

wise to a dispersion of lithium aluminum hydride, 0.19 g in 100 ml of anhydrous ether, and the reaction mixture was refluxed for 8 hr. The excess lithium aluminum hydride was decomposed by careful addition of water. The precipitated hydroxide was dissolved in ice-cold 1 N hydrochloric acid. The usual work-up gave 3.6 g (71%) of a fraction, bp 90–91°. Preparative vpc on a 15 ft × 0.25 in. 20% Carbowax 20M on Chromosorb P column (70°, He 80 cc/min) yielded pure (*R*)-2-methoxypentane (the fraction obtained

from distillation was approximately 98% pure). The vpc purified sample, n_D^{25} 1.3814 (known sample: n_D^{25} 1.3816), had retention time and infrared spectrum identical with a known sample.²⁸ It had α_D^{25} $-3.24 \pm 0.01^\circ$. Since the starting (*R*)-4-methoxy-1-pentene was of $20.9 \pm 0.4\%$ optical purity, the minimum rotation of (*R*)-2-methoxypentane should be $\alpha_D^{25} -15.5 \pm 0.3^\circ$, to be compared with $\alpha_D^{25} -16.3 \pm 0.1^\circ$ for the sample obtained by hydrogenation of (*R*)-4-methoxypentene.

Nuclear Magnetic Resonance Studies of Rate Processes and Conformations. V. Synchronous Inversion at Two Nitrogens¹

J. E. Anderson^{2a} and J. M. Lehn

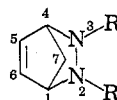
Contribution from the Institut de Chimie, Université de Strasbourg, Strasbourg 67, France.^{2b} Received August 19, 1966

Abstract: Temperature-dependent nmr spectra have been observed for compounds of the 2,3-diazabicyclo[2.2.1]-heptane and bicyclo[2.2.2]octane series. The activation parameters ΔF^\ddagger , ΔH^\ddagger , and ΔS^\ddagger have been calculated from the spectral data; they lie in the range of 11.8–13.9, 12.4–16.2 kcal/mole, and 2.8–11.5 eu, respectively. The nature of the rate process giving rise to the spectral changes is discussed. The data are best rationalized on the basis of a *consecutive inversion process at two nitrogens*. The shape of the potential curve and the origin of the inversion barrier are discussed. Solvent effects on the barrier height have been observed.

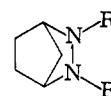
Of the different types of rate processes amenable to quantitative study by means of variable temperature nuclear magnetic resonance, nitrogen inversion is among the most fascinating for both physical and chemical reasons. Nitrogen inversion is usually very fast on the nmr time scale, but in certain compounds structural features may so slow down inversion that its effects are visible in the nmr spectrum. The first reported study was in the aziridine series,³ where ring strain leads to a high barrier to inversion. Temperature changes in the nmr spectrum of a sterically hindered benzoquinoline have been attributed to hindered nitrogen inversion.⁴ Recently, studies of an open-chain hydroxylamine ether⁵ and a perfluorohydroxylamine ether⁶ have provided further examples of hindered nitrogen inversion, which has also been observed in diazidine derivatives⁷ and in a fluorinated oxazetidine.⁸

In the course of an investigation of rate processes in nitrogen-containing heterocycles,^{1,9–11} we have become interested in the analogous bicyclic systems.¹¹

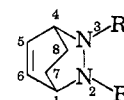
Several compounds of this type have been found to display temperature-dependent nmr spectra. We report here our studies of *double nitrogen inversions* in compounds of the 2,3-diazabicyclo[2.2.1]heptane and 2,3-diazabicyclo[2.2.2]octane series.



