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Flexibility vs Rigidity of Singly and Doubly Tethered Biphenyls: Structure, Dynamic Stereochemistry, and Resolution of Tribenzo[*a*,*c*,*f*]cyclooctane, Tetrabenzo[*a*,*de*,*h*,*kl*]bicyclo[6.6.0]tetradecane, and Their Alkyl Derivatives[†]

Lior Eshdat,[‡] Elad Shabtai,[‡] Sadiq A. Saleh,[§] Tamar Sternfeld,[‡] Mayuko Saito,[||]
Yoshio Okamoto,[||] and Mordecai Rabinovitz*[,‡]

*Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel,
Department of Chemistry, Yarmouk University, Irbid, Jordan, and Department of Applied Chemistry,
Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan*

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The barrier for enantiomerization of tribenzo[*a*,*c*,*f*]cyclooctane (**1a**) as acquired from dynamic ^{1}H NMR experiments was found to be $\Delta G^{\ddagger} = 19.5-20.1$ kcal mol^{-1}, and $\Delta G^{\ddagger} = 17.2-17.6$ kcal mol^{-1} for its alkylated derivatives (**1b**−**e**) at the coalescence temperatures. Tetrabenzo[*a*,*de*,*h*,*kl*]bicyclo[6.6.0]tetradecane (**2a**) and its tetraethyl derivative (**2b**) were separated to their enantiomers by chiral HPLC. The kinetic values for the enantiomerization were obtained by following the racemization rate of the pure enantiomer. Barriers of $\Delta G^{\ddagger}_{596} = 49.6$ kcal mol^{-1} and $\Delta G^{\ddagger}_{561} = 46.3$ kcal mol^{-1} for **2a** and **2b**, respectively, were obtained. Strong solvent and temperature effects on the ^{1}H NMR chemical shifts were observed. X-ray crystallography revealed torsional conformations for **1a**, **1b**, and **2a** with dihedral angles of 57.8°, 56.1°/58.2° (two conformations), and 57.7°, respectively. Semiempirical calculations (AM1) reveal higher relative strain energies and smaller biphenyl dihedral angles for the bulky alkyl substituents, which correspond to their lower $\Delta G^{\ddagger}$ values.

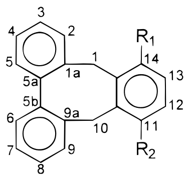
Introduction

Bridged biphenyls are generally twisted and can adopt two possible enantiomeric conformations, which represent right-handed or left-handed helices. The enantiomers are exchangeable due to rotation about the biphenyl axis. The stereochemistry of only few bridged biphenyls which form eight-membered rings were studied.[1−6]

We have previously prepared and studied the magnetic anisotropy of such systems, i.e., tribenzo[*a*,*c*,*f*]cyclooctane (**1a**) and tetrabenzo[*a*,*de*,*h*,*kl*]bicyclo[6.6.0]tetradecane (**2a**), and have revealed their unusual anionic rearrangement.[7] The biphenyl fragments, which are the backbone of these molecules, are bridged at their 2,2′ positions as in **1** or at 2,2′ and 6,6′ as in **2**. The bridges are anchored to the biphenyl fragment by benzylic carbons.

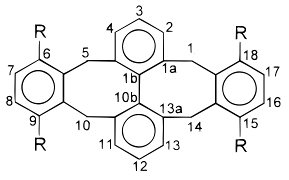
The benzylic sp^3 carbons of the bridge skeleton confer some flexibility on the molecule to rotate about the pivotal axis of the biphenyl. This leads to an inversion between the two helical enantiomers.[8] It has recently been shown that bridged biphenyls are related to optically active liquid crystals,[9] which by themselves have applicative advantages.[10] It is therefore of interest to evaluate the barrier of enantiomerization of this class of biphenyls, which are expected to be relatively rigid due to the presence of benzene components in their bridges.[1,2]

1



1a $R_1=R_2=H$
1b $R_1=R_2=Me$
1c $R_1=Me$ $R_2=Et$
1d $R_1=Me$ $R_2=i\text{-}Pr$
1e $R_1=Et$ $R_2=Et$

2



2a R=H
2b R=Et

In each of the symmetrical alkyl derivatives of **1**, a C_2 symmetry axis passes through the center of the biphenyl

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* Corresponding author. Phone: 2-6585281. Fax: 2-6527547. e-mail: mordecai@vms.huji.ac.il.

[†] This work is dedicated to the memory of Prof. Joseph Klein, a beloved teacher and scholar.

