

The Conformation of Biphenyls in Nematic Liquid Crystalline Solution. An Investigation of the Torsional Angles in 2,6-Dihalogenated Derivatives

Leslie D. Field, Sever Sternhell,* and Alan S. Tracey¹

Contribution from the Department of Organic Chemistry, University of Sydney, Sydney, New South Wales, 2006, Australia. Received January 17, 1977

Abstract: The ground-state torsional angles between the planes of the benzene rings in 2',6'-dihalogenated derivatives of 4-bromobiphenyl were determined from the NMR spectra of these compounds dissolved in nematic liquid crystalline solvents. The angles were found to be 68, 70, and 77° for the chloro, bromo, and iodo derivatives, respectively. These values compare with 35° for this angle when the 2' and 6' positions are not substituted. Changes in the structure of the phenyl rings on substitution of the 2' and 6' positions were observed.

Nuclear magnetic resonance studies of molecules and ions aligned in the nematic phase of liquid crystalline materials have provided a considerable amount of information concerning their structures.²⁻⁵ The vast majority of the compounds which have been investigated are rigid, i.e., they do not undergo intramolecular motion except for thermal vibrations. However, information concerning internal motion can often be obtained from the NMR spectra of conformationally averaging species if they are dissolved in nematic solvents.^{4,5} Thus several biphenyl derivatives have been investigated and information concerning the torsional angle, defined as the deviation from coplanarity about the inter-ring carbon-carbon bond, has been obtained.⁵⁻⁸ In one case, 4,4'-dichlorobiphenyl (1), an attempt was made to obtain both the preferred angle of rotation, or torsional angle, and parameters defining the potential energy function which describe the internal rotation.⁶ This method, in general, suffers from the fact that there will be insufficient dipolar coupling constants to define the potential energy function or that they will be insensitive to it. In an alternative approach, the angle of twist in 3,4,4',5-tetrabromobiphenyl (2) and 3,3',5,5'-tetrachlorobiphenyl (3) was determined by assuming that the calculated structure was a linear average of two equivalent highly populated rotamers having torsional angles of θ and $180^\circ - \theta$, where θ is zero for a planar molecule.^{7,8} For 4,4'-dichlorobiphenyl the discrepancy between the two approaches is about 6° in the calculated torsional angle, 38° for a fitted potential function compared to 32° for the simple average.⁶

In compounds 1, 2, and 3 the 2,6 and 2',6' positions are unsubstituted. This pattern of substitution was adopted because the close proximity of protons 2 and 6 to 2' and 6' results in the dipolar couplings between these two pairs of protons being particularly sensitive to the internal twist angle. However, it has been pointed out⁶ that for 4,4'-dichlorobiphenyl the calculated value of the dipolar coupling between nuclei 2,6 and 3',5' varied by about 165 Hz for angles of twist between 0° and 90°. This appears to be of adequate precision and should allow information concerning relative interactions of nonhydrogen substituents in the 2' and 6' positions to be obtained, thus leading to a possible correlation between the nature of the substituents and the torsional angle.

To this end 4-bromobiphenyls substituted in the 2',6' and 2',4',6' positions were prepared. The substitution patterns were such that the torsional angle as a function of Cl to H, Br to H, and I to H interactions could be examined.

The compounds prepared were 4-bromo-2',4',6'-trichlorobiphenyl (4), 4-bromo-2',6'-dichlorobiphenyl (5), 2,4,4',6-tetrabromobiphenyl (6), 2,4',6-tribromobiphenyl (7), and 4-bromo-2',6'-diiodobiphenyl (8).

Results and Discussion

A molecular coordinate system was chosen so that it is fixed in the para-disubstituted ring (Figure 1). θ is defined as the dihedral angle between the two rings.

Isotropic Solution. The NMR spectra obtained from the compounds dissolved in isotropic solutions gave the NMR parameters listed in Table I. The values from Table I, which are unexceptional, were subsequently used in the analysis of the spectra from anisotropic solutions.

Anisotropic Solution. The spectra from the anisotropic solutions were about 7 kHz in width. A typical spectrum, that of 4-bromo-2',6'-dichlorobiphenyl (5), is shown in Figure 2.

