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Steric Isotope Effects

IV.* The Deuterium Isotope Effect in the Racemization of the (+)-2-(*N*,*N*,*N*-Trimethyl)-2′-(*N*,*N*-dimethyl)-diamino-biphenyl-6,6′-d_2 Cation

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The title cation has been synthesized and its rate of configurational inversion in aqueous solution extrapolated to zero concentration to determine k_{0D}, the rate in the absence of salt effects, and compared with the rate (k_{0H}) of the corresponding protium compound. The isotopic rate ratio (k_{0D}/k_{0H}) was found to be 1.18 ± 0.04 at 97.73°C, and 1.16 ± 0.05 at 73.41°C. These results are compared with those of Heitner and Leffek on the 2-(*N*,*N*,*N*-tris-trideuteriomethyl)-2′-(*N*,*N*-bis-trideuteriomethyl)-diaminobiphenyl cation, for which essentially no isotope effect at all was observed.

Studies of deuterium isotope effects on the configurational inversion of suitably substituted biaryls,[1–3] in which the barrier to internal rotation is predominantly due to increased steric compression on going from the initial state to the transition state, have for the most part led to at least qualitative confirmation of the theory of steric isotope effects developed by Bartell.[4] That is, the deuterated compounds racemize faster than their protium analogs due to the smaller amplitude of the zero-point vibrational motion of the C—D bond compared to that of the C—H bond, which makes the deuterium in effect smaller than the protium and thus leads to less repulsive non-bonded interactions in the transition state with a lowered enthalpy of activation as the (theoretical) result.

One of the first attempts to check Bartell's theory as applied to the inversion of an optically active biaryl was the work of Mislow *et al.*[5] on the deuterated bridged biphenyl diketone I, which was found to racemize more slowly than the protium analog ($k_D/k_H = 0.94$), in apparent contradiction with the theory.

* For Part III see Ref. 3.

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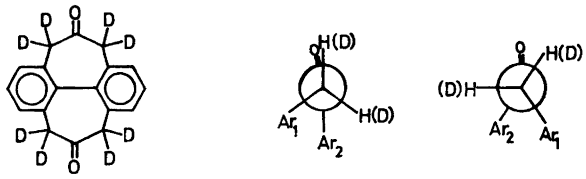
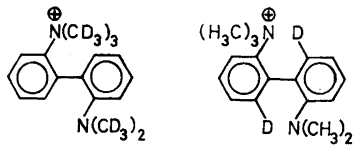


a b

I II

In a review of secondary deuterium isotope effects, Laszlo and Welvart [6] have suggested a rationalization for this result, *viz.* that the initial state of the deuterated molecule (*cf.* II*a*; Ref. 6) is stabilized due to a more favorable dipole-dipole interaction between the C—D bond and the carbonyl bond arising from the greater electropositive character of deuterium compared with protium. This then leads to a slower racemization rate for the deuterated compound, as the transition states in the two cases (*cf.* II*b*; Ref. 6) are expected to be of approximately the same energy. That IIa may represent the initial state of the molecule is considered reasonable on the basis of analogy with acetaldehyde, for which the conformation with eclipsed methyl C—H and C=O bonds has been shown to be the most stable by microwave measurements.[7]

A more serious contradiction of Bartell's theory appeared to be the work of Heitner and Leffek [8] on the (+)-2-(*N*,*N*,*N*-tris-trideuteriomethyl)-2′-(*N*,*N*-bis-trideuteriomethyl)-diaminobiphenyl cation (III), for which essentially no isotope effect at all was observed in spite of the presence of fifteen deuterium



III IV

atoms in the molecule. The results were qualitatively rationalized in two ways:[8] "either the non-bonded interactions during racemization are so great that they are not significantly changed by deuteration, or a second effect occurs in the molecule with deuteration which compensates for the change in mean-square amplitude." In view of the possibility, made plausible by the study of models, that the hydrogen atoms of the *N*-methyl groups are not *necessarily* involved in the non-bonded interactions which dominate the path to configurational inversion, we suggested [3] that the most important non-bonded repulsions might be between the 6- and 6′-protons and the nitrogen and carbon atoms of the 2- and 2′-substituents. Thus the 6,6′-d_2 compound (IV) would be predicted to exhibit a measurable isotope effect. The present work was undertaken in order to test this prediction.