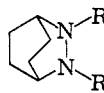
1, R = COOC₂H₅
2, R = CH₃
3, R = CD₃



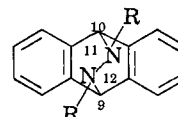
4, R = COOC₂H₅
5, R = CH₃
6, R = H



7, R = COOC₂H₅
8, R = CH₃



9, R = COOC₂H₅
10, R = CH₃



11, R = COOCH₃
12, R = CH₃

Results

Preparation of the Substrates. Diels–Alder addition of diethyl azodicarboxylate to cyclopentadiene¹² gives an adduct **1** which on reduction with lithium aluminum hydride (LAH) or lithium aluminum deuteride leads to *N,N'*-dimethyl-2,3-diazabicyclo[2.2.1]-5-heptene (**2**) or its *N,N'*-di(trideuteriomethyl) derivative **3**. Hydrogenation of adduct **1** produces the dihydro adduct¹³ **4** which by treatment with LAH gives *N,N'*-dimethyl-

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(2) (a) Salters' Co. Postdoctoral Research Fellow 1964–1966; (b) laboratory associated with the Centre National de la Recherche Scientifique.

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Table I. Variable-Temperature Nmr Spectra of Compounds 2, 3, 5, 6, 8, 10, 12^a

Compound	Temp, °C (solvent)	N-CH ₃	H-1, H-4	H-5, H-6	H-7 or H-7, H-8	H aromatic
2	57 (CDCl ₃)	2.45 (s, 6 H)	3.80 (m, 2 H)	6.40 (t, splitting 1.7 Hz, 2 H)	1.50 (d of t, 8.5, 1.2 Hz, 1 H) 2.10 (d of t, 8.5, 1.8 Hz, 1 H)	...
	-39 (CDCl ₃)	2.33 (s, 3 H) 2.60 (s, 3 H)	3.65 (m, 1 H) 4.05 (m, 1 H)	6.20 (q, 5.7, 1.7 Hz 1 H) 6.65 (oc, 5.7, 3.0, 1.4 Hz, 1 H)	1.55 (d of t) 2.15 (d of t)	...
	33 (pentane)	2.28 (s, 6 H)	3.60 (b m, 2 H)	6.20 (b s, 2 H)	<i>b</i>	...
	-46.5 (pentane)	1.13 (s, 3 H) 2.40 (s, 3 H)	3.40 (m, 1 H) 3.80 (m, 1 H)	6.0 (q, 5.7, 1.7 Hz 1 H) 6.45 (oc, 5.7, 3.0 1.4 Hz, 1 H)	<i>b</i>	...
3		Absent	Same as 2	Same as 2	Same as 2	...
5	33 (CDCl ₃)	2.40 (s, 6 H)	3.20 (b m, 2 H)	Complex multiplets from 1.2 to 2.2 ppm (6 H)		...
	-52 (CDCl ₃)	2.43 (s, 3 H) 2.52 (s, 3 H)	3.20 (s, 1 H) 3.50 (s, 1 H)	Complex multiplets from 1.2 to 2.35 ppm (6 H)		...
	25 (pentane)	2.25 (s, 6 H)	3.07 (b m, 2 H)	<i>b</i>	<i>b</i>	...
	-52 (pentane)	2.20 (s, 3 H) 2.30 (s, 3 H)	2.92 (b s, 1 H) 3.22 (b s, 1 H)	<i>b</i>	<i>b</i>	...
6	27 (CDCl ₃)	...	3.60 (s, 2 H)	Complex multiplets from 0.8 to 1.8 ppm		...
8	33 (CDCl ₃)	2.40 (s, 6 H)	3.30 (b m, 2 H)	6.45 (X ₂ part of A ₂ X ₂ , 2 H)	2.08-1.20 (b, A ₂ B ₂ , 4 H)	...
	-59 (CDCl ₃)	2.35 (s, 3 H) 2.60 (s, 3 H)	3.45 (b m, 2 H)	6.35 (q, 8.2, 5.4 Hz, 1 H) 6.80 (oc, 8.2, 6.8, 1.4 Hz, 1 H)	1.0-2.2 (vb m)	...
	25 (pentane)	2.25 (s, 6 H)	3.2 (b m, 2 H)	6.35 (X ₂ part of A ₂ X ₂ , 2 H)	<i>b</i>	...
	-57 (pentane)	2.12 (s, 3 H) 2.38 (s, 3 H)	3.22 (b m, 2 H)	6.20 (q, 8.2, 5.4 Hz, 1 H) 6.70 (oc, 8.2, 6.8, 1.4 Hz, 1 H)	<i>b</i>	...
10	27 (CDCl ₃)	2.48 (s, 6 H)	2.62 (b m, 2 H)	1.3-2.2 (broad multiplet of the A ₂ B ₂ type, 8 H)		...
	-55 (CDCl ₃)	2.55 (s, 6 H)	2.75 (b m, 2 H)	1.2-2.4 (broad multiplet different from multiplet at 27°, 8 H)		...
12	30 (CDCl ₃)	2.18 (s, 6 H)	4.63 (s, 2 H)	6.8-7.4 (complex m, 8 H)
	-50 (CDCl ₃)	2.22 (s, 6 H)	4.90 (s, 2 H)	7.1-7.7 (complex m differ- ent from m at 30°, 8 H)