All spectra were analyzed with the aid of a modified UEA computer program⁹ in which the spin Hamiltonian employed is given by

$$\begin{aligned} \mathcal{H} = & - \sum_i (1 - \sigma_i - \sigma_{ia}) \nu_0 \hat{I}_{zi} + \sum_{i < j} [(J_{ij} + D_{ij}) \hat{I}_{zi} \hat{I}_{zj} \\ & + \frac{1}{2} (J_{ij} - \frac{1}{2} D_{ij}) (\hat{I}_i^+ \hat{I}_j^- + \hat{I}_i^- \hat{I}_j^+)] + \sum_i B_i \hat{I}_{zi}^2 \quad (1) \end{aligned}$$

where σ_i and σ_{ia} are respectively the isotropic and anisotropic contributions to the chemical shift. J_{ij} is the isotropic indirect coupling constant between nuclei i and j . D_{ij} is the corresponding direct or dipolar coupling constant. B_i is the quadrupolar interaction term which arises when nuclei have a spin greater than $\frac{1}{2}$. \hat{I}_{zi} , \hat{I}_i^+ , and \hat{I}_i^- are spin operators. If σ_{ia} , D_{ij} , and B_i are zero the Hamiltonian is simply that describing NMR spectra from isotropic solution.

This modified program, renamed DIPUEA, accepts as input chemical shifts, isotropic couplings, and either dipolar couplings and quadrupolar splittings or molecular structure and order parameters. It iteratively fits transition frequencies to chemical shifts, isotropic couplings, dipolar couplings, and quadrupolar splittings. The program factors according to magnetic but not chemical equivalence, e.g., it treats methyl groups as a single spin with high multiplicity.

The NMR spectra of all the compounds studied contained a large number of overlapping transitions. As a consequence, the analysis proceeded in two steps. Initially all transitions where assigned, with multiple transition being assigned at a mean experimental frequency. This procedure provided acceptable solutions, but with large standard deviations in parameters. In the second step all unresolved transitions were disregarded in the final calculation. This meant the removal of over one-half of the previously assigned transitions. For example, the spectrum shown in Figure 2 consists of about 220 transitions of useful intensity of which only 84 were utilized in the final calculations. The problem of unresolved transitions

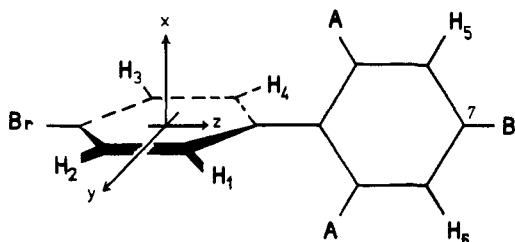


Figure 1. The system of coordinates and numbering of protons. 4, A = Cl, B = Cl; 5, A = Cl, B = H; 6, A = Br, B = Br; 7, A = Br, B = H; 8, A = I, B = H.

in the spectrum of 4-bromo-2',6'-diiodobiphenyl (**8**) was particularly severe and it was necessary to assign overlapping transitions. This accounts for the relatively large errors in the parameters determined for this compound. The results of the analyses are given in Table II.

Molecular Structures and Torsional Angles. The results in Table II provide information concerning: (i) the structures of the para-disubstituted phenyl rings; (ii) the equilibrium angle between the two phenyl rings of each compound; (iii) the relative positions of the protons in the trisubstituted phenyl rings (**5**, **7**, **8**).

The determination of the biphenyl structure was based on the assumption that the molecules are averaging conformationally between two well-defined rotamers with torsional angles of θ and $180 - \theta$ degrees from planarity. If we consider only one of the conformers then these biphenyl derivatives have C_2 symmetry and three orientation parameters S_{xx} , S_{zz} , and S_{xy} are required to describe the alignment of the molecule. With our choice of coordinate system the averaging resulting from internal rotation causes contributions from S_{xz} and S_{yz} to cancel and results in S_{xy} making no contributions to the dipolar couplings within the para-disubstituted ring. S_{xy} does affect the inter-ring couplings and scales the couplings within the second ring. As a consequence S_{xx} , S_{zz} , and the relevant structural parameters for the first ring may be determined by considering only the four dipolar couplings within that ring. Since the NMR data give only relative distances (but absolute angles), the distance $r_{14} = 4.300 \text{ \AA}$ (the value for biphenyl¹⁰) was adopted as a standard and other distances were determined relative to this.

