# Steric Isotope Effects

## III.* The Deuterium Isotope Effect in the Racemization of (−)-1,1′-Binaphthyl-2,2′-$d_2$

ROBERT E. CARTER** and LENNART DAHLGREN

*Department of Organic Chemistry, University of Göteborg and Chalmers Institute of Technology, Fack, S-402 20 Göteborg 5, Sweden*

(−)-1,1′-Binaphthyl-2,2′-$d_2$ has been synthesized and its rate of racemization compared with that of the protium compound at temperatures between 20 and 65°C. The isotopic rate ratio ($k_D/k_H$) was found to vary from 1.20 to 1.14 over this range, and a least-squares treatment of a plot of $\ln(k_D/k_H)$ *vs.* $1/T$ gave values for $\Delta\Delta H^{\ddagger} = \Delta H_H^{\ddagger} - \Delta H_D^{\ddagger} = 0.27 \pm 0.14$ kcal/mole and $\Delta\Delta S^{\ddagger} = 0.54 \pm 0.43$ e.u.

The results are discussed in terms of Bartell's theory of steric isotope effects and from the point of view of force constant changes between initial and transition states which lead to a change in zero-point energy. It is emphasized that these are two equivalent descriptions of the same vibrational phenomenon.

Since the original publication of the theory of steric isotope effects by Bartell,[1] much effort has been directed toward the estimation of the contribution of steric factors (non-bonded interactions) to the origin of secondary deuterium isotope effects.[2-5] Due to the *ca.* 17 % greater amplitude of the zero-point vibrational motion of a protium atom than a deuterium relative to the neighboring carbon in an organic molecule, the effective size of the deuterium is less than that of the protium. Non-bonded interactions involving deuterium are accordingly less repulsive than the corresponding interactions with protium, and in reactions in which non-bonded repulsions increase on going from the initial state to the transition state, it is to be expected that replacement of protium with deuterium at the "center of reaction" should lower the energy of activation and lead to faster rates. This expectation has been fulfilled by studies of the rates of racemization of appropriately deuterated

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atropisomeric molecules such as 9,10-dihydro-4,5-dideuteriomethylphenan-threne [3] (I) and 2,2'-dibromo-4,4'-dicarboxybiphenyl-6,6'-$d_2$ [4] (II). An apparent exception is the work of Heitner and Leffek,[5] who observed essentially no isotope effect at all in the racemization of the 2-($N,N,N$-trideuteriomethyl)-
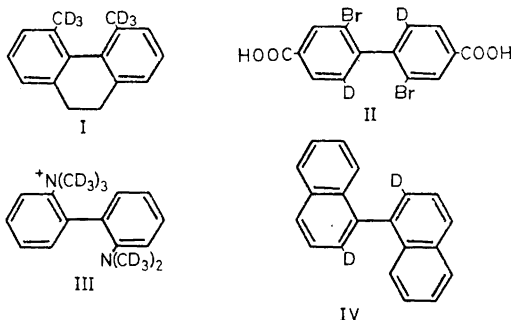


2'-($N,N$-dideuteriomethyl)-diaminobiphenyl cation (III). Two rationaliza-tions are suggested for the results:[5] either the change in non-bonded interac-tions on deuteration is insignificant due to the severity of the crowding during racemization, or a compensatory effect operates to nullify the decrease in vibrational amplitude due to deuteration. We suggest a third alternative, which is that the most important non-bonded repulsions are between the 6- and 6'-protons and the nitrogen and carbon atoms of the 2- and 2'-substituents. A study of the isotope effect in the racemization of the 6,6'-$d_2$ compound would be of great interest in this connection.

## RESULTS

The work described in this paper was undertaken in order to measure the (steric) deuterium isotope effect due to H···H non-bonded repulsion in an unsubstituted atropisomeric hydrocarbon. 1,1'-Binaphthyl is one of the simplest hydrocarbons that may be obtained in enantiomeric forms, and we thus turned our attention to the problem of synthesizing a specifically deu-terated optically active isomer, (−)-1,1'-binaphthyl-2,2'-$d_2$ (IV). Optical activity was secured *via* resolution of 2,2'-diamino-1,1'-binaphthyl,[6] and deuterium was introduced by reduction of the tetrazotized diamine with $D_3PO_2$ at −15°C.

