

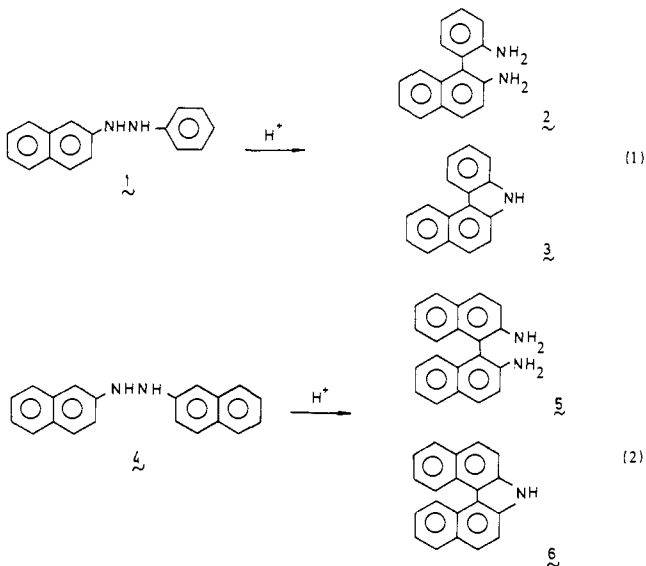
Heavy-Atom Kinetic Isotope Effects in the Acid-Catalyzed Rearrangement of *N*-2-Naphthyl-*N'*-phenylhydrazine. Rearrangement Is Shown To Be a Concerted Process^{1,2}

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Abstract: Heavy-atom kinetic isotope effects (KIE) have been measured in the acid-catalyzed rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine (**1**) into 1-(*o*-aminophenyl)-2-naphthylamine (**2**). A combination of whole-molecule-ion and isotope ratio mass spectrometry and scintillation counting has given KIE for ¹⁵N, ¹³C, and ¹⁴C. Use of [¹⁵N,¹⁵N']**1** and whole-molecule-ion mass spectrometry gave a KIE of 1.0434 (for two ¹⁵N atoms). Use of [1-¹³C]**1** and isotope-ratio mass spectrometry gave a KIE of 1.0196 for one naturally abundant ¹⁵N atom and 1.0042 for one ¹³C atom. Use of [2'-¹⁴C]**1** gave a KIE of 1.0142 for one ¹⁴C atom. The results show that this rearrangement is a concerted process, namely a [3,3]-sigmatropic shift. The transition state, furthermore, appears to be unsymmetrical. That is, the extents of N-N bond breaking and C-C bond forming appear to be unequal.

The acid-catalyzed rearrangement of *N*-2-naphthyl-*N'*-phenylhydrazine (**1**) has been reported to give 1-(*o*-aminophenyl)-2-naphthylamine (**2**) in up to 99% yield, along with a small amount (0.5%) of 3,4-benzocarbazole (**3**), eq 1. Neither another rearrangement product nor disproportionation was detected.⁴ The formation of **2** involves bonding at the so-called *o,o'*- or 2,2'-carbon atoms. In this respect this rearrangement is like that of 2,2'-hydrazonaphthalene (**4**), eq 2, which gives predominantly 2,2'-diamino-1,1'-binaphthyl (**5**) and the corresponding carbazole (**6**), but in distinct contrast with the rearrangements of hydrazobenzene and most of its derivatives, among which little or no *o,o'*-bonding is found.¹ Like **4**, **1** also rearranges when heated in solution in the absence of acid and again gives mostly **2** and **3**.^{5,6}



The acid-catalyzed and thermal rearrangements of **4** into **5** have been shown to be [3,3]-sigmatropic shifts with markedly unsymmetrical transition states.¹ We were interested in finding if the

acid-catalyzed and thermal rearrangements of **1** would have similar characteristics and hence fit the pattern of benzidine rearrangements which is developing, that is, that they comply with the requirements of orbital symmetry.¹ We were further interested in finding whether or not the difference found in the transition states of the acid-catalyzed and thermal rearrangements of **4** would also be seen in the rearrangements of **1**. To this end we synthesized [¹⁵N,¹⁵N']**1**, [1-¹³C]**1**, and *N*-2-naphthyl-*N'*-[2-¹⁴C]phenylhydrazine (hereinafter called [2'-¹⁴C]**1**) in order to measure the nitrogen and carbon kinetic isotope effects (KIE) in the formation of **2**.