^a Shifts are in ppm downfield from internal TMS. Coupling constants are in Hertz: s, singlet; d, doublet; t, triplet; q, quartet; oc, octet; m, multiplet; b, broad; v, very. ^b Hidden by solvent signals.

2,3-diazabicyclo[2.2.1]heptane (5).¹⁴ Alkaline hydrolysis of 4 leads to 2,3-diazabicyclo[2.2.1]heptane (6).¹³

Photochemical addition of diethyl azodicarboxylate to cyclohexadiene gives an adduct 7¹⁵ which on reduction with LAH gives N,N'-dimethyl-2,3-diazabicyclo[2.2.2]-5-octene (8). Catalytic hydrogenation of 7 leads to the dihydro adduct 9¹⁵ which on treatment with LAH gives N,N'-dimethyl-2,3-diazabicyclo[2.2.2]-octane (10).

Similarly the product 11¹⁶ from Diels-Alder addition of dimethyl azodicarboxylate to anthracene gives on reduction with LAH N,N'-dimethyl-9,10-dihydroanthracene-9,10-biimine (12).

Variable-Temperature Nmr Spectra. All compounds 1-12 show temperature-dependent nmr spectra. The spectra of the carbamates 1, 4, 7, 9, and 11 will be discussed separately as part of our studies of ring inversion

and hindered rotation in related systems.^{9,17} The main features of the nmr spectra of compounds 2, 3, 5, 6, 8, 10, and 12 at two temperatures (above and below the temperature range where kinetic effects are observed) are recorded in Table I. We will describe here the more prominent features of the spectral modifications observed as a function of temperature.

The nmr spectrum of 2 shows at 57° (Figure 1A) a singlet for the N-CH₃ groups, a multiplet for the bridgehead protons, and a triplet (XX' part of an AA'XX' spectrum) for the vinylic protons. The bridge methylene group shows the usual triplet AB pattern observed in norbornenes.^{18,19} At 32° these signals are broadened and fine structure is lost. At -39° the signals are again sharp (Figure 1B) and one observes two N-CH₃ signals of slightly different breadth (presumably due