[‡] The Hebrew University of Jerusalem.

[§] Yarmouk University.

[||] Nagoya University.

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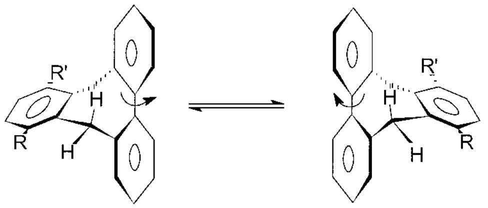
axis and the center of the *ortho*-disubstituted benzene plane, which is part of the bridge. Three C_2 axes exist in **2**, where the first one is positioned as in **1**, and the other two are perpendicular to it: one passes through the center of the biphenyl axis and the other includes it. The geminal benzylic-bridge hydrogens, described above, have an "axial-like" (H_a) or an "equatorial-like" (H_e) relationship to the eight-membered ring. These hydrogens are nonequivalent being exchangeable due to enantiomerization. Therefore, they could be employed in order to follow the process of enantiomerization by means of dynamic NMR.[11] When the barrier is higher than the upper limit of dynamic NMR, resolution of the enantiomers by chiral HPLC and a follow-up of the racemization process are efficient tools to determine the kinetic parameters.[12]



The enantiomerization process of the doubly bridged systems **2** could occur via a simultaneous motion of the two bridges or a consecutive motion of each bridge. In the consecutive motion the biphenyl benzene rings are expected to be highly distorted in the transition state. In a simultaneous process the contribution of the two bridges to the free energy of activation may be twice that of the single bridge. Thus, the expected barrier in both cases should be higher than the barrier for enantiomerization of the singly bridged system.

In the numerous bridged biphenyls studied,[1,2,5,13−16] the free energy of activation for the enantiomerization was found to depend on the degree by which the bridge restricts the freedom of rotation about the biphenyl axis. The degree of restriction is determined by the structure of the bridge, and by the functional groups present on the bridge and on the biphenyl component. The effect of substituents on the stereochemistry was investigated in systems bearing alkyl substituents in positions 11 and 14 of **1**, and in positions 6, 9, 15, and 18 of **2**.

We report a combined stereochemical and structural study of **1** and **2** carried out by applying NMR techniques, X-ray diffraction crystallography, chiral chromatography enantiomer resolution, racemization measurements, and semiempirical calculations.

Results and Discussion

Table 1. Dynamic ^{1}H NMR Data of 1a-e

compound	solvent	$\Delta\nu^{a,b}$ (Hz)	temp of coal.^{c} (K)	$\Delta G^{\ddagger\ d}$ (kcal mol^{-1})
1a	toluene-d_8	72	412	20.1
	CD_3NO_2	41	394	19.5
	THF-d_8	12^e	374^e	19.9^f
1b	$CDBr_3$	328	376	17.2
	toluene-d_8	253	373	17.3
1c	$CDBr_3$	333	376	17.2
1d	$CDBr_3$	352	383	17.5
1e	$CDBr_3$	337	383	17.6

[a] Values at the coalescence temperature; determined by extrapolation of $\Delta\nu$ vs temperature. [b] ±0.5 Hz. [c] ±3 K. [d] ±0.2 kcal mol^{-1}. [e] The two signals overlap due to the temperature effect on the chemical shift. [f] Average $\Delta G^\ddagger$ which was calculated by applying line shape analysis in the temperature range 352−374 K (see reference 10c).

Enantiomerization of Singly Bridged Systems. ^{1}H NMR spectra were recorded for **1a**−**e** at various temperatures in order to estimate the free energy of activation for the enantiomerization process. The $\Delta G^\ddagger$ values were calculated from the coalescence temperatures as well as from line shape analyses (Table 1).[11] The AB quartet of the benzylic-bridge hydrogens of **1a** that was recorded at low temperatures (toluene-d_8, 180 K, δ 3.49−3.69 ppm) coalesced into a singlet at 416 K. The $\Delta\nu$ of the AB quartet is solvent and temperature dependent.[17] The temperature dependence of $\Delta\nu$ in THF-d_8 was most significant, so the observed coalescence might be due to a coincidental overlap of the quartet. Therefore, only line shape analysis afforded a reliable value for $\Delta G^\ddagger$ (Table 1). Raising the temperature up to 453 K caused solvent independent narrowing of the singlets.