Unfortunately, the thermal rearrangement of **1** proved to be unamenable to our method of measuring KIE. Thermal rearrangement of **1** is comparatively slow. Shine and co-workers⁵ had found that even after 7 days in ethanol at 90 °C only 61% of a 0.058 M solution of **1** underwent rearrangement. Banthorpe reported that a 0.043 M solution of **1** in ethanol rearranged completely at 110 °C in 1 day and gave 90.7% of **2** and 6.7% of **3**. We were unable to obtain anything like complete rearrangement of **1** after heating at 90 °C in ethanol for many days, and at 100 °C during 4 days in *n*-propanol and aqueous *n*-propanol, which were chosen for their higher boiling points. More to the point, attempts to recover **2** quantitatively after low conversions of **1**, an essential feature of our KIE method, proved not to be possible. The rearrangement mixture appeared to be more complex at low conversions than the literature would suggest.^{5,6} Consequently, we were obliged to abandon attempts to measure KIE for the thermal rearrangement of **1**. We have, however, measured the ¹⁵N, ¹³C, and ¹⁴C KIE for the acid-catalyzed rearrangement. The combination of results, obtained from whole-molecular-ion and isotope-ratio mass spectrometry and scintillation counting, show that the acid-catalyzed rearrangement is a concerted process, and the transition state appears to be unsymmetrical. That is, the extents of N-N bond breaking and C-C bond forming in the transition state appear to be different.

Results

Syntheses of Labeled 1. Labeled **1** was made by the customary reduction of labeled 2-phenylazonaphthalene (**7**) with zinc and ammonium chloride in aqueous acetone. In each case **7** was made by condensation of appropriately labeled 2-naphthylamine and nitrobenzene. Thus, [¹⁵N,¹⁵N']**7** was made from condensation of 2-[¹⁵N]naphthylamine⁷ and commercial [¹⁵N]nitrobenzene, which contained 99% and 98% of ¹⁵N, respectively. [1-¹³C]**7** was made by condensation of nitrobenzene and 2-[1-¹³C]naphthylamine, the latter being available from earlier work.^{1,7} Finally,

(7) Gruszecka, E.; Shine, H. J. *J. Labelled Compd. Radiopharm.* 1983, 20, 1257.

(1) Part 21 in a series. For part 20 see: Shine, H. J.; Gruszecka, E.; Subotkowski, W.; Brownawell, M.; San Filippo, J., Jr. *J. Am. Chem. Soc.* 1985, 107, 3218.

(2) Supported by the National Science Foundation, Grant CHE-8314947, the Robert A. Welch Foundation, Grant D-028, and the Center for Energy Research, Texas Tech University.

(3) On leave from the Institute of Organic and Physical Chemistry, Technical University, Wrocław, Poland.

(4) Banthorpe, D. V. *J. Chem. Soc.* 1962, 2429.

(5) Shine, H. J.; Huang, F.-T.; Snell, R. L. *J. Org. Chem.* 1961, 26, 38.

(6) Banthorpe, D. V. *J. Chem. Soc.* 1964, 2854.

Table I. Yields of Products and Conversions in the Acid-Catalyzed Rearrangement of *N*-2-Naphthyl-*N'*-phenylhydrazine (**1**)^a

run	isotope	distribution, %			total recovery, ^b %	conversion, ^c %
		2	3	7		
1	¹⁵ N	5.3	1.0	91.7	98.0	8.3
		95.6	1.5	1.5	98.6	98.5
2		8.9	1.2	88.7	98.8	11.3
		95.3	1.9	1.4	98.6	98.6
3		16.9	2.5	79.7	99.1	20.3
		94.0	3.6	1.5	99.1	98.5
4	¹⁴ C	10.7	0.7	87.3	98.7	12.7
		94.3	1.2	2.8	98.3	97.2
5		15.7	1.7	81.5	98.9	18.5
		95.9	2.1	1.2	99.2	98.8
6		19.5	2.0	78.0	99.5	22.0
		95.4	1.8	1.4	98.6	98.6
7	¹³ C	6.7	1.4	90.0	98.1	10.0
		92.2	2.5	0.9	95.6	99.1
8		10.1	1.2	86.3	97.6	13.7
		96.7	2.7	0.4	99.8	99.6
9		16.7	1.6	81.5	99.8	18.5
		91.0	6.4	1.3	98.7	98.7

^aAt 0 °C in 60% aqueous dioxane. ^bSum of yields of **2**, **3**, and **7**. ^cBased on amount of **7** recovered.

[2'-¹⁴C]**7** was obtained by condensation of 2-naphthylamine with 1-nitro-2-[¹⁴C]benzene, the latter being made from commercially available 2-nitro-1-[¹⁴C]aniline.