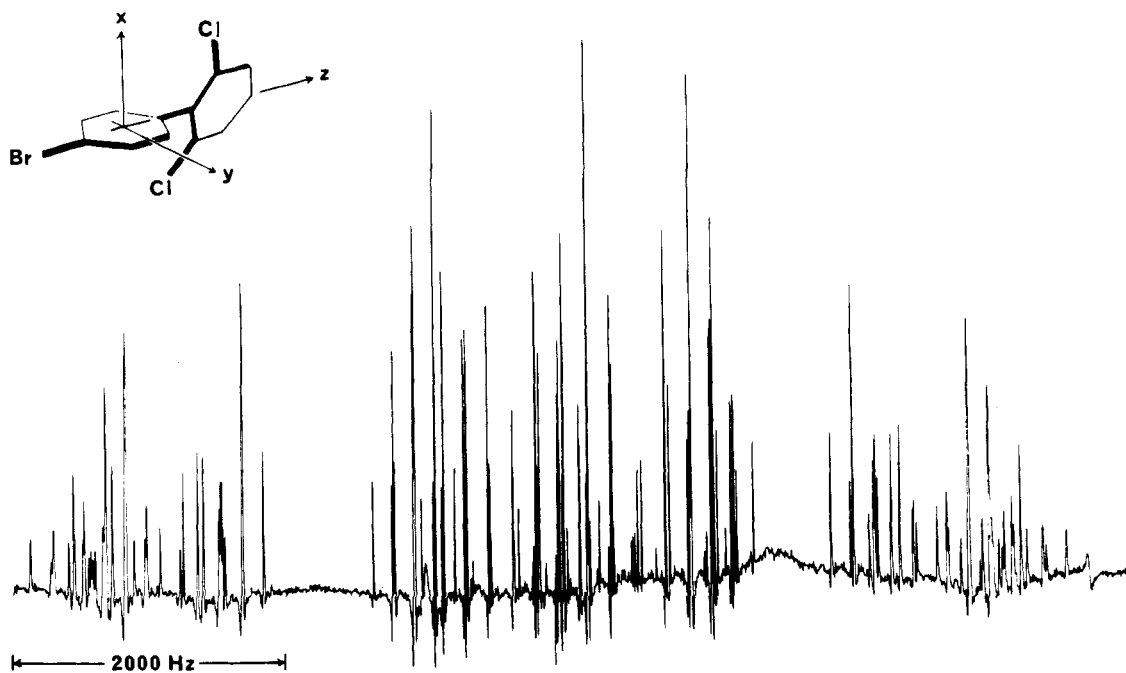


Figure 2. 270-MHz NMR spectrum of 4-bromo-2',6'-dichlorobiphenyl partially aligned in a nematic crystalline solvent.

The spectra of compounds **4** and **6** are defined by seven dipolar couplings. Of these, four are confined to the first ring. The remaining three couplings are not sufficient to define the twist angle, S_{xy} , r_{56} , and the z coordinate of nuclei H_5 and H_6 (where $z_1 = z_4 = 0$) and therefore for these two compounds a second structural assumption, $r_{56} = 4.300 \text{ \AA}$, was made. No such structural assumption is required for compounds **5**, **7**, and **8**. To make comparison easier, Table III gives the results for all compounds calculated on the basis $r_{56} = 4.300 \text{ \AA}$. These calculations were performed with the aid of the computer program SHAPE¹¹ which was modified to account for the averaging of the inter-ring dipolar couplings because of internal rotation. Table III also includes results of calculations using dipolar couplings reported⁴⁻⁶ for other biphenyl derivatives.

Entries **1a**, **2** and **3** of Table III show that for biphenyls with various substitution patterns but having only protons in the 2,6 and 2',6' positions the twist angles are essentially the same. In this regard **1b** is particularly interesting. In entry **1a**, θ was determined on the basis of the couplings from the first ring to nuclei 2' and 6' only. In **1b** the angle was determined on the basis of the couplings to the 3' and 5' protons only. The respective angles were calculated to be 31.8 and 35.3°. The corresponding angle in the gas phase¹⁰ has been found to be 42° while for nematic solution a value of 38° was obtained⁶ when a potential energy function for the torsional motion was included in the calculations. Thus it seems that although couplings from the 2,6 to the 2',6' positions are very sensitive to the equilibrium angle they are also sensitive to the shape of the potential energy function. The couplings to the 3',5' positions are also less sensitive to the shape of the potential energy function. The result is a better estimate of the equilibrium angle and suggests that a reasonable amount of confidence can be placed in the torsional angles for the remaining entries of Table III.

Table III shows that if the 2',6' hydrogens of biphenyl are replaced by chlorine there is a marked increase in the torsional angle, the value increasing from 35 to 68°. The angle increases only a further 2° when bromines replace chlorines. With the introduction of iodine a substantial increase in the angle to 78° occurs.