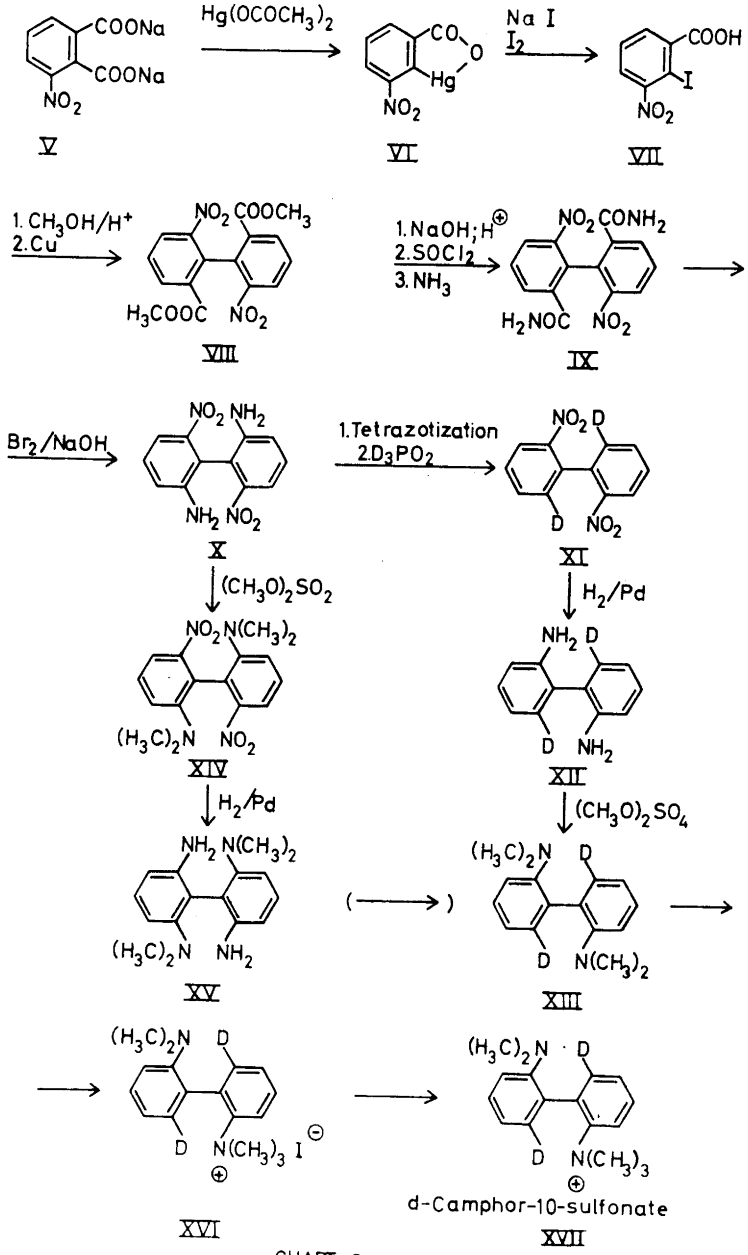

COONa
COONa
NO2
V
Hg(OCOCH3)2
CO
O
Hg
NO2
VI
Na I
I2
COOH
I
NO2
VII
1. CH3OH/H+
2. Cu
NO2 COOCH3
H3COOC NO2
VIII
1. NaOH; H⊕
2. SOCl2
3. NH3
NO2 CONH2
H2NOC NO2
IX
Br2/NaOH
NO2 NH2
NH2 NO2
X
1. Tetrazotization
2. D3PO2
NO2 D
D NO2
XI
(CH3O)2SO2
NO2 N(CH3)2
(H3C)2N NO2
XIV
H2/Pd
NH2 D
D NH2
XII
H2/Pd
NH2 N(CH3)2
(H3C)2N NH2
XV
(CH3O)2SO4
(H3C)2N D
D N(CH3)2
XIII
(H3C)2N D
D N(CH3)3 I⊖
⊕
XVI
(H3C)2N D
D N(CH3)3
⊕
d-Camphor-10-sulfonate
XVII