The calculated barriers (19.5−20.1 kcal mol^{-1}) are close to the inversion barrier which was found for 9,12-dihydrodibenzo[*a*,*c*]cyclooctene (19.5 kcal mol^{-1})[18] and are significantly lower than the corresponding less rigid 9,10,11,12-tetrahydrodibenzo[*a*,*c*]cyclooctane (23.2 kcal mol^{-1})[18] and its dicarboxylic derivative.[2] This shows that greater rigidity due to the presence of sp^2 carbons in the bridge does not lead to higher barriers.

The benzylic-bridge hydrogens of the alkyl derivatives possessed one or two AX quartets depending on the symmetry of the system. These quartets coalesced into broad singlets upon elevation of the temperature. The $\Delta G^\ddagger$ values were derived from the coalescence temperatures and were found to be in the range 17.2−17.6 kcal mol^{-1}. As the alkyl substituents become bulkier, the barrier for enantiomerization is increased. The enantiomerization process could also be followed by observing the ^{1}H NMR patterns of the benzylic hydrogens of the ethyl groups of **1c** ($CDBr_3$, 285 K, 2H, δ 2.78−2.83 ppm) and **1e** ($CDBr_3$, 280 K, 4H, δ 2.77−2.83 ppm), and the methyl hydrogens of the isopropyl group of **1d** ($CDBr_3$, 285 K, 6H, δ 1.15−1.40 ppm). The $\Delta G^\ddagger$ values for the enantiomerization of each compound, as derived from the benzylic-bridge hydrogens, were found to be essentially the same as when they were derived from the substituent alkyl groups.

Resolution, Racemization, and Dynamics of the Doubly Bridged Systems. The ^{1}H NMR of **2** did not show a typical enantiomerization-induced coalescence even at 450 K recorded on a 200 MHz spectrometer. We did not observe any dynamic process using NOE experi-

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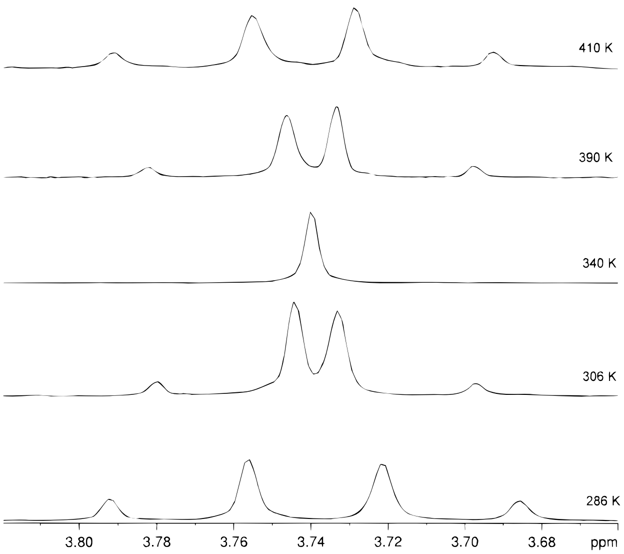

Figure 1. Temperature dependent ^{1}H NMR spectra of the benzylic-bridge region of **2a** (400 MHz, THF-d_8).

ments. Hence, for determination of the enantiomerization barrier, the optical resolution of **2a** and **2b** was obtained on a chiral HPLC column. The racemization of the dextrorotatory enantiomer of **2a** in squalane was followed at 582, 589, 596, 602, and 608 K by HPLC. From the observed data (Supporting Information), a barrier of $\Delta G^\ddagger = 49.6$ kcal mol^{-1} ($\Delta H^\ddagger = 49.2$ kcal mol^{-1}, $\Delta S^\ddagger = -0.612$ cal mol^{-1} K^{-1} (at 596 K))[19] was calculated for the enantiomerization process. The racemization of the levorotatory enantiomer of **2b** was followed in squalane at 549, 556, 561, 566, and 571 K (Supporting Information) and $\Delta G^\ddagger = 46.3$ kcal mol^{-1} ($\Delta H^\ddagger = 37.3$ kcal mol^{-1}, $\Delta S^\ddagger = -16$ cal mol^{-1} K^{-1} (at 561 K))[19] was obtained. Such values are surprisingly high. In other types of doubly bridged biphenyls the $\Delta G^\ddagger$ values are about twice as high as those of the singly bridged analogues.[1,13-15] The magnitude of the barrier by itself cannot provide a convincing answer to the question of whether the inversion of the bridges is consecutive or simultaneous.