The deuterium content of all batches used in the kinetic runs was deter-mined by mass spectrometry.* It was found that an ionization voltage of 10.5 eV minimized the height of $M^+-1$ and $M^+-2$ peaks which otherwise interfered with the determination of the percentages of $d_0$ and $d_1$ molecules in the samples. The mass spectrometric analyses are summarized in Table 4

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* We are indebted to Mr. Bengt Åkesson for carrying out the mass spectrometric analyses on the LKB A 9000 mass spectrometer at the Department of Organic Chemistry of the University of Lund.

*Table 1.* Kinetic data on the racemization of $(-)$-1,1'-binaphthyl and its 2,2'-dideuterio derivative in $N,N$-dimethylformamide solution.

| Temp., °K | Isotope | $10^5 \times k$, sec$^{-1}$ | Average and max. dev. $\times 10^5$ sec$^{-1}$ | $k_D/k_H$ | $\Delta\Delta G^{\ddagger}$, cal mole$^{-1}$ |
|---|---|---|---|---|---|
| 337.20 | H | 286.63 | | | |
| | H | 295.51 | | | |
| | H | 288.29 | $290.14 \pm 5.37$ | | |
| | D | 332.37 | | | |
| | D | 331.81 | | | |
| | D | 328.15 | $330.78 \pm 2.63$ | $1.14_0 \pm 0.03_0$ | $87.8 \pm 17.8$ |
| 330.77 | H | 156.34 | | | |
| | H | 153.19 | $154.77 \pm 1.58$ | | |
| | D | 178.59 | | | |
| | D | 175.92 | $177.26 \pm 1.34$ | $1.14_5 \pm 0.02_1$ | $89.0 \pm 11.7$ |
| 323.85 | H | 76.96 | | | |
| | H | 76.56 | | | |
| | H | 77.65 | | | |
| | H | 76.43 | | | |
| | H | 77.14 | $76.95 \pm 0.70$ | | |
| | D | 88.14 | | | |
| | D | 87.35 | $87.75 \pm 0.40$ | $1.14_0 \pm 0.01_3$ | $84.3 \pm 7.3$ |
| 316.33 | H | 33.85 | | | |
| | H | 33.36 | $33.61 \pm 0.25$ | | |
| | D | 38.98 | | | |
| | D | 38.70 | $38.84 \pm 0.14$ | $1.15_6 \pm 0.01_3$ | $91.1 \pm 7.1$ |
| 309.18 | H | 14.82 | | | |
| | H | 14.88 | | | |
| | H | 14.84 | $14.85 \pm 0.03$ | | |
| | D | 17.60 | | | |
| | D | 17.90 | | | |
| | D | 17.34 | $17.61 \pm 0.29$ | $1.18_6 \pm 0.02_2$ | $104.8 \pm 11.0$ |
| 302.43 | H | 6.595 | | | |
| | H | 6.718 | $6.657 \pm 0.062$ | | |
| | D | 7.899 | | | |
| | D | 7.778 | $7.839 \pm 0.061$ | $1.17_8 \pm 0.02_0$ | $98.4 \pm 10.3$ |
| 295.31 | H | 2.677 | | | |
| | D | 3.227 | | $1.20_5$ | 109.4 |
| 330.70 | H | 67.96[a] | | | |
| | D | 80.00[a] | | $1.17_7$ | 107.1 |

[a] Data determined in cyclohexane solution.

in the Experimental Section. The data show that in all of the samples about 80—86 % of the deuterated molecules contain two deuterium atoms, while about 99 % contain at least one.

An unidentified impurity at $m/e$ 289, which defied all attempts at removal by chromatography, was present in all of the samples to the extent of ca. 7—11 % of the total sample. The impurity parent peak was about 5—8 % of the height of the parent peak for the main component. In the mass spectrum of the protium compound, the impurity parent peak occurred at $m/e$ 288 and was about 1.5 % of the height of the parent peak for the main component; the impurity accounted for about 2.5 % of the total sample. It seems reasonable to ascribe both the relatively large percentage of $d_1$ molecules in the deuterated samples and the greater amount of impurity compared to that in the protium compound to a large primary isotope effect in the reduction of the tetrazotized diamine with $D_3PO_2$. Rekasheva and Miklukhin [7] estimated an isotopic rate ratio $(k_D/k_H)$ of ca. 0.3 for the transfer of a proton from hypophosphorous acid to the aromatic nucleus during reduction.