CHART I

RESULTS

Synthesis. The preparation of (+)-2-(*N*,*N*,*N*-trimethyl)-2′-(*N*,*N*-dimethyl)-diaminobiphenyl-6,6′-d_2 (+)-camphor-10-sulfonate (XVII), starting from the sodium salt of 3-nitrophthalic acid, is outlined in Chart I. Treatment of the sodium salt V with mercuric acetate [9] followed by iodination with sodium iodide and iodine in water,[9] led to 2-iodo-3-nitrobenzoic acid (VII). After esterification with methanol, Ullmann coupling afforded the diester [10] VIII, which was then hydrolyzed and the resulting acid converted to the diamide [10] IX *via* the acid chloride. Hofmann rearrangement of the diamide IX yielded 2,2′-diamino-6,6′-dinitrobiphenyl [10] (X), starting from which two routes to the desired product were investigated, as indicated in Chart I. The path found to be most convenient was that in which tetrazotization of X and introduction of deuterium by reduction with D_3PO_2 (X→XI) *preceded* reduction of the nitro groups with 0.5 % palladium on charcoal and methylation with dimethyl sulfate in the presence of dilute sodium hydroxide (XI→XII→XIII). The other path involved methylation of X with dimethyl sulfate in the presence of anhydrous potassium carbonate in refluxing 2-butanone (X→XIV), followed by reduction of the nitro groups and introduction of deuterium as described above (XIV→XV→XIII). The deuteration reaction was, however, not carried out, since we could more conveniently reach the desired compound by the alternate route, and we experienced difficulties in obtaining 2,2′-bis-dimethylamino-6,6′-diaminobiphenyl (XV) in good yield in a pure state.

The quaternization of the tetramethyl base (XIII) with methyl iodide was performed as described by Leffler and Graham,[11] and the resolution of the quaternary base was accomplished with the silver salt of (+)-camphor-10-sulfonic acid, following the method of Shaw and Turner.[12]

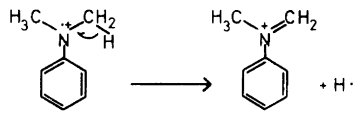
The deuterated dinitrobiphenyl XI had the same melting point as a sample of the corresponding protium compound, prepared by reduction of the tetrazotized diaminodinitrobiphenyl X with H_3PO_2. The protium compound was in turn shown to be identical with authentic 2,2′-dinitrobiphenyl prepared [12] by Ullmann coupling of 2-chloronitrobenzene.

Deuterium analysis. The deuterium content of each of the compounds XI, XII, XIII, XVI, and XVII was estimated by mass spectral analysis (see Table 1). In the case of XI, the peaks in the region of the parent peak at *m/e* 246 were inconveniently small for use in the deuterium analysis, apparently due to the facile loss of a $-NO_2$ group which gives the most abundant ion in the spectrum at *m/e* 200. The peaks in the range *m/e* 198—201 were used for the analysis.

In the 70 eV mass spectrum of the protium compound corresponding to the deuterated diaminobiphenyl XII, the height of the M^+-1 peak at *m/e* 183 was 42 % of that of the parent peak. This peak is assumed to arise from the loss of a hydrogen atom from an amino group, as shown to be the case for aniline.[13] As this would have interfered with the deuterium analysis, we obtained the mass spectrum at lower electron energies, and found that at 10 eV the M^+-1 peak was completely eliminated.

A similar problem arose in connection with the analysis of the mass spectra of XIII, XVI, and XVII. In the spectra of the latter two compounds, the

parent peak occurs at m/e 242 due to elimination in the spectrometer inlet, and we have assumed that this does not seriously interfere with the relative heights of the peaks used for the analysis. At 70 eV, the M^+-1 peaks in the spectra of the protium compounds were fairly small, *ca.* 8 % as intense as the parent peaks. The loss of a hydrogen atom is assumed to occur by a process analogous to that suggested [14] for *N,N*-dimethylaniline,



which yields the most abundant ion in the spectrum.[14] Surprisingly enough, we found that an electron energy of 11 eV essentially completely suppressed the peak for the parent ion, providing the M^+-1 peak at m/e 241 as the base peak in the spectrum, as shown by a careful comparison between the 70 eV and 11 eV spectra.

The absence of significant deuterium loss by exchange during the reduction of the dinitrobiphenyl XI to the diamine XII is demonstrated by a comparison of the data for these two compounds in Table 1. No deuterium

Table 1. Mass spectrometric deuterium analyses.