Conformational Studies. At low temperatures, the ^{1}H NMR spectrum of **2a** exhibited an AB quartet for the benzylic-bridge hydrogens (THF-d_8, 220 K, δ 3.64−3.85 ppm). As the temperature was elevated, there was a displacement of the two doublets toward each other until they superimposed to form one line δ 340 K, (3.74 ppm). Upon further elevation of the temperature, the line separated again to form a new AB system (Figure 1). The ^{1}H NMR spectra of **2b** did not exhibit as strong a temperature dependence as **2a**, and only a slight shift of the doublets could be observed.

It is well-known that the actual conformation of bridged biphenyls has a crucial influence on the chemical shift of the benzylic-bridge hydrogens.[13,14] Therefore, the temperature dependence of the chemical shifts of the doublets is most likely caused by one of the following: (a) an asymmetrical potential energy curve whereby a variation of temperature changes the average conformation of the molecule and thus alters the magnetic environment, (b) an interplay between two or more conformers of the same enantiomer, or (c) a temperature-dependent solvent effect.

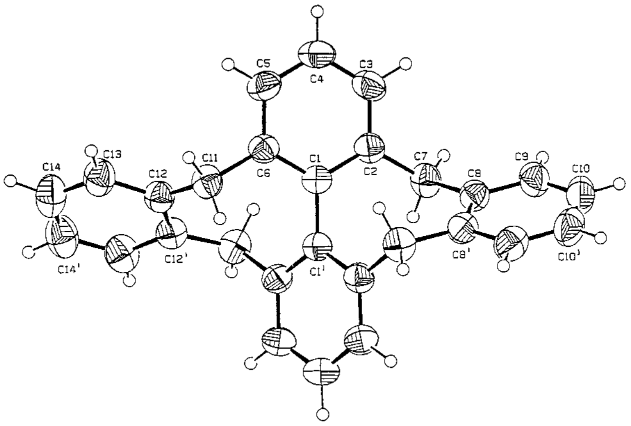

Figure 2. ORTEP diagram of tetrabenzo[*a*,*de*,*h*,*kl*]bicyclo-[6.6.0]tetradecane (**2a**).

The multiple local minima that were calculated for dibenzo[*a*,*c*]cyclooctane and its derivatives[4,5] may also point to the existence of several local minima for **2a**. A gradual elevation of the temperature, which changes the ratio of the populations among the different conformations, may gradually displace the chemical shift. This process continues until the averaged magnetic environment of both benzylic-bridge hydrogens is the same, but this does not actually exchange them. At higher temperatures, the average magnetic environment of each hydrogen differs again, causing the doublets to split and to shift away from each other. If the two enantiomers possess different conformations and the barrier between the conformers is high enough, then at low temperatures two sets of signals are expected. Yet, this has not been the case for **2a** and **2b** even at temperatures close to the freezing point of toluene-d_8 and of THF-d_8 (180 and 167 K, respectively). Molecular mechanics calculations (MMX)[20] which were performed on various starting conformations of **1** and **2** led to only one minimum energy conformation.[21] The findings that $\Delta\nu$ is dependent on the type of solvent and that the temperature dependence of $\Delta\nu$ decreases in solvents which give a larger $\Delta\nu$, lends strength to the explanation of this phenomenon in terms of solvent effects. Thus, we find that the temperature dependence of the chemical shift is best ascribed to an asymmetrical potential energy curve, i.e., a, or to a temperature-dependent solvent effect, i.e., c.

The singly bridged biphenyl systems **1** have lower enantiomerization barriers; therefore, they exhibit coalescence (due to enantiomerization) prior to the crossing of the doublets.

In attempt to find whether conformational differences can account for the large gap between the $\Delta G^\ddagger$ values of **1** and **2**, an X-ray diffraction study was performed on single crystals of **1a** and **2a** (Figure 2). A single crystal of **1b** was also studied in order to gain information concerning the effect of the alkyl derivative on the conformation.

According to the X-ray pattern, all these molecules have twisted conformations, where the unit cells include

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[19] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were evaluated by plotting $-\ln k$ vs $1/T$ where k is the rate constant of racemization and T is temperature ($-\ln k = -\ln A + E_a/(RT)$). The rate constant ($-\ln(\mathrm{ee}) = 2kt$) was determined by plotting $-\ln(\mathrm{ee})$ vs time.

[20] MMX as implemented by PCMODEL-PI (Serena Software, Box 3076, Bloomington, IN 47402).

[21] MM2-91 calculations were performed on **1** and **2** by a referee to give single minimum energy conformations in addition to the calculations mentioned here.