Before reduction to labeled **1** the labeled **7** was diluted with unlabeled **7** by co-crystallization. In this way, the mixtures used contained respectively 5 mol% of [¹⁵N,¹⁵N']**7** and [1-¹³C]**7**, while the radioactive **7** was labeled to the extent of 8 mCi/mol. Reduction of labeled **7** gave [¹⁵N,¹⁵N']**1** with mp 107–108.5 °C, [1-¹³C]**1** with mp 102–104 °C, and [2'-¹⁴C]**1** with mp 106–107.5 °C. Shine and co-workers⁵ reported mp 104 °C, while Banthorpe⁴ reported mp 90 °C. We have not tried to resolve this difference. Since **1** rearranges thermally in the solid state⁶ it may be that the lower melting point derives from some rearrangement having occurred during a slower rate of heating. One of us has noted before that 2,2'-dimethoxyhydrazobenzene, used in related work, was also occasionally obtained with a sharp but lower melting point (83–85 °C) than ordinarily obtained (102–103 °C), and in that case the lower-melting product appeared to be analytically no different from the higher.⁸ Possibly, therefore, some hydrazoarenes may have more than one crystalline form, each with its own melting point.

Rearrangement of 1. The kinetic order in acid in the rearrangement of **1** ranges from 1.0 to 2.0 depending on the concentration of acid.⁴ In our method of measuring KIE it is necessary to take samples at known, chosen extents of conversion, and this means that the rearrangement should occur over a reasonable period of time. We chose the conditions, therefore, already established by Banthorpe, for rearrangement of 0.004 M **1** at 0 °C in 60% aqueous dioxane which was 0.10 M in HClO₄.⁴ The rate constant for rearrangement under these conditions is given as 1.78 × 10⁻⁴ s⁻¹, and the rearrangement is second order in acid. Times of low conversions were calculated with this rate constant, while for 100% conversion rearrangement was allowed to go for 48 h. Acid solutions were made alkaline with 40% sodium hydroxide at the chosen times. Unrearranged **1** was then oxidized by air to **7**, and **1**, **2**, and **7** were separated in standard ways (see Experimental Section).

Separations by column chromatography were quite satisfactory in giving excellent recovery of **2** and **7**. The errors in recovery of the small amounts of **3** may have been fairly large, however. Also, 1–2% of amine-like product(s) was obtained at the end of the silica chromatography but could not be identified. These small

uncertainties have a bearing on the extent of conversion which is used in calculating KIE. The data for recovery of **2**, **3**, and **7** are given in Table I. Because the recovery of **7** was more certain than that of **3**, and because 1–2% of unknowns was obtained, we have used the amount of **7**, rather than the sum of **2** and **3**, as a measure of the low conversions. As for the 100% conversions, these, too, gave small amounts of **7**. We cannot say if these represent unrearranged **1** which was oxidized to **7** after rearrangement was quenched or if the **7** was formed by small amounts of disproportionation or adventitious oxidation of **1** during rearrangement. These possibilities have been taken into account in calculating KIE, as noted below.

The **2** thus separated was crystallized from 95% ethanol and then converted into its bis(trifluoroacetyl) derivative. This derivative was purified by sublimation twice for mass spectrometric measurements and three times for scintillation counting.

KIE Measurements and Calculations. KIE were calculated from the relative abundances of light and heavy isotopes in the product at low and 100% conversions. The product **2** was not used itself, however, but, after isolation, it was converted quantitatively into its bis(trifluoroacetyl) derivative. The reason for this was initially connected with measuring relative abundances by whole-molecule-ion mass spectrometry. For this, **2** itself is not so well suited because its mass spectrum has a substantial (M - 1) peak, whereas an (M - 1) peak is negligibly small in the mass spectrum of the derivative. At the same time also the ease of purifying the derivative by crystallization and sublimation made it the choice in the other methods of measuring relative abundances: scintillation counting and isotope-ratio mass spectrometry.

Nitrogen KIE were obtained first with doubly enriched substrate, [¹⁵N,¹⁵N']**1**. The ratio of the (M + 2)/M ions, namely 428/426, in the product's derivative was measured by high precision, multiscan, whole-molecule-ion mass spectrometry. The enrichment of mass 428 in the derivative was then normalized for the natural abundance, because we had used substrate containing only 5 mol% of [¹⁵N,¹⁵N']**1**, and the normalized data were used in calculating KIE for two ¹⁵N atoms. The results are given in Table II.