Compound [a]	Deuterium content, %				Electron energy, eV
	d_0	d_1	d_2	d_3	
XI	2.1	15.8	80.1	2.0	70
XII	0.8	14.4	83.5	1.6	10
XIII	1.8	14.1	83.5	0.8	70 [b]
XVI	1.0	14.8	82.0	2.1	11
XVII	1.4	14.5	82.6	1.5	11

[a] See Chart I.
[b] Corrections based on the height of the M^+-1 peak in the spectrum of the protium compound (*ca.* 8 % of M^+) were applied to the data for XIII in order to estimate the deuterium content.

exchange was observed in the methylation reaction (XII→XIII) that follows the reduction as shown by the estimated deuterium contents of XII and XIII presented in Table 1. Furthermore, a control experiment was carried out, in which the methylation of undeuterated 2,2′-diaminobiphenyl was performed in D_2O. The mass spectrum of the resulting tetramethyl base showed that no deuterium incorporation had taken place.

The positions of the deuterium atoms in the dinitro and diamino compounds XI and XII indicated in Chart I were shown to be correct by 100 MHz

NMR spectra. A comparison of the spectra for the deuterium and protium compound pairs established unequivocally which protons had been replaced by deuterium atoms, in view of the well-known effects of amino and nitro substituents on aromatic proton chemical shifts and the characteristic aromatic proton-proton coupling constant ranges.

The position of the deuterium atoms in the final product XVII was similarly established by a 100 MHz NMR spectrum on a sample recovered after the completion of the polarimetric runs (see below), and thus we may safely assume that no significant deuterium scrambling occurs in the methylation (XIII→XVI) and resolution (XVI→XVII) steps, nor under the experimental conditions in the kinetic runs.

Kinetics. The change in optical rotation of aqueous solutions of the diastereomeric salt XVII was followed on a Perkin-Elmer 141 automatic reading polarimeter at 73.41° and 97.73°C. The protium compound was similarly treated in parallel experiments.

The lengthy synthetic route provided a rather limited amount of deuterated material, and we found it necessary to make a choice between runs at one concentration at four or five temperatures in order to be able to extract reasonable activation parameters from the data, or runs at several concentrations at two temperatures in order to take salt effects into account. Our previous experience of the difficulty in obtaining activation parameters reliable enough to separate enthalpy and entropy contributions to steric isotope effects,[2,3] and our recent work on salt effects in the racemization of biphenyls,[15,16] which emphasized the importance of obtaining thermodynamically well-defined rate constants by extrapolation to zero ionic strength (J) on a plot of ln k *vs.* J, left no doubt as to which choice was to be preferred. We thus followed the change in optical rotation of the deuterium cation at four different concentrations at each temperature, and that of the protium cation at four to ten concentrations at the same temperatures, as well as at 79.15° and 88.87 °C. In Table 2 the kinetic data are summarized, including the ionic strength in each run and the intercepts from plots of ln k *vs.* J according to eqn. (1),

$$\ln k = \ln k_0 + (B - B^{\ddagger})J \qquad (1)$$

where k_0 is the rate of configurational inversion in the absence of salt effects and $B-B^{\ddagger}$ is the slope of the plot. $B-B^{\ddagger}$ provides an indication of the sensitivity of the inversion reaction to dissolved ions, *i.e.* in this case to the concentration of the biphenyl cation itself and its counter-ion, and was found to be 2.01 at 97.73°C and 2.52 at 73.41°C for the protium ion (*cf.* Ref. 15).

The larger number of concentrations at which the runs with the protium compound could be carried out allowed somewhat greater accuracy in the determination (by the method of least squares) of the slope in the ln k *vs.* J plot in this case. We have assumed that the introduction of two deuterium atoms into the molecule will have a negligible effect on the $B-B^{\ddagger}$ term in eqn. (1). It is thus possible to use the least-squares slope calculated for the protium compound to calculate a k_{0D} value from the points for the deuterium compound. The results of such computations for data obtained at 97.73°C and 73.41°C are recorded in Table 2. The ratio k_{0H}/k_{0D} was found to be 1.18 ± 0.04 at 97.73°C and 1.16 ± 0.05 at 73.41°C. The errors in these values

Table 2. Kinetic data on the configurational inversion of the (+)-2-(*N*,*N*,*N*-trimethyl)-2′-(*N*,*N*-dimethyl)-diaminobiphenyl cation and its 6,6′-dideuterio derivative in aqueous solution at various ionic strengths (J).