Table 2. Crystal Data for 1a, 1b, and 2a

	1a	**1b**	**2a**
formula	$C_{20}H_{16}$	$C_{22}H_{20}$	$C_{28}H_{22}$
fw, g mol^{-1}	256.35	284.40	358.48
cryst system	monoclinic	triclinic	orthorhombic
space group	$P2_1/c$	$P\bar{1}$	$Aba2$
a, Å	10.426(2)	12.286(3)	11.130(1)
b, Å	13.350(3)	14.847(4)	11.232(2)
c, Å	11.229(2)	9.885(4)	15.585(6)
α, deg		104.02(3)	
β, deg	116.03(2)	98.69(3)	
γ, deg		66.96(2)	
V, Å^3	1404.4(7)	1606.7(9)	1948.4(8)
Z	4	4	2
d (calcd), g cm^{-3}	1.21	1.18	1.22
μ(Cu Kα), cm^{-1}	4.82	4.64	4.87
R	0.035	0.063	0.034
R_W	0.062	0.109	0.052

Table 3. AM1 Calculations

compound	R_1	R_2	RSE[a] (kcal/mol)	biphenyl dihedral angle (deg)[b]	H_e-H_{near}[c] (Å)
1a	H	H	0	59.50	2.99
1b	Me	Me	4.38	55.80	2.19, 2.17[d]
1c	Me	Et	5.49	55.41	2.18, 2.10[d]
1d	Me	i-Pr	6.16	55.30	2.18, 1.92[d]
1e	Et	Et	6.61	55.27	1.97
2a	H	H	0	62.22	2.19
2b	Et	Et	13.17	58.52	1.95

[a] For method of calculation, see text. [b] The biphenyl dihedral angles are determined by the carbons common to the two phenyl rings and to a cyclooctane ring (i.e., carbons 1a, 5a, 5b, and 9a in **1** and carbons 1a, 1b, 10b, and 13a in **2**). [c] The distance between the equatorial bridge hydrogen (H_e) and the nearest hydrogen in space. [d] When the calculated distances were different for each H_e, both values are given.

both enantiomers (Table 2). In the case of **1b** there are two types of flexible and close conformations in the same unit cell.[22] The biphenyl dihedral angles are 57.8° for **1a**, 56.1° and 58.2° for the two conformations of **1b**, and 57.7° for **2a**. The deviations from the mean plane of the benzene rings are small and do not exceed 0.0249 Å in any of the compounds tested. There are slight deviations from the C_2 symmetry axis which **1a** and **1b** possess in solution as emphasized by ^{1}H NMR. These values may indicate that in the solid state, there are minor differences between doubly bridged and singly bridged systems, or between substituted and unsubstituted derivatives.

To gain more information on the effect of substituents on the enantiomerization process, we carried out semiempirical AM1 calculations.[23,24] These calculations afforded twisted conformations similar to those that were found by X-ray crystallography. Table 3 shows the correlation between the relative strain energy (RSE) and structural parameters of the systems studied. We chose to calculate RSE applying an isodesmic reaction.[25] As the reaction coordinate of the enantiomerization follows changes of the biphenyl dihedral angle, we compared it with the RSE and with the kinetic parameters (Table 1). This comparison shows the following trend: as the substituents are bulkier, the biphenyl dihedral angle decreases and the relative strain energy increases. The most significant difference is shown between the parent and the substituted systems. A higher RSE corresponds to an elevated energy of the ground state, which consequently leads to a lower barrier for enantiomerization. This holds assuming that the transition state of the systems which belong to the same family, i.e., **1** or **2**, is similar. This general trend is in line with the kinetic parameters that were derived by the dynamic-NMR and racemization experiments. Our calculations strengthen the argument of Mislow et al.,[13] for systems that undergo similar inversion processes: a less twisted ground state conformation is energetically closer to the energy of the transition state, and results in a lower $\Delta G^{\ddagger}$.

Substituent Effects on the ^{1}H NMR Spectra. The AX quartets assigned to the benzylic-bridge hydrogens in the alkyl derivatives (**1b**−**e** and **2b**) differ from the pattern of the benzylic-bridge hydrogens of **1a** and **2a** (AB quartets). Although all the molecules examined adopt a similar twisted conformation, according to the crystallographic study and on the basis of the calculations, the slight variations in the dihedral angle of the biphenyl rings may still account for the difference in the ^{1}H NMR pattern. Since these hydrogens are located in a region where the anisotropic effects of three benzene rings overlap, it follows that the magnetic environment is highly dependent on the relative orientations of the benzene rings vis à vis the benzylic-bridge hydrogens.