The kinetic data were obtained at seven temperatures between 20 and 65°C in $N,N$-dimethylformamide solution on a Perkin-Elmer 141 automatic reading polarimeter. The results are presented in Table 1 along with isotopic rate ratios and the isotopic differences in free energy of activation calculated according to eqn. (1). No attempt was made to correct

$$\Delta\Delta G^{\ddagger} = \Delta G_H{}^{\ddagger} - \Delta G_D{}^{\ddagger} = RT \ \ln(k_D/k_H) \tag{1}$$

the isotope effect for the protium content of the deuterated samples. The rate constants were obtained from a least-squares treatment of the polarimetric data on an Olivetti Programma 101 desk computer. The error limits given in Table 1 are all maximum deviations.

The presence of the impurity had no effect on the kinetic results, as excellent straight lines (standard error ca. 0.3 %) were obtained in all of the runs

Table 2. Activation parameters for racemization of (−)-1,1′-binaphthyl and its 2,2′-dideuterio derivative in $N,N$-dimethylformamide solution.[a]

| Compound | $\Delta H^{\ddagger}$ kcal mole$^{-1}$ | $\Delta S^{\ddagger}$ e.u. |
|---|---|---|
| (−)-1,1′-Binaphthyl | $21.49 \pm 0.19$ | $-8.00 \pm 0.57$ |
| (−)-1,1′-Binaphthyl [b] | 21.9 | $-5.2$ |
| (−)-1,1′-Binaphthyl-2,2′-$d_2$ | $21.21 \pm 0.14$ | $-8.60 \pm 0.44$ |
| | $\Delta\Delta H^{\ddagger}$ kcal mole$^{-1}$ | $\Delta\Delta S^{\ddagger}$ e.u. |
| | $0.28 \pm 0.23$ | $0.60 \pm 0.72$ |
| | $0.27 \pm 0.14^{c}$ | $0.54 \pm 0.43^{c}$ |

[a] Errors are given as three times the standard deviation obtained from the least-squares calculation.

[b] Data from Cooke and Harris, Ref. 8.

[c] From a least-squares treatment of a plot of $\ln(k_D/k_H)$ vs. $1/T$.

reported in Table 1, and there was no residual rotation outside the experimental error (about $\pm 0.002°$) after complete racemization of the binaphthyl sample.

Variations in binaphthyl concentration from 3.5 to 8.5 mg/ml had no measurable effect on the observed rate of racemization.

The influence of solvent polarity on the isotope effect was briefly investigated by kinetic runs in cyclohexane solution at $330.70°K$, the results of which are also given in Table 1. The calculated rate ratio, $k_D/k_H = 1.17_7$, and the value of $\Delta\Delta G^{\neq}$, 107.1 cal/mole, may be compared with the corresponding data at the same temperature in $N,N$-dimethylformamide solution, $k_D/k_H = 1.14_5 \pm 0.02_1$ and $\Delta\Delta G^{\neq} = 89.0 \pm 11.7$ cal/mole. These data indicate that, taking into consideration the limits of experimental error, solvent polarity is not of great significance in determining the magnitude of the isotopic rate ratio.

A least-squares treatment of the rate data in Table 1, plotted as $\ln(k/T)$ vs. $1/T$, led to the thermodynamic activation parameters presented in Table 2. The errors are given as three times the standard error derived from the least-squares calculation. The parameters for the undeuterated compound may be compared with those previously obtained by Cooke and Harris [8] in $N,N$-dimethylformamide solution: $\Delta H^{\neq} = 21.9$ kcal/mole, $\Delta S^{\neq} = -5.2$ e.u.

Values for $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ along with limits of error determined by statistical combination of the errors given for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are included in Table 2. In view of the observed trend in the isotopic rate ratio as a function of temperature (see Table 1), it was of interest to perform a least-squares analysis of a plot of $\ln(k_D/k_H)$ vs. $1/T$ in order to extract more reliable estimates of $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ and their limits of error. These data are also presented in Table 2, from which it is obvious that it is impossible to state with certainty that in this case $\Delta\Delta G^{\neq} = \Delta\Delta H^{\neq}$ as required by Bartell's theory.[1] However, in order to be able to use the theoretical treatment without modification in our discussion of the results, we have somewhat arbitrarily chosen an approximate value of 100 cal/mole for $\Delta\Delta H^{\neq}$, which is in line with the data in the last column of Table 1 as well as with the lower limits of the data derived from the plot of $\ln(k_D/k_H)$ vs. $1/T$. (See Table 2.)