Since the assumption $r_{56} = 4.300 \text{ \AA}$ is not necessary for

Table I. Chemical Shifts (Hz at 100 MHz) and Isotropic (J) Coupling Constants (Hz) Characterizing the NMR Spectra of Biphenyls Dissolved in Acetone- d_6

Compd	$\nu_1 = \nu_4$	$\nu_2 = \nu_3^a$	$\nu_5 = \nu_6$	ν_7	$J_{12} = J_{34}$	$J_{13} = J_{24}$	$J_{14}(J_{23})^b$	$J_{57} = J_{67}$
4	44.10 \pm 0.01	0	8.4 \pm 0.2		8.33 \pm 0.02	0.45 \pm 0.02	2.26 \pm 0.02	
5	44.17 \pm 0.02	0	15.56 \pm 0.04	26.49 \pm 0.05	8.29 \pm 0.03	0.44 \pm 0.03	2.24 \pm 0.03	8.16 \pm 0.04
6	49.32 \pm 0.02	0	-24.9 \pm 0.02		8.30 \pm 0.03	0.40 \pm 0.03	2.31 \pm 0.04	
7	49.47 \pm 0.02	0	-6.57 \pm 0.04	42.24 \pm 0.04	8.19 \pm 0.02	0.34 \pm 0.02	2.12 \pm 0.02	8.09 \pm 0.05
8	59.89 \pm 0.02	0	-34.34 \pm 0.02	84.40 \pm 0.02	8.25 \pm 0.02	0.40 \pm 0.02	2.23 \pm 0.02	7.87 \pm 0.02

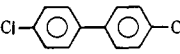
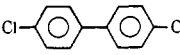
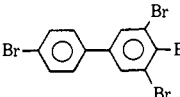
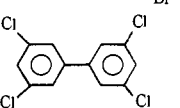
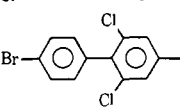
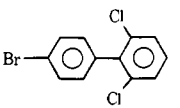
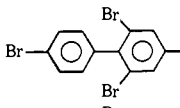
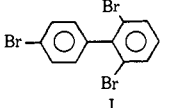
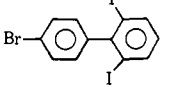
^a Set arbitrarily at 0. ^b J_{14} and J_{23} could not be determined independently.

Table II. The Parameters Describing the 270-MHz NMR Spectra of Biphenyls Dissolved in Anisotropic Media (Hz)

	4	5	6	7	8
$D_{12} = D_{34}$	-6734.7 \pm 0.1	-3885.1 \pm 0.1	-4977.6 \pm 0.2	-3349.3 \pm 0.2	-2821.8 \pm 0.4
$D_{13} = D_{24}$	194.2 \pm 0.1	190.1 \pm 0.1	165.0 \pm 0.2	208.6 \pm 0.2	224.7 \pm 0.3
D_{14}	826.7 \pm 2.3 ^a	637.5 \pm 1.1 ^a	654.4 \pm 0.2 ^b	641.1 \pm 1.5 ^a	639.8 \pm 0.3 ^b
D_{23}	824.9 \pm 2.4 ^a	635.3 \pm 1.1 ^a		638.4 \pm 1.5 ^a	
$D_{15} = D_{16} = D_{45} = D_{46}$	-393.0 \pm 0.2	-225.7 \pm 0.4	-284.7 \pm 0.9	-189.1 \pm 0.5	-154.3 \pm 1.2
$D_{25} = D_{26} = D_{35} = D_{36}$	-193.6 \pm 0.3	-111.0 \pm 0.4	-141.6 \pm 0.5	-95.1 \pm 0.5	-80.5 \pm 1.2
D_{56}	386.7 \pm 0.2	3.75 \pm 0.2	245.5 \pm 0.3	-83.0 \pm 0.4	-164.5 \pm 0.8
$D_{17} = D_{47}$		-210.3 \pm 0.6		-176.5 \pm 0.8	-143.2 \pm 1.8
$D_{27} = D_{37}$		-90.7 \pm 0.6		-76.2 \pm 0.8	-64.7 \pm 1.8
$D_{57} = D_{67}$		-919.4 \pm 0.1		-1124.5 \pm 0.1	-1312.6 \pm 0.3
$\nu_1 = \nu_4$	86.7 \pm 1.3	108.4 \pm 0.9	91.7 \pm 2.3	120.2 \pm 1.2	149.7 \pm 2.9
$\nu_2 = \nu_3$	0.0	0.0	0.0	0.0	0.0
$\nu_5 = \nu_6$	282.3 \pm 0.1	274.2 \pm 0.1	271.8 \pm 0.2	285.7 \pm 0.1	288.1 \pm 0.2
ν_7		140.9 \pm 0.2		224.6 \pm 0.2	351.6 \pm 0.4
Rms error (No. of transitions assigned)	0.33 (46)	0.44 (84)	0.51 (40)	0.58 (80)	1.41 (113)

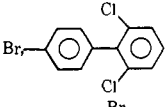
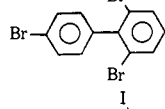
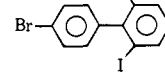
^a D_{14} and D_{23} have a large covariance (a 1-Hz increase in D_{14} is accompanied by a 1-Hz decrease in D_{23}). ^b D_{14} and D_{23} could not be independently determined.