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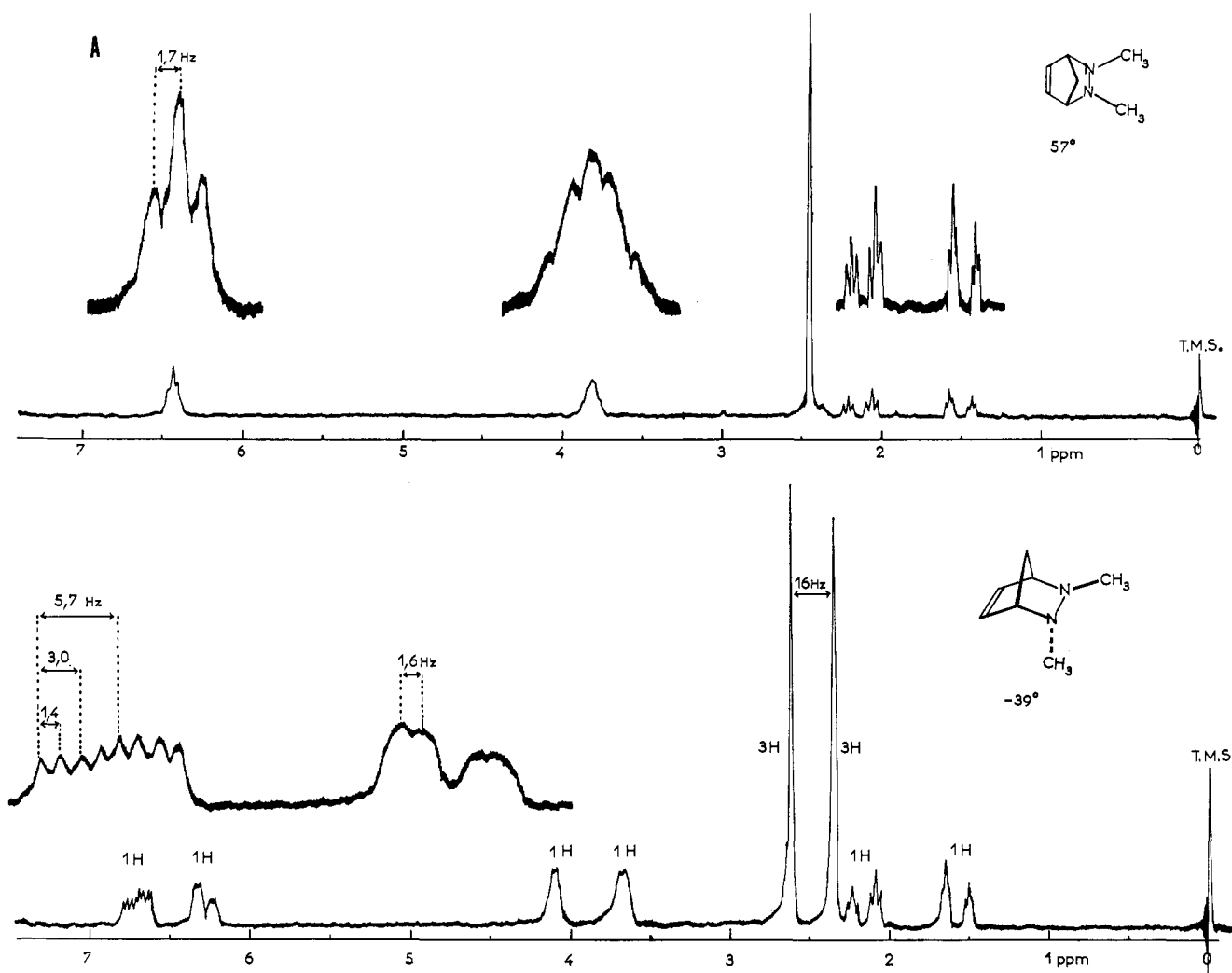


Figure 1. Nmr spectrum of compound 2 (A) at +57°, (B) at -39° in CDCl₃ at 60 MHz.

to different stereospecific long-range couplings) and of equal areas, *two* signals for the bridgehead protons, and an AB spectrum for the vinylic protons, whose A and B parts show different vicinal and allylic coupling constants to the bridgehead protons.²⁰ The signals of the bridge methylene group do not change appreciably. Compound 3 shows exactly the same spectra as 2 except that the N-CH₃ signals are absent and fine structure of the bridgehead protons is slightly better resolved. The spectrum of compound 5 contains only one signal for the N-CH₃ protons and one multiplet for the bridgehead protons at 32° and above. At -56° however two N-CH₃ signals are present as well as two multiplets for the bridgehead protons. The signal due to the bridgehead protons of compound 6 is appreciably broadened at -74° (the line width at half-height at 30° is 4 Hz and is 16 Hz at -74°; the TMS line width is about 0.5 Hz at both temperatures) but could not be split into two bands with the available equipment. The temperature dependence of the spectrum of compound 8 is similar to that observed for 2. At 62.5° one observes a singlet for the N-CH₃ groups, a multiplet for the bridgehead protons, an XX' part of an AA'XX' spectrum for the vinylic protons, and a complex pattern for the -CH₂-CH₂- bridge. At -59.5° the spectrum comprises an even more complex pat-

(20) This remarkable feature will be discussed in a forthcoming communication.