## DISCUSSION

It is quite unlikely that the transition state in the configurational inversion of 1,1'-binaphthyl is planar due to the extremely short $H \cdots H$ non-bonded distance of 0.67 Å which may be calculated from the geometry of the molecule if planarity and normal bond distances and angles are assumed. Harris and co-workers [8,9] have discussed in detail the problem of non-planar transition states in the 1,1'-binaphthyl series, and have reached the conclusion that considerable bending of the interannular (pivot) bond probably occurs. Furthermore, they have proposed [8,9] that inversion may take place in two discrete steps, one for each pair of opposing atoms. Due to the uncertainties concerning the exact conformation of the molecule in the transition state(s), and in particular the non-bonded $H \cdots H$ distance between the opposing

atoms, we have not attempted a calculation of the isotope effect according to the theory of Bartell.[1] However, in view of the existence of several different $H \cdots H$ non-bonded potential functions, it was of interest to make an attempt at using the observed isotope effect in conjunction with a suitable potential function as a probe for estimating the $H \cdots H$ distance in the transition state(s), and at the same time as an approach to the force constant between the non-bonded hydrogen atoms, $i.e.$ the second derivative of the potential function at the equilibrium $H \cdots H$ distance in the transition state.

An approximate expression for the isotopic difference in activation energy, $\Delta\Delta E^{\ddagger}$, may be derived from the equations of Bartell,[1,4] neglecting derivatives of the potential function higher than the fourth:

$$\Delta\Delta E^{\ddagger} = \Delta E_{\mathrm{H}}^{\ddagger} - \Delta E_{\mathrm{D}}^{\ddagger} = 0.13_5 l_{m(\mathrm{H})}{}^2 [V''(r_g) + (1/2)l_{t(\mathrm{H})}{}^2 V^{\mathrm{iv}}(r_g)] \qquad (2)$$

In this equation, $l_{m(\mathrm{H})}{}^2$ is the mass-sensitive component of $l_{t(\mathrm{H})}{}^2$, the mean square of the amplitude of vibration of the pair of hydrogen atoms involved in the non-bonded interaction. $V''(r_g)$ and $V^{\mathrm{iv}}(r_g)$ are the second and fourth derivatives of the non-bonded potential function $V$ at the mean interatomic distance $r_g$, which is the same for all isotopes in the first approximation. The parameters $l_{m(\mathrm{H})}$ and $l_{t(\mathrm{H})}$ are taken to be [1,4] 0.09 Å and 0.25 Å, respectively.

Using the approximate value of 100 cal/mole $= 6.95 \times 10^{-15}$ erg/molecule for $\Delta\Delta E^{\ddagger} = \Delta\Delta H^{\ddagger} = \Delta\Delta G^{\ddagger}$ ($vide\ supra$), and an appropriate potential function, it is possible to find the value of $r_g$ at which the sum $V''(r_g) + (1/2)l_{t(\mathrm{H})}{}^2 V^{\mathrm{iv}}(r_g)$ satisfies eqn. (2). The use of eqn. (2) as given above involves the tacit assumption that the isotopic difference in activation energy is due to $one$ $H \cdots H$ non-bonded point of contact, $i.e.$ a two-stage reaction path with two identical transition states is assumed. For a one-stage reaction path the right-hand side of eqn. (2) must be multiplied by a factor of two.

The data in Table 3, where values of $r_g$, $V''(r_g)$, and $(1/2)l_{t(\mathrm{H})}{}^2 V^{\mathrm{iv}}(r_g)$ for one and two points of contact are collected, were obtained from various $H \cdots H$ potential functions, including the simple exponential type $V(r) = a \exp(-r/b)$ (Howlett [10]), the so-called "6—12" type containing an attractive

*Table 3.* Estimated values of $H \cdots H$ transition state distances $[(r_g)_{\mathrm{t.s.}}]$ in the inversion of $(-)$-1,1'-binaphthyl from the second and fourth derivatives of various potential functions and Bartell's theory of steric isotope effects (see text).