Table III. Internuclear Distances (Å), Torsional Angles (deg), and Order Parameters^a

	$r_{12} = r_{34}$	r_{14}^b	r_{23}	$z_5 = z_6^c$	θ^d	S_{xx}	S_{zz}	S_{xy}	Ref
 (1a)	2.467 \pm 0.001	4.300	4.296 \pm 0.002	1.897 \pm 0.003	31.8 \pm 0.03	-0.2273	0.4319	0.0064	6
 (1b)	2.467 \pm 0.001	4.300	4.296 \pm 0.002	4.289 \pm 0.017	35.3 \pm 0.7	-0.2273	0.4319	0.0081	6
 (2)	2.461 \pm 0.003	4.300	4.300 \pm 0.007	1.905 \pm 0.007	32.5 \pm 0.05	-0.2520	0.4117	0.0570	8
 (3)	4.300 ^b		4.300 ^b	1.882 \pm 0.007	35.4 \pm 0.1	-0.4066	0.2346	0.1983	7
 (4)	2.479 \pm 0.002	4.300	4.303 \pm 0.004	4.282 \pm 0.005	68.1 \pm 0.4	-0.1535	0.4272	0.0610	
 (5)	2.479 \pm 0.002	4.300	4.305 \pm 0.003	4.318 \pm 0.016	68.3 \pm 0.5	-0.0356	0.2467	0.0849	
 (6)	2.478 \pm 0.001	4.300	4.300 ^b	4.303 \pm 0.014	69.6 \pm 0.6	-0.0988	0.3155	0.0487	
 (7)	2.479 \pm 0.002	4.300	4.306 \pm 0.004	4.313 \pm 0.020	71.7 \pm 0.7	-0.0003	0.2125	0.0816	
 (8)	2.478 \pm 0.001	4.300	4.300 ^b	4.265 \pm 0.056	77.6 \pm 2.2	0.0329	0.1789	0.0782	

^a It is assumed that $r_{14} = r_{56} = 4.300$ Å. ^b Assumed distance. ^c Referenced to $z_1, z_4 = 0$. ^d Calculated on the basis that $r_{56} = 4.300$ Å.

Table IV. Torsional Angles, Structure, and Order Parameters, Utilizing the Scale Factor $r_{14} = 4.300 \text{ \AA}$

	$r_{12} = r_{34}$	r_{23}	z_7^b	r_{56}	$r_{57} = r_{67}$	θ	S_{xx}	S_{zz}	S_{xy}	
	(5)	2.479 ± 0.002	4.305 ± 0.002	5.577 ± 0.006	4.363 ± 0.014	2.526 ± 0.015	67.4 ± 0.5	-0.0355	0.2466	0.0848
	(7)	2.479 ± 0.002	4.306 ± 0.002	5.587 ± 0.009	4.365 ± 0.007	2.533 ± 0.010	69.8 ± 0.8	-0.0003	0.2125	0.0836
	(8)	2.478 ± 0.001	4.300^a	5.586 ± 0.019	4.322 ± 0.042	2.535 ± 0.020	77.1 ± 3.7	0.0330	0.1788	0.0793

^a Assumed distance. ^b Referenced to $z_1, z_4 = 0$.

compounds **5**, **7**, and **8** further calculations in which this parameter was allowed to vary were carried out. Table IV gives the results of these calculations and shows that there is a decrease in the calculated torsional angle by about 1° from the values reported in Table III and that r_{56} is slightly greater than the previously assumed distance, increasing to 4.363 ± 0.014 , 4.365 ± 0.007 , and $4.322 \pm 0.042 \text{ \AA}$ for compounds **5**, **7**, and **8**, respectively.

It is interesting to find from Tables III and IV that the relative structure of the para-disubstituted phenyl ring is changed when the 2' and 6' positions are halogenated. For compounds **1** and **2** (Table III), the distances r_{12} and r_{23} fall in the ranges 2.465 ± 0.004 and $4.298 \pm 0.002 \text{ \AA}$, respectively. Upon replacement of hydrogen by chlorine, bromine, or iodine the average distance r_{12} is increased to $2.479 \pm 0.001 \text{ \AA}$ while r_{23} changes to $4.305 \pm 0.001 \text{ \AA}$.