Temp., °K	Isotope	$10^2 \times J$	$10^6 \times k$, sec^{-1}	$10^6(k_0 \pm$ std.dev.) sec^{-1}	k_{0D}/k_{0H} [a]
370.88	H	2.09	42.57		
		2.69	43.56		
		4.92	44.25		
		5.31	45.05		
		6.18	45.76	40.67 ± 0.63	
		7.64	48.62		
		7.68	46.37		
		8.84	48.29		
		9.19	48.37		
		10.08	51.04		
					1.18 ± 0.04
370.88	D	1.97	48.73		
		3.21	51.04	48.06 ± 0.83 [a]	
		4.28	52.40		
		6.25	55.11		
362.02	H	2.22	16.18		
		4.20	18.04	16.27 ± 0.45	
		6.70	18.64		
		8.88	19.36		
352.30	H	2.51	5.74		
		3.02	5.83		
		4.50	6.17	5.51 ± 0.08	
		6.69	6.53		
		7.06	6.42		
		10.97	6.91		
346.56	H	2.35	2.82		
		3.05	3.16		
		4.09	3.11		
		5.53	3.26	2.81 ± 0.08	
		6.70	3.42		
		8.01	3.55		
		8.78	3.48		
		9.76	3.46		
					1.16 ± 0.05
346.56	D	2.06	3.49		
		3.60	3.50	3.25 ± 0.05 [a]	
		5.43	3.73		
		6.59	3.84		

[a] For calculation of k_{0D} and errors, see text.

$[\Delta(k_{0D}/k_{0H})]$ were obtained by combination of the standard deviations in k_{0H} and k_{0D} *via* the relation

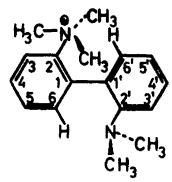
$$\Delta(k_{0D}/k_{0D}) = [(\Delta k_{0H}/k_{0H}) + (\Delta k_{0D}/k_{0D})](k_{0D}/k_{0H})$$

This should give at least the correct order of magnitude of the errors in the isotopic rate ratios.

A least-squares treatment of the rate data for the protium compound, plotted as $\ln(k_{0H}/T)$ *vs.* $1/T$, led to the following values for the activation parameters: 27.37 ± 0.14 kcal/mole for $\Delta H^{\ddagger}$ and -5.3 ± 0.4 e.u. for $\Delta S^{\ddagger}$. In view of the small number of points in the plot, the standard errors given here should be replaced by more appropriate values estimated as described by Petersen, Markgraf and Ross [17] (*vide infra*): ± 0.62 kcal/mole in $\Delta H^{\ddagger}$ and ± 1.8 e.u. in $\Delta S^{\ddagger}$.

DISCUSSION

The isotope effect measured in this work is especially interesting in comparison with the data of Heitner and Leffek [8] on III, for which they report $k_H/k_D = 0.996 \pm 0.007$ and 1.02 ± 0.01 in aqueous solution at 100.0° and 119.9°C, respectively. Studies of molecular models indicate that the two methyl groups on the 2′-nitrogen need not be subjected to extraordinary steric compression during the inversion reaction, since a simple rotation about the aryl C—N bond places them at a comfortable distance from the passing proton on the opposite ring. This clearly leaves the H···N non-bonded interaction as the

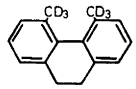


dominant steric factor on the "2′-side" of the molecule. The situation is perhaps not quite so straightforward with regard to the passage of the 6′-proton past the 2-trimethylammonium group, but we suggest that an appropriate rotation about the aryl C—N bond will allow the aryl proton to "intermesh" between two of the methyl groups, whereupon the dominant effect again becomes the H···N interaction. However, it should be pointed out that in neither case can a contribution from an aryl H···methyl C interaction be totally disregarded.

Of course the positive charge on the ammonium nitrogen is most likely solvated by water molecules during the course of the inversion, but this will only add details to our picture and not affect its substance. Even if there is a change in solvation between the initial and transition states, the effect of the presence of deuterium in the molecule on such a change can probably be rather safely neglected in this case, since the charge on the nitrogen is the same throughout and is expected to be the dominant factor in determining the "organization" of the solvation shell.

