrier in **1** and even more than that in **2**, according to our analyses.

2,2′-Dilithio-1,1′-binaphthyl·2EDA (**3a**) racemizes most favorably stepwise on the *anti* side (MNDO). The less favorable *syn* pathway leads to exchange of the lithiums between the C(2) and C(2′) atoms. Stabilization through lithium double bridging lowers the rotational barrier of the *syn*-TS of **3a** compared to that of 1,1′-binaphthyl (**1**) by 6.3 kcal/mol (MNDO). For *anti* rotation, this difference is increased to 11.7 kcal/mol due to the stepwise pathway of **3a**.

After using ab initio results to calibrate the favorable MNDO *anti* activation barrier of **3a** (22.1 kcal/mol), the corrected estimate should be in reasonable agreement with an experimental estimate for **3** (18.4 kcal/mol). PM3 reproduces the experimental value (22.5 kcal/mol) for the racemization energy of **1** (23.1 kcal/mol). The PM3 activation barrier for **2** (30.3 kcal/mol) is lower than the experimental guess for 2,2′-dimethyl-1,1′-binaphthyl (**4**) (37–40 kcal/mol).

Semiempirical methods appear to be well suited for calculating the rotational barriers in biphenyl-type systems and provide detailed insights into the pathways and mechanisms involved.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft, the Volkswagenstiftung, and the Convex Computer Corp.

Supplementary Material Available: Archive entries of all ground and transition structures of **1**, **2**, and **3a** as well as MP2/6-31G*//6-31G* archive entries for **6a–d** (35 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.