This could be attributed to the decrease in π orbital overlap between the two phenyl rings due to the observed increase in torsional angle. Of further interest is the fact that the distances r_{57} and r_{67} are about 2.530 \AA compared with the distances r_{12} , which are considerably shorter, being 2.479 \AA . Since r_{12} and r_{57} both represent distances between hydrogens ortho to each other then there are substantial structural differences between the two rings of these biphenyl derivatives.

Conclusions

The results of the investigation show that the torsional angle in biphenyls is strongly dependent on substitution in the positions ortho to the inter-ring bond.

The equilibrium angles of biphenyls substituted with chlorine, bromine, or iodine in the 2' and 6' positions were determined and compared with each other and with those for biphenyls unsubstituted in these positions. On the basis of a model in which averaging occurs between two well-defined rotamers with torsional angles of θ and $180^\circ - \theta$, the angles were found⁵⁻⁸ to be about 35° for biphenyls unsubstituted in the 2', 6' positions and 68, 70, and 77° for biphenyls with Cl, Br, and I substitution, respectively.

The equilibrium angle is determined by the potential energy function for internal rotation. This function is essentially the sum of two terms, one of which describes the nonbonded interaction between atoms and is dependent on their "size" among other factors, while the other arises from the energy of conjugation.¹² Since the conjugation energy is unlikely to change significantly within the series considered here, the different angles obtained can be attributed to changes in the nonbonded interaction terms.

Experimental Section

NMR Spectra. Nematic phase NMR spectra were recorded on the Bruker HX270 spectrometer at the National NMR Centre, Canberra, Australia operated in the FT mode. Approximately 1200 interfero-

grams of 8K data points were accumulated at 25°C (regulated). Spectral widths of 10 kHz, pulse widths of $4 \mu\text{s}$, and pulse delays of 500 ms were used. The interferograms were deconvoluted¹³ and transformed over 32K data points to yield spectra with a digital resolution of 0.625 Hz.

Isotropic NMR spectra were recorded on a Varian XL100 spectrometer operating in the FT mode.

Nematic Phases. The compounds (ca. 50 mg) were each dissolved in mixtures of *N*-(*p*-ethoxybenzylidene)-*p*-butylaniline (200 mg) and Nematic Mixture X11643 (300 mg, Eastman).

Syntheses. All compounds were purified by preparative column chromatography on neutral alumina using light petroleum (boiling range $40\text{--}60^\circ \text{C}$) as eluent, followed by preparative thin-layer chromatography on silica (Merck Kieselgel 60PF) eluted also with light petroleum. Halogen ratios and molecular weights were verified by low resolution mass spectrometry on an AEI MS902 mass spectrometer. UV spectra were recorded on a Perkin-Elmer Model 402 Ultraviolet Spectrometer, within the range 200–400 nm.

Melting points were recorded on a Kofler heating stage and are uncorrected.

4-Bromo-2',4',6'-trichlorobiphenyl (4) was prepared by coupling *p*-bromiodobenzene (4.6 g, 16 mmol) and iodo-2,4,6-trichlorobenzene (2.5 g, 8 mmol) over copper powder (6 g) at 230°C for 3 h in a sealed vessel. The mixture was extracted with chloroform and the extracts were purified. Crystallization from light petroleum (boiling range $30\text{--}40^\circ \text{C}$) gave **4** as a colorless crystalline solid: mp $91\text{--}92^\circ \text{C}$; λ_{max} (MeOH) 226 (sh), 224 nm (sh) ($\log \epsilon$ 4.44, 4.09); *m/e* 334:336:338:340, calcd for $\text{C}_{12}\text{H}_6\text{BrCl}_3$ 51.0:100.0:65.4:18.0, found 51:100:63:18. Anal. ($\text{C}_{12}\text{H}_6\text{BrCl}_3$) C, H, Br, Cl.

4-Bromo-2',6'-dichlorobiphenyl (5) was prepared by coupling *p*-bromiodobenzene (6.0 g, 21 mmol) with 2,6-dichloriodobenzene (2.9 g, 10.5 mmol) over copper powder (9 g) at 200°C for 3.5 h in a sealed vessel. The mixture was extracted with chloroform and the extracts were purified to yield **5** as a colorless liquid: λ_{max} (MeOH) 225 (sh), 244 nm (sh) ($\log \epsilon$ 4.37, 4.02); *m/e* 300:302:304, calcd for $\text{C}_{12}\text{H}_7\text{BrCl}_2$ 61.2:100.0:46.0, found 61:100:46. Anal. ($\text{C}_{12}\text{H}_7\text{BrCl}_2$) C, H, Br, Cl.