| Points of contact | 1 | 2 | 1 | 2 | 1 | 2 |
|---|---|---|---|---|---|---|
| Potential function [a] | $V''(r_g) \times 10^{-5}$ dynes/cm | | $(1/2)l_{t(\mathrm{H})}{}^2 V^{\mathrm{iv}}(r_g) \times 10^{-5}$ dynes/cm | | $(r_g)_{\mathrm{t.s.}}$ Å | |
| K | 0.350 | 0.174 | 0.277 | 0.146 | 1.755 | 1.885 |
| B | 0.445 | 0.212 | 0.194 | 0.105 | 1.745 | 1.930 |
| H | 0.530 | 0.264 | 0.108 | 0.053 | 1.725 | 2.000 |
| S | 0.225 | 0.116 | 0.417 | 0.203 | 2.010 | 2.100 |
| A | 0.308 | 0.152 | 0.330 | 0.166 | 2.225 | 2.370 |

[a] K = Kivelson $et\ al.$, Ref. 13; B = Bartell, Ref. 12; H = Howlett, Ref. 10; S = Scott and Scheraga, Ref. 11; A = Allinger $et\ al.$, Refs. 14, 15.
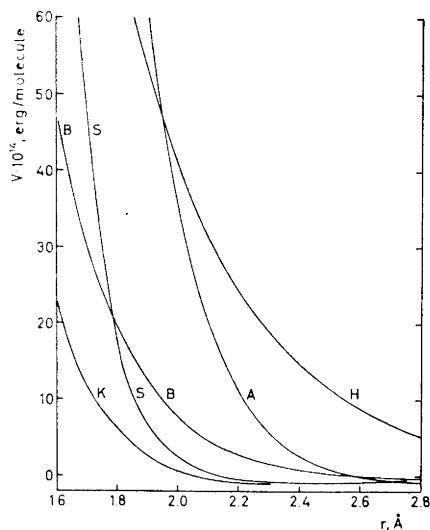
*Fig. 1.* Plots of various H···H non-bonded potential functions taken from the literature. For references, see note *a*, Table 3.
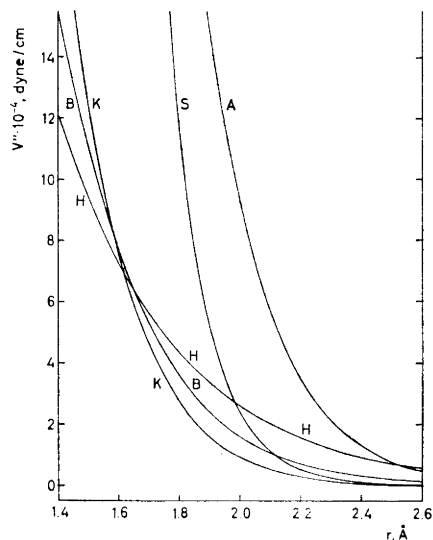
*Fig. 2.* Plots of the second derivative of the potential functions in Fig. 1.

and a repulsive term, $V(r)=ar^{-12}-br^{-6}$ (Scott and Scheraga [11]), and the mixed exponential-$r^{-6}$ type with three constants, $V(r)=a\ \exp(r/b)-c\ r^{-6}$ (Bartell,[12] Kivelson *et al.*,[13] Allinger *et al.*[14,15]). These functions and their second and fourth derivatives are plotted in Figs. 1, 2, and 3, respectively.

The values of $r_g$ in Table 3 suggest that about 2.0 Å would be a reasonable approximation to the non-bonded H···H distance in the transition state(s). The potential taken from the recent work of Allinger *et al.*,[14,15] designed primarily for the calculation of the equilibrium conformations and energies of hydrocarbons, gives a larger value of $r_g$. This is in part due to the fact that Allinger *et al.*[14,15] chose a value of 1.45 Å for the van der Waals' radius of hydrogen to obtain the best agreement between experimental and theoretically calculated heats of formation.*

The magnitude of the second derivative of each potential function at $r_g$ may be compared with that of the force constant for the in-plane bending mode of an aromatic C—H bond,[16] about $0.64 \times 10^5$ dynes/cm. Force constants arise from interactions between atoms, either bonded or non-bonded. $V''(r_g)$ corresponds to a force constant for the interaction of the non-bonded hydrogen atoms at the particular interatomic distance $r_g$, and reflects the "hardness" of the potential function.