In synthesizing [1-¹³C]**1** we had planned to measure the ¹³C KIE by whole-molecule-ion mass spectrometry, too, that is, from the relative abundances of masses 427 and 426 in the product's derivative. However, we were not able to obtain satisfactorily reproducible data by this method, and, therefore, we turned to isotope-ratio mass spectrometry. In the latter method the sample is converted into CO₂ and mass ratio 45/44 is measured relative

(8) Shine, H. J.; Park, K. H.; Brownwell, M. L.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 7077.

Table II. KIE for the Acid-Catalyzed Rearrangement of *N*-2-Naphthyl-*N'*-phenylhydrazine (**1**)^a

run	isotope	method ^b	conv, ^c %		KIE _{app} ^d	KIE ^e	10 ³ σ ^f
1	¹⁵ N, ¹⁵ N	A	8.3	98.5	1.0434	1.0468	3.1
2	¹⁵ N, ¹⁵ N	A	11.3	98.6	1.0434	1.0466	2.6
3	¹⁵ N, ¹⁵ N	A	20.3	98.5	1.0340	1.0368	2.2
7 ^g	¹⁵ N	B	10.0	99.1	1.0170	1.0186	
8	¹⁵ N	B	13.7	99.6	1.0204	1.0210	
9	¹⁵ N	B	18.5	98.7	1.0180	1.0194	
4	¹⁴ C	C	12.7	97.2	1.0125	1.0140	2.7
5	¹⁴ C	C	18.5	98.8	1.0128	1.0136	5.6
6	¹⁴ C	C	22.0	98.6	1.0139	1.0149	3.8
8	¹³ C	B	13.7	99.6	1.0042	1.0043	
9	¹³ C	B	18.5	98.7	1.0039	1.0041	

^aAt 0 °C in 60% aqueous dioxane. ^bA, multiscan whole-molecular-ion mass spectrometry; B, isotope-ratio mass spectrometry on N₂ and CO₂ obtained from samples enriched in ¹³C but having only naturally abundant nitrogen; C, scintillation counting. ^cBased on recovered azo compound **7**. ^dCalculated with eq 3 or 6 and assuming high conversion was 100%. ^eCalculated with eq 4 or 6 and using conversions shown in the table. ^fStandard deviation in KIE calculated from standard deviation of the mean in whole-molecule-ion mass ratio measurements and scintillation counts. ^gThe ¹³C KIE obtained by method B for run 7 was 1.0202 and is so obviously in error that it is omitted from the table.

to the ratio in an arbitrary standard. Ordinarily, this method is best used with compounds whose ¹³C content is close to that in the standard. This turned out to be the case in our use of enriched **1**, because we had carried out rearrangements of mixtures containing only 5 mol % of [1-¹³C]**1**. The enrichment in atom % was thus 0.25, well within the range for precise isotope-ratio measurements on CO₂. These measurements led, then, to the ¹³C KIE in Table II.

The combustion of samples to give CO₂ for isotope-ratio measurements also gave N₂. The N₂ thus obtained from our ¹³C samples was naturally abundant nitrogen. It was possible, therefore, to obtain by isotope-ratio mass spectrometry the ratio of masses ²⁹N₂/²⁸N₂ as well as that of ⁴⁵CO₂/⁴⁴CO₂ in the product at low and 100% conversions. From these data we were able to calculate the nitrogen KIE for one ¹⁵N atom. The results are given in Table II.

A carbon KIE was also measured for ¹⁴C in the product by scintillation counting. We had used [1-¹³C]**1** for measuring ¹³C KIE because 2-[1-¹³C]naphthylamine was available from earlier work.¹⁷ Rather than laboriously construct 2-[1-¹⁴C]naphthylamine for ¹⁴C KIE we chose to use [2-¹⁴C]**1** because it could be made easily from 1-nitro-2-[¹⁴C]benzene whose precursor was available commercially. Thus, although we thereby obviated making a direct comparison of ¹³C and ¹⁴C KIE by having each label in the same position, we were able to compare the effect of each of these heavy atoms in the same bonding process. The results are given in Table II.