2,2',4',6'-Tetrabromobiphenyl (6) was prepared by coupling *p*-bromiodobenzene (1.1 g, 4 mmol) and 2,4,6-tribromiodobenzene (3.0 g, 7 mmol) over copper powder (3 g) at 220°C for 2 h in a sealed vessel. The mixture was extracted with chloroform and the extracts were purified. Crystallization from light petroleum gave **6** as a colorless crystalline solid: mp $103\text{--}104^\circ \text{C}$; λ_{max} (MeOH) 226 nm (sh) ($\log \epsilon$ 4.53); *m/e* 468:470:472:474, calcd for $\text{C}_{12}\text{H}_6\text{Br}_4$ 67.8:100.0:65.7:16.4, found 67:100:65:18. Anal. ($\text{C}_{12}\text{H}_6\text{Br}_4$) C, H, Br.

2,4,6-Tribromobiphenyl (7) was prepared by coupling *p*-bromiodobenzene (3.0 g, 10.5 mmol) and 2,6-dibromiodobenzene (1.9 g, 5.2 mmol) over copper powder (4.5 g) at 200°C for 3.5 h in a sealed vessel. The mixture was extracted with chloroform and the extracts were purified to yield **7** as a colorless liquid: λ_{max} (MeOH) 227 nm (sh) ($\log \epsilon$ 4.35); *m/e* 388:390:392:394, calcd for $\text{C}_{12}\text{H}_7\text{Br}_3$ 33.9:100.0:98.5:32.7, found 33:100:97:33. Anal. ($\text{C}_{12}\text{H}_7\text{Br}_3$) C, H, Br.

4-Bromo-2',6'-dinitrobiphenyl was prepared by coupling *p*-bromiodobenzene (6 g, 21 mmol) and bromo-2,6-dinitrobenzene (2.8 g, 11.5 mmol) over copper powder (9 g) at 165°C for 2.5 h in a sealed vessel. The mixture was extracted with chloroform. The solvent was removed and the residue was washed with boiling light petroleum. The

product was recrystallized from ether/light petroleum to yield 4-bromo-2',6'-dinitrobiphenyl as a yellow crystalline solid: mp 100–101 °C; λ_{\max} (MeOH) 230 nm ($\log \epsilon$ 4.43); NMR (acetone- d_6 , Hz at 100 MHz referenced to $\nu_2 = 0$, protons numbered as in Figure 1) $\nu_1 = 33.39$, $\nu_2 = 0$, $\nu_5 = -63.09$, $\nu_7 = -30.45$; $J_{12} = 8.29$, $J_{13} = 0.42$, $J_{14}(J_{23}) = 2.23$, $J_{57} = 8.21$. Anal. ($C_{12}H_7BrN_2O_4$) C, H, Br, N.

4-Bromo-2',6'-dinitrobiphenyl was reduced to the diamine using tin/hydrochloric acid.

4-Bromo-2',6'-diiodobiphenyl (8) was prepared from the diazonium salt of the diamine using standard techniques and was purified and obtained as a colorless oil: λ_{\max} (MeOH) 232 nm ($\log \epsilon$ 4.44); m/e 484:486, calcd for $C_{12}H_7BrI_2$ 100.0:98.7, found 100:99. Anal. ($C_{12}H_7BrI$) C, H, Br, I.

Acknowledgments. The authors wish to acknowledge support (Grant No. 15407) from the Australian Research Grants Commission to S.S. and a University of Sydney Postdoctoral Research Fellowship to A.S.T. We are also grateful to the staff of the National NMR Centre for cooperation in obtaining the NMR spectra.