tern for the -CH₂-CH₂- bridge, two singlets for the N-CH₃ groups, a broad multiplet for the bridgehead protons, and an AB spectrum for the two vinylic protons, whose A and B parts again show different vicinal and allylic coupling constants with the bridgehead protons.²⁰ In the symmetrical molecule 10 important changes of the signals due to the -CH₂-CH₂- groups are observed as the temperature is lowered. However the N-CH₃ and bridgehead protons show each one band which remains unchanged at different temperatures. Similarly the spectrum of the bridged anthracene derivative 12 contains a singlet for the N-CH₃ protons and a singlet for the bridgehead protons, and both signals are independent of temperature. The aromatic protons however give a symmetrical multiplet of the A₂B₂ type at 32° which on lowering the temperature changes markedly and becomes unsymmetrical (presumably an ABCD spectrum), indicating that the molecule is undergoing a hindered rate process.

The variable temperature spectra of compounds 2, 5, and 8 have been measured in both deuteriochloroform and pentane. In pentane the high-temperature average signals occur at the mean position of the low-temperature pairs of signals; this is not so in CDCl₃ because of temperature-dependent solvent effects.

Activation Parameters. From the temperature-dependent spectra obtained for compounds 2, 3, 5, and 8 the activation parameters of the rate process involved

Table II. Spectral Parameters and ΔF_c^* Values^a

	Solvent	Compound			
		2	3	5	8
$\Delta\nu$, Hz	CDCl ₃	15.6	24.6	5.7	14.6
	Pentane	16.0	...	6.3	14.9
T_c , °C	CDCl ₃	+15.5	+22	-19	-27
	Pentane	+8	...	-26	-37.5
ΔF_c^* , ^b kcal/mole	CDCl ₃	14.5	14.5	13.2	12.3
	Pentane	14.1	...	12.8	11.8

^a Refers to N-CH₃ signals, except for 3, which refers to bridgehead signals. ^b Calculated using eq 2. Estimated accuracy ± 0.2 kcal/mole.

line shapes of the N-CH₃ signals as a function of temperature (see Experimental Section for details of the determination of k). Figure 2 shows the plots $\log(k/T) = f(1/T)$ for the pentane solutions of compounds 2, 5, and 8. The calculated activation parameters ΔH^* , ΔS^* , and ΔF_T^* (ΔF^* at temperature T , °K) are listed in Table III for both pentane and deuteriochloroform solutions. Compound 3 presents no suitable signal for line-width measurements. The same is true for compounds 10 and 12 for which only a *very* rough value of ΔF_c^* can be calculated. For 10 T_c , $\sim -30^\circ$ and $\Delta F_c^* \sim 12$ kcal/mole; for 12 $T_c \sim +5^\circ$ and $\Delta F_c^* \sim 14$

Table III. Activation Parameters from Line-Shape Measurements

	Solvent	Compound		
		2	5	8
ΔH^* , ^a kcal/mole	CDCl ₃	16.9 \pm 0.6	14.8 \pm 0.5	14.9 \pm 0.8
	Pentane	16.2 \pm 0.8	15.7 \pm 1.0	12.4 \pm 0.6
ΔS^* , ^a eu	CDCl ₃	+8.3 \pm 2.1	+6.0 \pm 2.0	+10 \pm 3.0
	Pentane	+7.6 \pm 2.6	+11.5 \pm 4.0	+2.8 \pm 2.5
ΔF_T^* , ^b kcal/mole	CDCl ₃	14.5 \pm 0.2	13.0 \pm 0.2	12.2 \pm 0.2
	Pentane	13.9 \pm 0.2	12.6 \pm 0.4	11.8 \pm 0.3

^a Values obtained from the plot of Figure 2 and from eq 3. ^b These values are obtained directly from the line shapes at temperature $T = 264^\circ\text{K}$ (CDCl₃) and $T = 268^\circ\text{K}$ (pentane) using eq 2.

may be calculated.²¹⁻²³ However, knowledge of the nature of this process and of the shape of the potential barrier is necessary. From the discussion given below it follows that the present rate process is best described as a case of exchange between two sites A and B with equal populations and lifetimes $\tau_A = \tau_B = 2\tau$.