In addition to the effect of the dihedral angle, a crowding of the alkyl substituent and of the “equatorial-like” bridge hydrogen (H_e) also plays a role in determining their ^{1}H NMR pattern. The calculated distances between the bridge hydrogen and the benzylic hydrogen of the adjacent alkyl substituent in the singly bridged molecules **1b**−**e** are at least 0.7 Å shorter than the distance between the bridge hydrogen in **1a** and the nearest benzene hydrogen (Table 3). There is a smaller difference of 0.23 Å in the alkyl-substituted **2b** and nonsubstituted **2a** doubly bridged molecules. This may result in a growing electronic repulsion, which lowers the electron density on H_e compared to the axial hydrogen in the alkyl derivatives in both families. Therefore, the chemical shift of H_e should be shifted downfield. This agrees with the finding that only the lower field doublet of the benzylic-bridge hydrogens AX pattern showed a NOE cross-peak with the signal of the methyl group.

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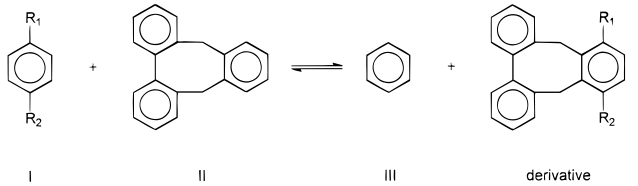
(24) AM1 as implemented by Spartan (version 4.1; Wavefunction, Inc., Irvine, CA 92715) was used.

(25) Analyzing the relative energetic contribution of strain and overcrowding (RSE) to the energy of the various derivatives was performed by using the following isodesmic reaction (a similar reaction was designed for the doubly bridged systems):



E_{ref} is the heat of formation of a hypothetical derivative, which is free of contributions from steric strain and intramolecular overcrowding due to the substituent. It may be calculated by computing the energies of the reference molecules (I−III) and assuming a zero energy of the above reaction:

$$E_{ref} = E(\mathrm{I}) - E(\mathrm{II}) - E(\mathrm{III})$$

RSE is evaluated by subtracting E_{ref} from the computed heat of formation of the derivative (E_{deriv}):

$$\mathrm{RSE} = E_{deriv} - E_{ref}$$

See: George, P.; Trachtman, M.; Bock, C. W.; Brett A. M. *Tetrahedron* **1976**, *32*, 317−323.

Table 4. Solvent Effect on $\Delta\nu$ (283 K) of the Benzylic-Bridge Doublets of 1a

solvent	chemical shifts (ppm)	chemical shift difference (Hz)
bromoform-*d*	3.61, 3.68	28.1
chloroform-*d*	3.59, 3.63	16.9
cyclohexane-d_6	3.56, 3.65	36.1
THF-d_8	3.55, 3.70	45.4
nitrobenzene-d_5	3.48, 3.63	58.2
nitromethane-d_3	3.59, 3.72	79.3
benzene-d_6	3.48, 3.74	105.2

An intermolecular factor explaining the ^{1}H NMR pattern of the benzylic-bridge hydrogens, i.e., the reduction of a stacking effect due to steric repulsion, was ruled out since no significant change was seen in the chemical shift upon dilution of samples of **1a** and of **1b**.

The Solvent Effect on the ^{1}H NMR Spectra. Samples of **1a** (0.02 M) were prepared using different solvents. Aromatic and nonaromatic solvents of different polarities were chosen and measurements were taken at 283 K. A clearly pronounced solvent dependence of the $\Delta\nu$ between the axial and the equatorial positions could be seen (Table 4). This dependence neither correlates with the dipole moment of the solvent nor with its aromaticity. It is rather unusual that simple hydrocarbons exhibit such a strong solvent effect on the chemical shift,[26] which is a known phenomenon for molecules that bear heteroatoms.[27]

In the alkyl derivatives, the solvent effect is less pronounced as $\Delta\nu$ is large, regardless of the solvent used. We therefore suggest that in these cases the dominant contribution to $\Delta\nu$ is a result of the presence of the alkyl substituent and its effect on the magnetic environment and on the conformation of the compound.

Conclusions

The structure and dynamic behavior of biphenyls, which are singly or doubly bridged by chains that form semirigid eight-membered rings, are described. The $\Delta G^{\ddagger}$ of enantiomerization of the doubly bridged systems is significantly higher than that of the singly bridged systems.