KIE may be calculated from isotope distributions in either the product or unreacted substrate of a reaction. If the product is used product sampling must be carried out at low and 100% conversions. The distribution of isotopic molecules at 100% conversion is the same as that in the initial substrate, so that one could, in principle, use the initial substrate for measuring the ratio of isotopes rather than taking the reaction to 100% conversion. When measuring the ratio of isotopic molecules by whole-molecule-ion mass spectrometry, though, it is advisable to compare mass ratios obtained with the same rather than different molecules, that is with product always or with substrate always. In working with hydrazoarenes the substrate is not suitable for mass ratio measurements because it is so susceptible to oxidation in handling. Instead of the substrate, therefore, the precursor azoarene can be used. However, the mass spectra of azoarenes are not overly suitable for the whole-molecule-ion technique, in that the parent ion is usually only of modest intensity, there is usually a large contribution from the (M - 1) peak, and the fragment ions are not suitable for use. In the case of ¹⁴C KIE, the azoarenes are not suitable for use because they are colored, and hence cause quenching in scintillation counting. Consequently, it is better to aim for the product when applying the whole-molecular-ion and scintillation counting methods to the rearrangements of hydrazoarenes. These disadvantages to using the azoarene for KIE measurements would not apply to the isotope-ratio mass spectrometry method, because the sample is converted into gases.

Nevertheless, where we resorted to isotope-ratio mass spectrometry we again used the product since the product samples were ready for use.

In any event, it was necessary for us to isolate product for the two methods described. The timing of product isolation was calculated from Banthorpe's rate constant,⁴ but this was used only as a guide. The extent of conversion was determined more meaningfully from the amounts of products formed and the amount of unreacted **1**, isolated, though, as the azoarene **7**. The product of rearrangement of **1** is **2**. However, the carbazole **3** is formed in the same rate-determining way, not from **1** itself but from the same carbon-carbon bonded precursor.⁹⁻¹¹ Therefore, the extent of conversion should be given by the sum of the yields of **2** and **3**. However, the amounts of **3** formed were so small (a few mg) that we feel that there is some uncertainty in the reported yields of **3**. Again, as mentioned earlier, very small amounts of another product or products appeared in the final elutions from the silica chromatography column. Consequently, we feel that the azoarene **7**, representing recovered **1**, is a better measure of low conversions. This measure is listed in Tables I and II.

The time calculated for 99.9% conversion was 11 h. We allowed 48 h for 100% conversion. Nevertheless, 1-2% of azoarene was always obtained on workup. It is possible that this could be attributed to incomplete conversion of **1**. Therefore we have calculated KIE in two ways. In the first we have assumed that conversion was complete and have calculated KIE from eq 3.¹² The results are reported in Table II as KIE_{app}.

$$R_p/R_o = [1 - (1 - F)^{k_2/k_1}] / F \quad (3)$$

In the second, we have assumed that the high conversions were, in fact, not 100% but as listed in Tables I and II. We have calculated KIE with the low and high conversion data using eq 4 and an iterative procedure developed by Professor W. H. Saunders, Jr., and described earlier.¹ The results are reported as KIE in Table II.

$$R_p/R_p' = \frac{F'[1 - (1 - F)^{k_2/k_1}]}{F[1 - (1 - F)^{k_2/k_1}]} \quad (4)$$

In the isotope-ratio method mass ratios, i.e., of ²⁹N₂/²⁸N₂ and ⁴⁵CO₂/⁴⁴CO₂, were obtained as they related to arbitrary standards and were expressed as "del" values (δ), as shown, for example, for nitrogen in eq 5. From this equation it was possible to calculate

$$\delta(29/28)_s = \frac{(29/28)_s - (29/28)_{std}}{(29/28)_{std}} 1000 \quad (5)$$

(9) Banthorpe, D. V.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1964**, 2864.

(10) Shine, H. J. "Aromatic Rearrangements"; Elsevier: New York, 1967; pp 126-179.

(11) Cox, R. A.; Buncl, E. In "The Chemistry of the Hydrazo, Azo, and Azoxy Groups"; Patai, S., Ed.; Wiley: New York, 1975; pp 775-859.

(12) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley-Interscience: New York, 1980; p 100.

the mass ratio, $(29/28)_s$, in a sample at a given conversion and to use the data to calculate KIE with eq 6, according to Ayrey et al.¹³ In eq 6, shown here for nitrogen KIE, f is the extent of

$$k_{14}/k_{15} = \frac{\ln(1-f)}{\ln(1-rf)} \quad (6)$$

conversion and r is given by either $(28/29)_{100}/(28/29)_{\text{low}}$ or $(28/29)_{\text{high}}/(28/29)_{\text{low}}$, the subscripts referring to percent conversion. The results thus obtained are given in Table II as KIE_{app} and KIE. Arbitrary standards were ordinary nitrogen with a mass ratio $(28/29)$ of 136.0 and a carbon source with a mass ratio $(44/45)$ of 88.992.