From the Eyring rate equation the rate constant k is

$$k = \frac{1}{\tau_A} = \frac{1}{2\tau} = \frac{kfT}{h} e^{-\Delta F^*/RT} \quad (1)$$

Incorporating a transmission coefficient $f = 1/2$ (see discussion below), eq 1 can be rewritten as

$$\Delta F^* = 4.57T[10.02 + \log T/k] \quad (2)$$

At the coalescence temperature one has $T_c = \sqrt{2}/2\pi\Delta\nu$, where $\Delta\nu = \nu_A - \nu_B$ is the separation of the lines A and B when the rate process is slow. From the coalescence temperature, T_c , of the N-CH₃ signals and from the corresponding $\Delta\nu$ value the free energy of activation at coalescence temperature ΔF_c^* may be obtained. In the case of the deuterated compound 3 the calculations are based on the coalescence and $\Delta\nu$ value of the bridgehead proton signals. These are in fact the same as for compound 2. The calculations are more approximate in the case of 3, as the bridgehead protons are coupled to other protons in the molecule (Table II lists the values of $\Delta\nu$, T_c , and ΔF^* for compounds 2, 3, 5, and 8).

Equation 1 may be rewritten as

$$\log(k/T) = 10.02 + \Delta S^*/R - \Delta H^*/RT \quad (3)$$

Plotting $\log(k/T)$ against $1/T$ yields a straight line from which the activation enthalpy ΔH^* and the activation entropy ΔS^* may be calculated. k is obtained from the

(21) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution N.M.R.," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.

(22) L. W. Reewes, *Advan. Phys. Org. Chem.*, **3**, 18 (1965).

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kcal/mole. These values have been obtained from the temperature of maximum broadening of complex multiplets assuming, arbitrarily, a $\Delta\nu$ value of 20 Hz. For compound 6 an *upper* limit to ΔF_c^* of 10 kcal/mole is obtained, assuming $\Delta\nu$ for the bridgehead protons is approximately the same as in the case of compound 5 and taking $T_c \leq -74^\circ$. These values for 6, 10, and 12 are for solutions in CDCl₃.

Discussion

Nature of the Rate Process. In the present discussion we will use compound 2 as an example. The conclusions may be extended to the other compounds 3, 5, 6, 8, 10, and 12.

The changes in the variable-temperature nmr spectra of 2 described above (see also Figure 1) show that at 57° the species observed has, in effect, a plane of symmetry, whereas at -39° this symmetry element is lost. Possible conformational changes in the present system are rotation about the N-CH₃ bond and nitrogen inversion. Rotation about the N-CH₃ bonds is expected to have a very low hindering potential²⁴ and slow rotation would not explain the observed changes. Nitrogen inversion however may have a much higher potential barrier.³⁻⁸

Furthermore the observed spectral modifications require that: (i) the different types of protons in the molecule (except the bridge methylene group) exchange between two different sites of equal populations (as shown by integration at -39° ; see Table I), (ii) these two different sites are within the same molecule. This is what is expected for a rate process of the type $13 \rightleftharpoons 14$. When the interconversion is fast, the nmr spectrum observed is an average spectrum of the equilibrating

(24) The potential barrier to rotation about the C-CH₃ bond in neopentane is 4.8 kcal/mole and is the highest barrier found for a process of this type.²⁵

(25) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, Inc., New York, N. Y., 1965.