References and Notes

- (1) University of Sydney Postdoctoral Fellow, 1976.
- (2) P. Diehl and C. L. Khetrapal, "NMR-Basic Principles and Progress", Vol. 1, Springer-Verlag, Berlin, 1969.
- (3) C. L. Khetrapal, A. C. Kunwar, A. S. Tracey, and P. Diehl, "NMR-Basic Principles and Progress", Vol. 9, Springer-Verlag, Berlin, 1975.
- (4) P. Diehl, "Specialist Periodical Reports, Nuclear Magnetic Resonance", Vol. 5, R. K. Harris, Ed., The Chemical Society, London, 1977.
- (5) J. W. Emsley and J. C. Lindon, "NMR Spectroscopy Using Liquid Crystal Solvents", Pergamon Press, Oxford, 1975.
- (6) W. Niederberger, P. Diehl, and L. Lunnazzi, *Mol. Phys.*, **26**, 571 (1973).
- (7) A. d'Annibale, L. Lunnazzi, A. C. Bolcelli, and D. Macciantelli, *J. Chem. Soc., Perkin Trans. 2*, 1396 (1973).
- (8) L. Lunnazzi and D. Macciantelli, *Gazz. Chim. Ital.*, **105**, 657 (1975).
- (9) J. A. Ferretti, R. K. Harris, and R. B. Johannesen, *J. Magn. Reson.*, **3**, 84 (1970).
- (10) A. Almendingen and O. Bastiansen, *K. Norske Videnskab. Selskabs. Skrifter*, No. 4, 1 (1958).
- (11) P. Diehl, P. M. Henrichs, and W. Niederberger, *Mol. Phys.*, **20**, 139 (1971).
- (12) I. Fischer-Hjalms, *Tetrahedron*, **19**, 1805 (1963).
- (13) I. D. Campbell, C. M. Dobson, R. J. P. Williams, and A. V. Xavier, *J. Magn. Reson.*, **11**, 172 (1972).

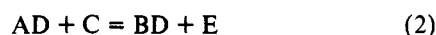
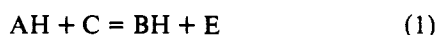
The Calculation of Isotopic Partition Functions Ratios by a Perturbation Theory Technique. 2. Dissection of the Isotope Effect

Stephen A. Skaron and Max Wolfsberg*

Contribution from the Department of Chemistry, University of California, Irvine, California 92717. Received December 3, 1976

Abstract: Statistical mechanical perturbation theory is applied to the evaluation of molecular partition functions and (reduced) isotopic partition function ratios $[(s_2/s_1)f]$ are calculated. The unperturbed vibrational problem corresponds to noninteracting stretches, bends, torsions, etc. It is demonstrated that an analysis of the unperturbed problem yields important insights into the magnitude of $(s_2/s_1)f$ values and into the isotope effects on chemical equilibria which can be calculated from these quantities. In such an analysis, one does not need to consider normal mode vibrational frequencies but one considers instead the frequencies corresponding to noninteracting individual coordinates. The contributions of the individual coordinates to $(s_2/s_1)f$ values and to isotope effects on equilibrium constants are presented.

Isotope effects on gas phase chemical equilibrium constants can be expressed in terms of ratios of isotopic molecular partition function ratios.^{1,2} Consider, for example, the reactions



Here AD (BD) refers to a compound in which the deuterium isotope of hydrogen has been substituted for the protium isotope in AH (BH). The molecular species C and E are not isotopically substituted. Then

$$K_1/K_2 = K_3 = (Q_{AD}/Q_{AH})/(Q_{BD}/Q_{BH}) \quad (4)$$

where Q refers to molecular partition function. Calculations of such isotope effects are usually carried out within the framework of the Born-Oppenheimer approximation so that, for a given molecule in a given electronic state, the equilibrium molecular geometry and force constants for vibrational motion are independent of isotopic substitution.³ It is usually adequate to consider only ground electronic states at room temperature. It can then be demonstrated that there are no isotope effects on chemical equilibria if the molecules are subject to classical

mechanics ($K_3[\text{classical}] = 1$) or, equivalently, in the limit of infinite temperature for quantum mechanical molecules, except for the relevant symmetry number factors which are of little interest. Symmetry number factors will usually be dropped here. The interest is therefore in the reduced isotopic partition function ratio, the ratio of the quantum mechanical partition functions of two isotopic molecules divided by the corresponding ratio of partition functions calculated classically.

While corrections must be taken into account for very precise calculations,⁴ isotopic partition function ratios for ideal gas phase molecules are usually evaluated by a model in which the nuclear motion degrees of freedom of an N atomic molecule are 3 classical translations, 3 classical rigid rotations (2 if the molecule is linear), and $3N - 6$ harmonic vibrations ($3N - 5$ for a linear molecule). Bigeleisen and Mayer¹ derived the expression for the reduced isotopic partition function ratio $(s_2/s_1)f$ corresponding to this model,

$$(s_2/s_1)f = \frac{(Q_2/Q_1)}{(Q_2/Q_1)[\text{classical}]} = \frac{(Q_2/Q_1)_{\text{vib}}}{(Q_2/Q_1)_{\text{classical}}[\text{vib}]} \\ = \prod_i^{3N-6} \frac{u_{2i}}{u_{1i}} \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}} e^{(u_{1i}-u_{2i})/2} \quad (5)$$

Here $u = h\nu/kT$; T is the absolute temperature; ν refers to