Discussion

The results in Table II show that there are only small differences between KIE_{app} and KIE. For the purposes of discussion we will use the KIE data as the maximum we could measure in the effects of the heavy isotopes on the rate of rearrangement.

The average of the KIE for two ¹⁵N atoms (runs 1–3) is 1.0434 ± 0.0047 . The average of the KIE for one ¹⁵N atom (runs 7–9) obtained by isotope-ratio mass spectrometry is 1.0197 ± 0.0009 . The two results are in excellent agreement, since from the isotope-ratio result we can calculate an anticipated KIE for two ¹⁵N atoms as 1.0398.

The average of the KIE for one ¹⁴C atom (runs 4–6) is 1.0142 ± 0.0005 . Only two results for ¹³C are listed for use. A third result (run 7, see Table II) was so obviously in error that we report the result but exclude it from use. The average ¹³C KIE (runs 8 and 9) then is 1.0042 ± 0.0001 . We cannot make a strict comparison of the effects of the ¹³C and ¹⁴C atoms since they were at the opposite ends of the bond being formed. However, each atom occupies a ring position and is undergoing similar changes in bonding when the C–C bond is being formed. Therefore, we can accept that the two results would not be seriously different if the two heavy atoms had occupied the same bonding site. We can calculate from eq 7¹⁴ that the ¹³C KIE for the same site as ¹⁴C should be 1.0074. The experimental result, 1.0042, is in

$$\frac{\log(k(^{12}\text{C})/k(^{14}\text{C}))}{\log(k(^{12}\text{C})/k(^{13}\text{C}))} = 1.9 \quad (7)$$

reasonable agreement and tells us that the ¹³C KIE for bond formation is indeed very small. It is the size of the ¹⁴C KIE, in fact, which establishes firmly that C–C bonding is part of the transition state of the rearrangement.

The ¹⁵N and ¹³C KIE, each for one heavy atom differing from its light isotope by one mass unit, suggest that although rearrangement is concerted its transition state is not symmetrical. That is, it appears that the breaking of the N–N bond is the more significant process. Whether or not this is a correct diagnosis must be sought, however, in calculations on transition-state models, a challenge which, we hope, can elicit response in other laboratories.

Recently, we have reported KIE for the one-proton rearrangement of 2,2'-hydrazonaphthalene (**4**).¹ This rearrangement, found to be a [3,3]-sigmatropic shift, also appears to have a decidedly unsymmetrical transition state. From the data in that case single-atom ¹⁵N and ¹³C KIE are calculated to be 1.0442 and 1.0043, respectively. The ¹³C KIE is seen again to be very small.

The small KIE for bond formation in these rearrangements can be attributed to the competition of two effects, best identified in the Bigeleisen equation (eq 8).¹⁵ As C–C bonding in the transition state becomes more advanced, the size of the square-bracket term becomes smaller, and the term ν_{1L}^*/ν_{2L}^* , itself always greater than 1.0, is reduced in size. The net effect in the rearrangements of

1 and **4** is to have carbon KIE close to 1.0.

$$k_1 k_2 = (\nu_{1L}^*/\nu_{2L}^*) \left[1 + \sum_i^{3n-6} G(u_i) \Delta u_i - \sum_i^{3n-7} G(u_i^*) \Delta u_i^* \right] \quad (8)$$

If we can speculate on the rearrangements of **1** and **4** in the absence of model calculations it appears that the transition state in the rearrangement of **1** is "tighter" than that in the rearrangement of **4**. That is, less extensive N–N bond breaking may have occurred in the rearrangement of **1** than of **4** when C–C bond formation has its effect. Possibly this reflects the need, in the rearrangement of **4**, to bring two naphthalene rings close together, but not necessarily overlapping,¹ in the transition state, a process which appears intuitively to be more difficult than bringing together one naphthalene and one benzene ring in the rearrangement of **1**. That the rearrangement of **1** involved two protons while that of **4** involved only one may also contribute to the difference in transition states. That is, if we look upon the rearrangement in the polar-transition-state sense, with one part of the heterolyzing molecule delocalizing two units of positive charge and the other part delocalizing a pair of amino-group electrons, the two parts of the transition state may be held in closer proximity, by charge-attraction effects, in rearranging **1** than the two parts of the singly charged transition state in rearranging **4**. We have commented on the effect of charge in comparing the transition state of the acid-catalyzed and thermal rearrangements of **4**.¹

Experimental Section

Dioxane was distilled from lithium aluminum hydride just before use. For column chromatography silica gel was from J. T. Baker (3405 R, 60–200 mesh) and neutral alumina was from MCB (Type F-20, 80–200 mesh).