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* It should be noted that the potential function as given by Allinger *et al.*[14] is incorrect, probably due to a printing error. The factor before the exponential term should read $8.28 \times 10^5\ \varepsilon$ instead of $8.28\ \varepsilon$. (*Cf.* Hill, T. L. *J. Chem. Phys.* **16** (1948) 399.)
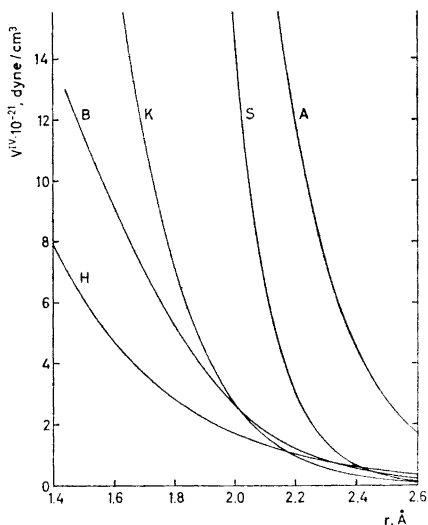
*Fig. 3.* Plots of the fourth derivative of the potential functions in Fig. 1.

The general theoretical treatment of isotope effects as developed by Bigeleisen and Wolfsberg [17] and by Melander [18] predicts that a change in the vibrational energy levels of a molecule between the initial and transition states of a reaction will lead to a kinetic isotope effect upon replacement of appropriate atoms in the molecule with their isotopes. This prediction is probably equally valid for both primary and secondary deuterium isotope effects, and indicates that zero-point energy differences are most likely to be decisive in both cases. Implicit in this argument is the important conclusion, discussed by Thornton [2] in a recent review, that the interpretation of a given experimental observation of a secondary isotope effect may always be made in terms of those effects, whether "inductive", "steric" or other, which can directly or indirectly bring about vibrational changes.

The present results may be understood from the above point of view if it is borne in mind that an increase in steric "pressure" on going from the initial to the transition state is expected to lead to a force constant increase for the bond undergoing compression.

In the harmonic approximation the relation between the frequency in $cm^{-1}$ ($\bar{\nu}$) and the force constant $k$ is given by eqn. (3). Using

$$\bar{\nu} = \left(\frac{1}{2\pi c}\right)\left(\frac{k}{\mu_H}\right)^{1/2} \tag{3}$$

this relationship, the equation derived for the secondary isotopic rate ratio [19,20] (eqn. 4) may be converted to eqn. (5).

$$k_D/k_H = \exp[(0.130 hc/kT)\sum_i(\bar{\nu}_{i(H)}{}^{\ddagger} - \bar{\nu}_{i(H)})] \tag{4}$$

$$k_D/k_H = \exp\left\{\frac{0.130\,h}{2\pi k\,T\,\mu_H{}^{1/2}}\sum_i[(k_i{}^{\ddagger})^{1/2} - k_i{}^{1/2}]\right\} \tag{5}$$

In this expression, $\mu_H$ is the reduced mass of the hydrogen atom in a C—H bond, which is assumed to be identical for all modes in the initial and transition states. The force constants are expressed in dynes/cm, and the summation is taken over the three vibrational modes of each isotopic C—H bond.

The degree to which each of these vibrational modes will be affected by steric compression cannot be estimated without rather detailed information about molecular conformations along the reaction coordinate in the inversion of 1,1'-binaphthyl, and thus an *a priori* calculation of the isotopic rate ratio is rendered impossible at present. However, it is interesting to use eqn. (5) together with the experimental isotope effect to estimate a transition-state force constant. At $T=302.43°K$, the isotopic rate ratio was found to be $k_D/k_H=1.17_8$ (see Table 1). If these data are inserted into eqn. (5) and it is assumed that the in-plane bending mode, for which $k=0.64 \times 10^5$ dynes/cm (*vide supra*), will suffer the major part of the force constant change, a value of $k^+=0.81 \times 10^5$ dynes/cm is obtained for the corresponding transition-state bending constant. If on the other hand it is assumed that the greatest part of the force constant change occurs in the stretching mode $(k=5.0 \times 10^5$ dynes/cm[16]), the corresponding $k^+$ is $5.4 \times 10^5$ dynes/cm. These $k^+$ values are calculated on the basis of two points of non-bonded contact. The corresponding values for one point of contact are $0.99 \times 10^5$ and $5.9 \times 10^5$ dynes/cm for the bending and stretching modes, respectively.