Semiempirical calculations suggest that the alkyl derivatives have smaller torsional angles and higher ground state strain energies, as the substituents are bulkier. Thus, their ground state energies are relatively closer to the energy of the transition state. This explains the fact that the $\Delta G^{\ddagger}$ values for the alkyl derivatives are lower than those of the parent molecules. The calculations also show that the presence of alkyl substituents creates a more crowded environment near the benzylic-bridge hydrogens in the singly and in the doubly bridged biphenyls.

The ^{1}H NMR chemical shift of the bridge protons of the doubly bridged systems is highly sensitive to the conformation of the enantiomer. Each enantiomer in this group may have an asymmetrical potential curve, and possibly even more than one local minimum. The methylated singly bridged **1b** exists in two flexible and close conformations in the solid state.

Experimental Section

The ^{1}H NMR and 2D NMR spectra were recorded on a 400 MHz and a 200 MHz spectrometer. Samples were sealed in 5 mm glass tubes. Chemical shifts were measured relative to a solvent peak, which was calibrated according to the temperature.[28] The temperature was calibrated with methanol or with ethylene glycol.

Compounds **1a** and **2a** were prepared by reaction of benzene and 2,2′-bis(hydroxymethyl)biphenyl or 2,2′,6,6′-tetrakis(hydroxymethyl)biphenyl, respectively, in the presence of concentrated sulfuric acid according to the literature.[7] The preparation of **1b**−**e** was carried out by the same reaction using 2,2′-bis(hydroxymethyl)biphenyl and *p*-xylene, *p*-ethyltoluene, *p*-cymene, or *p*-diethylbenzene, respectively. Compound **2b** was yielded in the reaction of 2,2′,6,6′-tetrakis(hydroxymethyl)-biphenyl with *p*-xylene in concentrated sulfuric acid. All compounds gave satisfactory elemental analyses and ^{1}H NMR spectra.

Chromatography was performed on a chromatograph equipped with UV and polarimetric detectors for HPLC.

X-ray crystallographic studies were performed on single crystals, which were grown from petroleum ether (40−60 °C). Data were measured on a computer-controlled diffractometer. CuKα (λ = 1.54178 Å) radiation with a graphite crystal monochromator in the incident beam was used.

Tribenzo[*a*,*c*,*f*]cyclooctane (1a): ^{1}H NMR (400 MHz, 170 K, THF-d_8) δ 3.50 (d, 2H, J = 14.7 Hz, CH_2), 3.82 (d, 2H, J = 14.7 Hz, CH_2), 7.26 (m, 4H, ArH), 7.40 (m, 8H, ArH) ppm. Mp = 138−140 °C (lit.[8] mp = 137−139 °C).

11,14-Dimethyltribenzo[*a*,*c*,*f*]cyclooctane (1b): ^{1}H NMR (400 MHz, 280 K, $CDBr_3$) δ 2.46 (6H, Me), 3.22 (d, 2H, J = 15.0 Hz, CH_2), 4.06 (d, 2H, J = 15.0 Hz, CH_2), 6.93 (s, 2H, ArH), 7.25−7.42 (m, 8H, ArH) ppm. Mp = 131−132 °C.

11-Ethyl-14-methyltribenzo[*a*,*c*,*f*]cyclooctane (1c): ^{1}H NMR (400 MHz, 280 K, $CDBr_3$) δ 1.23 (t, 3H, J = 7.5 Hz, Me), 2.46 (s, 3H, Me), 2.78 (dq, 1H, J = 14.6, 7.5 Hz, CH_2), 2.83 (dq, 1H, J = 7.5, 14.6 Hz, CH_2), 3.21 (d, 1H, J = 14.9 Hz, CH_2), 3.22 (d, 1H, J = 14.9 Hz, CH_2), 4.06 (d, 1H, J = 14.9 Hz, CH_2), 4.07 (d, 1H, J = 14.9 Hz, CH_2), 6.96 (d, 1H, J = 7.7 Hz, ArH), 7.01 (d, 1H, J = 7.7 Hz, ArH), 7.30−7.33 (m, 6H, ArH), 7.39−7.40 (m, 2H, ArH) ppm. Mp > 300 °C (dec).