An alternative explanation for the absence of an isotope effect in the racemization of III, based on compensatory $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ terms in the expression $\ln(k_D/k_H) = (\Delta\Delta H^{\ddagger}/RT) - (\Delta\Delta S^{\ddagger}/R)$, was discussed by Heitner and Leffek,[8] who suggested that $\Delta\Delta H^{\ddagger} = 0.17$ kcal/mole and $\Delta\Delta S^{\ddagger} = 0.46$ e.u.

were reasonable values which could well reproduce the observed results. These values were compared with the data reported by Mislow *et al.*[1] for 9,10-dihydro-4,5-bis(trideuteriomethyl)phenanthrene and the corresponding protium compound in benzene solution: $\Delta\Delta H^{\ddagger}=0.24$ kcal/mole and $\Delta\Delta S^{\ddagger}=0.53$ e.u.



In this connection we wish to emphasize the fact that values for $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ obtainable from the polarimetric determination of kinetic data for isotopic molecules are often associated with error limits of the same order of magnitude, and may therefore not be significantly distinguishable from zero. This is especially true when kinetic data have been determined at only a few temperatures, because then the application of standard statistical analyses (the method of least squares, for example) is not very meaningful. In such a case, more realistic error limits may be estimated by the procedure described by Petersen, Markgraf and Ross,[17] in which $\Delta H^{\ddagger}$ is calculated from rate constants k and k' determined at the two ends of the temperature scale (T and T') and the maximum possible error in $\Delta H^{\ddagger}$ (δ) is given by

$$\delta = 2R[T'T/(T'-T)]\alpha$$

where R is the gas constant and α is the maximum possible fractional error in k and k'. The maximum possible error in $\Delta S^{\ddagger}$ (σ) is related to δ *via* the equation

$$\sigma = (\delta/T)+R\alpha$$

Thus for a temperature range of 30° in the neighborhood of 300—350°K and an error in k and k' of ± 1 %, $\delta=0.13$ kcal/mole and $\sigma=0.43$ e.u. Using these values, the maximum possible errors for $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ would be 0.26 kcal/mole and 0.86 e.u., respectively. Even if the reproducibility of the k's were as good as 0.5 %, the maximum possible errors in $\Delta\Delta H^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ ($\sim$0.1 kcal/mole and $\sim$0.4 e.u.) are still quite significant.

EXPERIMENTAL

Melting points were determined on a Kofler Hot-Stage Microscope. NMR spectra were recorded on Varian A60 and/or HA-100 instruments, using tetramethylsilane (TMS) as internal standard. Mass spectra were obtained on an LKB 9000 A spectrometer.

Kinetic runs were carried out on test solutions contained in 10 cm jacketed polarimeter tubes. The temperature of the circulating water was maintained within $\pm 0.01°$ with a Haake FT thermostat. A correction for the difference between the temperature of the water in the thermostat bath and that of the test solution, due to heat loss in the polyvinylchloride tubing connecting the bath and the polarimeter tube, was determined at each temperature by means of a copper-constantan thermocouple with one junction in the bath and the other in the test solution. Voltages were measured with a Croydon type P3 potentiometer.

In each run, the sample was allowed to reach constant rotation, and the rate constant was calculated by the method of least squares from the equation

$$2kt = \ln[(\alpha_0-\alpha_\infty)/(\alpha_t-\alpha_\infty)]$$

where k is the first-order rate constant for inversion, t is the time, and α_0, α_t, and α_∞ are the observed optical rotations at $t=0$, $t=t$, and after ten half-lives. All calculations were made on an Olivetti Programma 101 desk computer.

2,2'-Dinitrobiphenyl-6,6'-d_2 *(XI)*. 2,2'-Diamino-6,6'-dinitrobiphenyl [10] (X) (2 g) was suspended in CH_3COOD (10 ml), and D_2SO_4 (10 ml) was added with stirring. The resulting solution was cooled in an ice bath, and the following steps were all carried out in the cold. A solution of $NaNO_2$ (1.2 g) in D_2O (5 ml) was added dropwise with efficient stirring. The diazonium salt solution was stirred another hour, and then poured into D_3PO_2 (5 ml, *ca.* 50 % in D_2O) and D_2O (10 ml) containing a small amount of Cu_2O. After standing in the refrigerator overnight, the mixture was filtered, and the filter cake dried on the filter by suction and then dissolved in a small amount of chloroform. The solution was dried and filtered, and the filtrate was placed on a column of silica gel and eluted with chloroform. The yellow band that was first eluted was collected, the eluate evaporated, and the product crystallized from ethanol to yield 0.9 g (50 %), m.p. 124–125°. The m.p. of the protium compound is variously reported as 127–128° [18] and 124.5°.[19] A 100 MHz NMR spectrum in $CDCl_3$ solution showed that only a residual proton spectrum remained from the resonances assigned to the 6,6'-protons (at $\delta=7.27$) in the spectrum of the corresponding protium compound.