In view of the fact that bond-bending requires of the order of ten times less potential energy than bond-stretching (or compression) for the same linear deviation, it is probably reasonable to suggest that at the non-bonded distances involved in the present and previous [3,4] work, relief of non-bonded repulsions is primarily achieved by bond-bending. Westheimer's calculation [21] of the contribution of various angle deformations and atom displacements to the energy of the transition state in the inversion of 2,2'-dibromo-4,4'-dicarboxybiphenyl shows that the contribution due to deformation of the C—C—H angles involved in the H···Br interaction (0.96 kcal/mole) is more than three times as great as the contribution from compression of C—H bonds (0.30 kcal/mole). Furthermore, about 40 % of the total energy of activation arises from deformation of the C—C—Br angles, *i.e.* from carbon-bromine bond-bending.

Finally, it should be emphasized that the discussion of the isotope effect in terms of steric interactions described by a H···H non-bonded potential function, and the explanation in terms of force constant changes leading to a change in zero-point energy, are two equivalent descriptions of the same vibrational phenomenon. Thornton [2] gives a lucid analysis of this fact in his review.

## EXPERIMENTAL

Melting points were determined on a Kofler Hot-Stage Microscope.

Kinetic runs were made on a Perkin-Elmer 141 polarimeter; the deviation in each reading was assumed to be about $\pm 0.002°$. The test solution was contained in a 10 cm jacketed tube, and the temperature of the circulating water was maintained within $\pm 0.01°$ with a Haake FT thermostat.

*Trideuteriohypophosphorous acid* was prepared as previously described.[4,22]

*2,2'-Diamino-1,1'-binaphthyl* was prepared according to the modified procedure of Cohen and Oesper.[23] The crude amine hydrochloride was extracted with dilute hydrochloric acid, the amine precipitated with sodium hydroxide, filtered off and dried on the filter. The product was recrystallized from hot ethanol; yield 37 %, based on β-naphthylamine. M.p. 193°C; lit.[6] m.p. 193°C.

*(+)-2,2'-Diamino-1,1'-binaphthyl* was prepared as described by Kuhn and Goldfinger.[6]

*(−)1,1-'-Binaphthyl-2,2'-d₂.* To a cooled flask containing deuterium oxide (7 g) and fitted with an efficient stirrer, acetyl chloride (7 g) was carefully added, followed by (+)-2,2'-diamino-1,1'-binaphthyl (1 g) and a cool solution of sodium nitrite (0.6 g) in deuterium oxide (10 ml). The cool diazonium salt solution was slowly added to a cool solution of trideuteriohypophosphorous acid (5 ml, *ca.* 50 % in deuterium oxide) and deuterium oxide (20 ml). A small amount of cupric oxide was added to catalyze the reduction. After standing in the refrigerator overnight, the product was filtered off, washed with water and dried. The crude material was dissolved in benzene (40 ml), petroleum ether was added (b.p. 40−60°, 40 ml) and the precipitate was filtered off. The red solution was chromatographed on a column of aluminium oxide and eluted with benzene-petroleum ether (b.p. 40−60°) 1:1 until the red impurity band began to come out. Evaporation of the eluate gave white crystals (0.2 g, 22 %), m.p. 152−153°.

*Table 4.* Mass spectrometric analyses of binaphthyl samples.

| Sample | $d_0$, % | $d_1$, % | $d_2$, % | Impurity, % [a] |
|--------|----------|----------|----------|-----------------|
| 7 | 97.5 | — | — | 2.5 |
| 4 | 0.7 | 12.8 | 86.5 | 11 |
| 5 | 1.2 | 17.3 | 81.5 | 8 |
| 8 | 1.3 | 17.6 | 81.1 | 10 |
| 10 | 1.4 | 17.7 | 80.7 | 10 |
| 11 | 1.0 | 13.0 | 86.0 | 7 |

[a] The amount of impurity is given in per cent of the *total* sample.

The purity was checked by mass spectrometry, the results of which are given in Table 4 (samples 4, 5, 8, 10, and 11). $[\alpha]_{4360}^{36} = +230°$ (c=0.85 g/100 ml, l=1 dm, DMF).

*(−)-1,1'-Binaphthyl* was prepared from the corresponding protium compounds; m.p. 158−159°, lit.[8] m.p. 157−159°. Mass spectrometry showed that the sample contained about 2.5 % of an impurity with its main peak at $m/e$ 288 (see Table 4, sample 7). $[\alpha]_{4360}^{51} = +250°$ (c=0.57 g/100 ml, l=1 dm, DMF).

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