11-Isopropyl-14-methyltribenzo[*a*,*c*,*f*]cyclooctane (1d): ^{1}H NMR (400 MHz, 285 K, $CDBr_3$) δ 1.15 (d, 3H, J = 4.2 Hz, CH_3), 1.40 (d, 3H, J = 4.2 Hz, CH_3), 2.46 (s, 3H, CH_3), 3.18 (d, 1H, J = 15.0 Hz, CH_2), 3.20 (d, 1H, J = 15.0 Hz, CH_2), 3.44 (m, 1H, J = 4.2 Hz, CH), 4.09 (d, 1H, J = 15.0 Hz, CH_2), 4.18 (d, 1H, J = 15.0 Hz, CH_2), 7.05 (d, 1H, J = 7.7 Hz, ArH), 7.08 (d, 1H, J = 7.7 Hz, ArH), 7.31 (m, 6H, ArH), 7.40 (m, 2H, ArH) ppm. Mp = 120−121 °C.

11,14-Diethyltribenzo[*a*,*c*,*f*]cyclooctane (1e): ^{1}H NMR (400 MHz, 285 K, $CDBr_3$) 2.77 (dq, 2H, J = 14.6, 7.5 Hz, CH_2), 2.83 (dq, 2H, J = 14.6, 7.5 Hz, CH_2), 3.23 (d, 2H, J = 15.0 Hz, CH_2), 4.09 (d, 2H, J = 15.0 Hz, CH_2), 7.02 (s, 2H, ArH), 7.34 (m, 6H, ArH), 7.41 (m, 2H, ArH) ppm. Mp = 110−111 °C.

Tetrabenzo[*a*,*de*,*h*,*kl*]bicyclo[6.6.0]tetradecane (2a): ^{1}H NMR (400 MHz, 210 K, THF-d_8) 3.65 (d, 4H, J = 14.4 Hz, CH_2), 3.83 (d, 4H, J = 14.4 Hz, CH_2), 7.16 (m, 4H, ArH), 7.27 (m, 4H, ArH), 7.27−7.35 (m, 6H, ArH) ppm. Mp = 278 °C (lit.[7a] mp = 278 °C).

6,9,15,18-Tetraethyltetrabenzo[*a*,*de*,*h*,*kl*]bicyclo[6.6.0]-tetradecane (2b): ^{1}H NMR (400 MHz, 210 K, THF-d_8) (1.24 (t, 12H, J = 7.5 Hz, Me), 2.72 (dq, 8H, J = 14.4 Hz, CH_2), 2.99 (dq, 8H, J = 14.4 Hz, CH_2), 3.36 (d, 4H, J = 14.4 Hz, CH_2), 4.26 (d, 4H, J = 14.4 Hz, CH_2), 7.00 (s, 4H, ArH), 7.21−7.27 (m, 6H, ArH) ppm. Mp = 273−275 °C.

Resolution of 2a. Preparative optical resolution of racemic **2a** was performed with a cellulose tris(3,5-dimethylphenyl-carbamate) HPLC column 50 × 2 (i/d) cm) (eluent hexane/2-

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[28] The chemical shift of each solvent was measured at several different temperatures and was calibrated relative to TMS in different concentrations. For the temperature correction of THF-d_8 see: Nir, M.; Shapiro I. O.; Hoffman R. E.; Rabinovitz, M. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1607−1616.

propanol (95.5/0.5 (v/v)), flow rate 10 mL/min, pressure 10 kg/cm^2). Racemization of optically active **2a** (ca. 4.6 mg/mL) in squalane was monitored by HPLC with CHIRALCEL OD column (eluent hexane/2-propanol (95.5/0.5 (v/v)), flow rate 0.5 mL/min, pressure 9 kg/cm^2).

Resolution of 2b. Preparative optical resolution of racemic **2b** was carried out with three CHIRALCEL OD columns connected in tandem (eluent isooctane, flow rate 0.5 mL/min, pressure 46 kg/cm^2). Racemization of optically active **2a** (ca. 4.6 mg/mL) in squalane was monitored by HPLC with a silica gel column (25 × 0.46 (i/d) cm) using hexane as eluent (flow rate 0.5 mL/min, pressure 16 kg/cm^2). Enantiomeric excess (ee) of samples were estimated from the intensity ratio of UV and polarimetric detectors.

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Supporting Information Available: Tables of structure solution and refinements, atomic coordinates, bond lengths and angles, least-squares planes, dihedral angles between least-squares planes, anisotropic thermal parameters, and stereoviews for **1a**, **1b**, and **2a**; racemization data for **2a** and **2b**; dynamic ^{1}H NMR spectra of the benzylic-bridge region of **1a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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