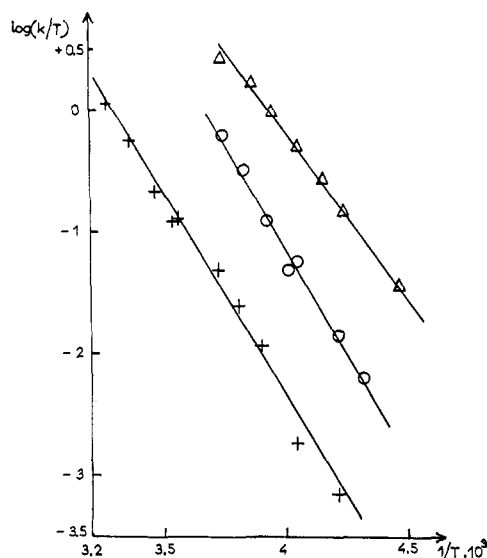
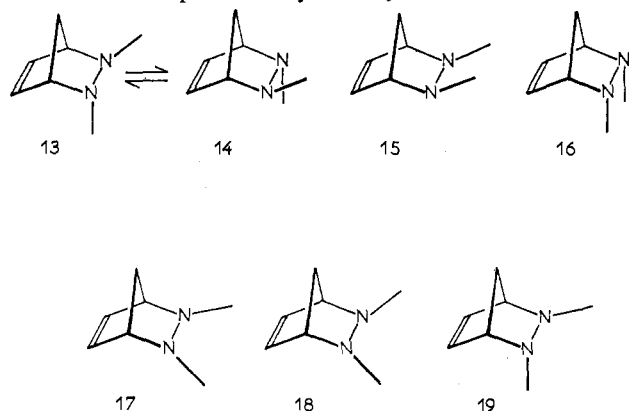


Figure 2. Plots of $\log(k/T) = f(1/T)$ for compounds **2** (+), **5** (O), and **8** (Δ) in pentane solution.

species **13** \rightleftharpoons **14**, and the molecule in effect has a plane of symmetry. On the other hand, in the case of slow interconversion one observes the superimposed identical spectra of the two optical antipodes **13** and **14**, which do not have a plane of symmetry. Forms **15** and **16**



are expected to have higher energies than **13** and **14** by at least 3 kcal/mole because of the presence of eclipsed methyl groups.^{25,26} That no measurable amount of these forms **15** and **16** is present is shown by the absence of any N-CH₃ signal in the low-temperature spectrum of **2** (see Figure 1) other than those two described. Furthermore one observes only one signal for N-CH₃ in the symmetrical bicyclooctane **10** and bridged anthracene **12** compounds at low temperatures, where changes in the spectrum of other protons in the molecule indicate that the rate process is slow.²⁸ The rate process observed in the present systems is therefore best described as a *synchronous inversion of the two nitrogens* interconverting forms **13** and **14**. By this we mean that for the interconversion to occur, the two nitrogens must undergo inversion in some synchronized or correlated fashion.

(26) Nonbonded interactions involving lone pairs of nitrogen may also be present, but their effects are difficult to estimate due to uncertainties about the "size" of the nitrogen lone pairs.^{26,27}

(27) N. L. Allinger, J. G. D. Carpenter, and F. M. Karkowski, *J. Am. Chem. Soc.*, **87**, 1232 (1965).

(28) It might be argued that the signals from forms of type **15** and **16** are hidden under those of **13** and **14**. However it is unlikely that this would be true for *all* signals in *all* compounds studied.

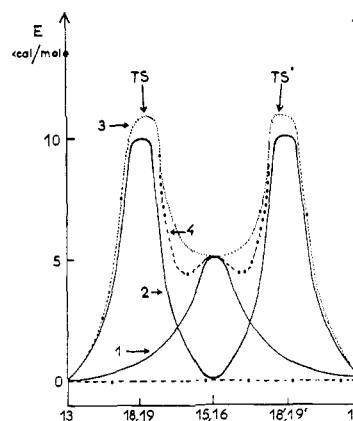


Figure 3. Schematic potential curves for consecutive double nitrogen inversion: **13** \rightleftharpoons **14**, **18'**, **19'**, and **TS'** are the mirror images of forms **18**, **19**, and of the transition state **TS**. The energy scale merely indicates an order of magnitude (see text).

Mechanism of the Interconversion. The interconversion **13** \rightleftharpoons **14** may proceed through different transition states. We shall discuss the two extreme paths by which this process might occur, considering again compound **2**.

Clearly the highest energy conformation **17** of the system is reached when both nitrogen sites are planar and the N-CH₃ groups eclipsed; this corresponds to a *simultaneous inversion* at the two nitrogen atoms.