Labeled 2-phenylazonaphthalenes (7) were prepared by the method of Ramart-Lucas;¹⁶ an example is given: A mixture of 2.67 g (18.7 mmol) of 2-naphthylamine and 2.0 g (16.3 mmol) of nitrobenzene was heated to 180 °C and to it was slowly added 1.7 g of powdered sodium hydroxide. Heating was continued for 30 min, and the mixture was cooled and dissolved in ether. The ether solution was washed with dilute hydrochloric acid, dried over sodium sulfate, and evaporated. The residue was chromatographed on alumina with use of 4:1 benzene:petroleum ether (30–60 °C), giving 1.4 g (6.0 mmol, 32%) of **7**, mp 83–84 °C, after crystallization from ethanol (lit.¹⁶ mp 84 °C).

[¹⁵N,¹⁵N]**7** was prepared from 2-[¹⁵N]naphthylamine⁷ and [¹⁵N]-nitrobenzene (98% ¹⁵N, Cambridge Isotope Labs). Dilution with unenriched **7** and crystallization from ethanol gave a mixture containing 5 mol % of [¹⁵N,¹⁵N]**7**.

[2-¹⁴C]**7** was prepared from 2-naphthylamine and nitro-2-[¹⁴C]-benzene. The latter was prepared from 2-nitro-1-[¹⁴C]aniline (American Hoechst, Frankfurt, FRG) as described earlier.¹⁷ Dilution with unenriched **7** and crystallization from ethanol gave [2-¹⁴C]**7** with activity approximately 8 mCi/mol.

[1-¹³C]**7** was prepared from 2-[1-¹³C]naphthylamine and nitrobenzene. The 2-[1-¹³C]naphthylamine was a mixture containing 5 mol % of the enriched molecule and was obtained by hydrogenolysis (H₂-Pd/C in benzene) of 5 mol % [1,1'-¹³C₂]-2,2'-azonaphthalene available from earlier work.¹

The mixtures of labeled **7** were reduced to labeled **1** with zinc dust and ammonium chloride¹⁸ immediately before rearrangements were carried out. The **1** thus obtained had an acceptable melting point (see text) and was used without recrystallization.

Acid-Catalyzed Rearrangement of 1. A solution of 936 mg (4.0 mmol) of **1** in 300 mL of dioxane and 200 mL of water (60% aqueous dioxane) was cooled to 0 °C. A solution containing 8.75 mL of 70% perchloric acid and 191.25 mL of water in 300 mL of dioxane was similarly cooled. A 75-mL aliquot of each solution was withdrawn and the aliquots were mixed and placed in the refrigerator for 48 h. This mixture served for 100% conversion. The remaining solutions, each of 425 mL, were mixed and kept at 0 °C for 10 min while being stirred under a slow current of oxygen-free argon. The solution was then quenched with 45 mL of 40% aqueous sodium hydroxide. Air was bubbled into the alkaline solution for 48 h to oxidize the remaining **1** to **7**. The solution was then diluted with 500 mL of water and extracted successively with 450, 300, and 150

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mL of ether. The ether solution was dried over magnesium sulfate and evaporated to give 796 mg (100% by weight) of orange-colored solid residue which was chromatographed on silica gel, using 98:2 chloroform:cyclohexane. Separation was clean, giving fractions containing, in order of elution, 703 mg of mainly **7**, 5.15 mg of a mixture of **7** and **3**, 70.7 mg (0.302 mmol, 8.9%) of reasonably pure **2**, and 1.7 mg of unknown amine-like product(s). **7** and the mixture of **3** and **7** were further purified and separated on a column of alumina, using 8:3 benzene: petroleum ether as eluent to remove 699 mg (88.7%) of **7** and methanol to remove 9.7 mg (1.22%) of **3**. The final results are listed in run 2, Table I.

The solution which had been kept for 48 h in the refrigerator was treated similarly. Workup gave finally 133.9 mg (0.572 mmol, 95.3%) of **2**, 2.5 mg (1.9%) of **3**, and 2.0 mg (1.4%) of **7**.

Rearrangements to other conversions were carried out similarly for all KIE runs.