2,2'-Diaminobiphenyl-6,6'-d_2 *(XII)*. 2,2'-Dinitrobiphenyl-6,6'-d_2 (XI) (8.9 g) was dissolved in absolute ethanol (50 ml) and ethyl acetate (150 ml) in the presence of palladium catalyst (0.5 % on C, 0.8 g), and hydrogenated at *ca.* 50 psi with a Parr hydrogenator. The reaction was complete in less than one hour. The resulting solution was filtered and the solvent evaporated. The residue was crystallized from ethanol to yield 5.6 g (83 %), m.p. 78–79°; lit.[20] m.p. (protium compound) 79–80°. In the 100 MHz NMR spectrum (in $CDCl_3$ solution) a triplet centered at $\delta=7.14$, assigned to the 4,4'-protons, and the residual proton spectrum due to the 6,6'-protons ($\delta=7.04$ in the spectrum of the protium compound) at the base of the triplet, was all that remained of the *ca.* 16 peaks observed in this region in the spectrum of the protium compound. The rest of the spectrum appeared as expected on the basis of the assignments made for the protium compound.

2,2'-Bis(dimethylamino)biphenyl-6,6'-d_2 *(XIII)*. 2,2'-Diaminobiphenyl-6,6'-d_2 (XII) was methylated by the method of Shaw and Turner.[12] The product had m.p. 72–73° (lit.[12] m.p. for protium compound 72–73°).

2-(N,N,N-*Trimethyl)-2'-*(N,N-*dimethyl)-diaminobiphenyl-6,6'-*d_2 *iodide (XVI)* was prepared by quaternization of XIII with methyl iodide in dry acetone, as described by Leffler and Graham [11] for the protium compound; m.p. 190° (decomp.). Lit.[12] m.p. (protium compound) 190–192°(corr.).

(±)-2-(N,N,N-*Trimethyl)-2'-*(N,N-*dimethyl)-diaminobiphenyl-6,6'-*d_2 *(+)-camphor-10-sulfonate (XVII)*. Resolution of the racemic cation of XVI was carried out with silver (+)-camphor-10-sulfonate as described by Shaw and Turner [12] for the protium compound; $[\alpha]_{436}^{98}=106°$ (H_2O), m.p. 190° (decomp.). Lit.[12] m.p. 189–190° (corr.).

2,2'-Bis(dimethylamino)-6,6'-dinitrobiphenyl (XIV). 2,2'-Diamino-6,6'-dinitrobiphenyl (X) (2 g) was dissolved in 2-butanone (40 ml). The solution was refluxed for 2 h after the addition of anhydrous K_2CO_3 (1.6 g) and dimethyl sulfate (1 ml). The same amounts of K_2CO_3 and dimethyl sulfate were then added once again and the mixture was refluxed overnight, cooled and filtered. The filtrate was evaporated to dryness, and recrystallization from ethanol afforded 0.8 g (70 %), m.p. 163–164°. The 60 MHz NMR spectrum (in acetone-d_6 solution) contained the expected peak for the $-N(CH_3)_2$ groups at $\delta=2.38$, and a strongly coupled ABC pattern in the region $\delta=7.4-7.8$ (aryl H).

2,2'-Bis(dimethylamino)-6,6'-diaminobiphenyl (XV) was prepared by the reduction of XIV with hydrogen over palladium on charcoal, as described for the preparation of XII from the corresponding dinitro compound (XI). The yield was, however, low and the product discolored. Sublimation gave the pure amine, m.p. 110–111°, and its identity was confirmed by NMR at 60 MHz, which showed peaks at $\delta=2.46$ ($-N(CH_3)_2$), 3.92 ($-NH_2$), and an A_2B-type pattern in the region $\delta=6.3-7.2$ (aryl H).

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