The **2** obtained from silica gel chromatography was dissolved in 5 mL of benzene to which 5 mL of trifluoroacetic anhydride was added. After being left to stand overnight the mixture was evaporated to dryness. The bis(trifluoroacetyl) derivative of **2** thus obtained was purified by sublimation, twice for mass spectrometric analyses (^{15}N and ^{13}C) and three times for scintillation counting (^{14}C). Each sample of the bis(trifluoroacetyl) derivative had mp 183-184 or 184-185 °C.

KIE Measurements. (A) Whole-molecular-ion mass ratios in the bis(trifluoroacetyl) derivative of **2** were determined with a Hewlett-Packard Model 5995 mass spectrometer, using the selected-ion-monitoring (SIM) mode. All samples were introduced into the mass spectrometer via the solid sample inlet, using the direct insertion probe.

Samples were heated as required to maintain a constant source pressure of 8×10^{-7} torr. Data collection for nitrogen KIE was achieved by monitoring the abundances of ions of m/e 426 and 428 at 70 eV. The average dwell time was 50 ms/ion. Three runs of approx 5000 scans each were made for each sample. The data were normalized for 100% m/e 426 and then corrected for the abundances of ions 426 and 428 in the unenriched derivative of **2**, measured similarly. In this way the enrichment of ion m/e 428 was determined in samples at each conversion. Calculations of KIE were made as described earlier.¹

(B) Mass ratios $^{29}\text{N}_2/^{28}\text{N}_2$ and $^{45}\text{CO}_2/^{44}\text{CO}_2$ were measured in the laboratories of Krueger Geochron with use of a VG Micromass model 903 triple collector isotope-ratio mass spectrometer. In this method a sample was mixed with preburned CuO, sealed in an evacuated tube, and heated at 550 °C for 8 h to convert the sample into a mixture of nitrogen, carbon dioxide, and water. The gases were separated cryogenically for mass ratio analyses. The method has been described by Sofer.¹⁹

(C) The ^{14}C content of samples was measured by scintillation counting with use of a Beckman Model LS 7000 counter with its appropriate programs. Approximately 3 ± 0.001 mg of sample was weighed on a Cahn balance and dissolved in 10.0 mL of cocktail (Packard SC INT-O No. 6013183). Three samples were weighed for each conversion, and each sample was counted 18 times. The average count per sample was in the range of 38500-39100, and the standard deviation in counting ranged from 0.05 to 0.55%. KIE were calculated with the use of eq 3 and 4; the iteration procedure for eq 4 has been described earlier.¹

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Synthesis and Diatropicity of a Phenanthrene-Annulated *trans*-Dimethyldihydropyrene: A Novel Molecule To Indicate the High π -Bond Order of the 9,10 Bond of Phenanthrene

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Revised Manuscript Received June 8, 1985

Abstract: The *trans*-phenanthrodimethyldihydropyrene **6** has been synthesized from phenanthraquinone and 2,6-dichlorotoluene in 0.3-0.5% overall yield by using Stevens or Wittig rearrangements and a Hofmann elimination sequence on the thiacyclophane **8B** followed by valence tautomerization of the resulting cyclophanediene **9**. This novel aromatic molecule **6** is used as a model to study the effect of phenanthroannulation on the diatropicity of an annulene. The internal methyl protons of **6** appear at δ -3.32, indicating a strong diamagnetic ring current. As predicted, the high π -bond order of the 9,10 bond of phenanthrene has resulted in much less bond localization in the 14π macrocyclic ring compared to the related benzannulated system **7**. An unexpectedly low 1.0:6.1 ratio of **6:9** was obtained in the synthesis, which represents the first example of the dimethyldihydropyrene \rightleftharpoons [2.2]metacyclophanediene system to have the latter as a major tautomer. This is believed to be due to adverse steric strains caused by the interaction between the H(1)-H(16) and H(8)-H(9) protons when **6** achieves planarity. Reduction in diatropicity of **6** compared with the parent **3** is discussed in terms of effects of annelation, deviation from planarity, and conjugation.

The works by Sondheimer,¹ Nakagawa,² Vogel,³ Boekelheide⁴ and Mitchell⁵ on different families of nonbenzenoid [$4n + 2$]-annulenes have collectively led to the better understanding of

various aspects of aromaticity. One of the more interesting areas is the effect of annelation, in particular benzannulation,^{5,6} on the diatropicity of the annulenes. The effect could be clearly observed from ^1H NMR studies of changes in chemical shifts of the "internal" protons or substituents of the annulenes. For example, benzannulated [14]annulenes **2**⁷ and **4**^{8a,8} have internal protons and methyl protons significantly shifted compared with their respective parent [14]annulene systems **1**⁹ and **3**.¹⁰ Although

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