However the configurations at the two nitrogen atoms might also invert one after the other. This is a *consecutive inversion* process. In this case the shape of the potential barrier and the transition state are difficult to define. They depend on two energy terms essentially: a term E_{nb} arising from nonbonded interactions (of which methyl-methyl interaction is the dominant) and a term E_i due to a nitrogen inversion process. E_{nb} is maximum for the bipyramidal forms **15** and **16** (which do not have the same energy) and minimum for **13** and **14**. E_i is maximum for the "half-planar" forms **18** and **19** (where one nitrogen site is planar) and minimum for the forms **13**, **14**, **15**, and **16** (where both nitrogens are pyramidal). The contribution of E_i should be at least as great as the inversion barrier of trimethylamine, *i.e.*, *ca.* 10 kcal/mole²⁹ (neglecting ring strain and reduced mass effects). On the other hand, E_{nb} should not increase by more than *ca.* 5 kcal/mole (eclipsed methyl-methyl interaction + various methyl-hydrogen interactions²⁵) on going from **13** (or **14**) to **15** (or **16**). Taking then forms **13** and **14** as the origin of energy, a schematic diagram, which *grossly* represents the variations of E_{nb} and E_i as consecutive inversion proceeds, may be drawn as given in Figure 3 (curve 1 for E_{nb} ; curve 2 for E_i). Depending on the exact shape of the potential curves 1 and 2, the resulting total potential curve may be represented by either curve 3 or 4 in Figure 3. On this basis, the transition state, **TS**, might be considered as resembling the "half-planar" forms **18** or **19**.

In any case, the transition state **17** for simultaneous inversion which incorporates *two* planar nitrogens and eclipsed methyl groups is of higher energy than any

(29) J. F. Kincaid and F. C. Henriques, Jr., *J. Am. Chem. Soc.*, **82**, 1471 (1960). These authors calculated a value of 15 kcal/mole for the inversion barrier of trimethylamine, but this value is presumably too high.^{3a}

possible transition state for consecutive inversion where at least *one* nitrogen is pyramidal. One might estimate the corresponding energy difference to be at least as great as the inversion barrier of trimethylamine, *i.e.*, *ca.* 10 kcal/mole²⁹ (neglecting nonbonded interactions and strain effects which can only further disfavor 17). Consequently, one may consider the rate process described here as a *consecutive inversion process at two nitrogens*, along a path resembling the potential curves 3 or 4 in Figure 3.

Furthermore, in such a case of a minimum in between two identical transition states, the transmission coefficient, f , in eq 1-3 should be taken as equal to $1/2$.³⁰ Accordingly, the ΔF^* and ΔS^* values of Tables II and III have been calculated using $f = 1/2$. The widely used value $f = 1^{22,23}$ would lead to values of ΔF^* greater by *ca.* 0.4 kcal/mole and to values of ΔS^* smaller by *ca.* 1.4 eu than those given in Tables II and III.

Inversion through nitrogen tunneling should also be considered. The rate of tunneling is faster the "lower" and the "thinner" the potential barrier. For aziridines the tunneling effect is thought to be negligible, the barrier to inversion being high.^{3,29,31} In the present case the activation energies obtained are quite high compared to ammonia.^{3,29} Furthermore the potential barrier is much "thicker" than in ammonia and in amines, as *both* nitrogens have to invert for interconversion $13 \rightleftharpoons 14$ to be realized. In addition the tunneling rate decreases exponentially with the mass of the substituents on the nitrogen, which is here very high. Thus increase of the rate of interconversion through tunneling should be negligible and the measured rates should then be close to the rates for going over the barrier.

Origin of the Potential Barrier. The activation enthalpies ΔH^* given in Table III may be considered as being approximately equal to the potential barriers ΔE^* .^{30,32,33}

The values of ΔH^* and of ΔS^* are however much less accurate than the ΔF^* values.³⁴ In the present series of closely related systems the activation entropies ΔS^* should be quite similar, so that it is more meaningful to compare the ΔF^* values (at the same temperature) than the ΔH^* values obtained for the different compounds.³⁴ Essentially three types of intramolecular factors are expected to influence the barrier height: nonbonded interactions, strain effects, and reduced-mass effects.

Smaller nonbonded interactions in the transition state and a smaller reduced mass lead to an appreciable decrease of the activation energy in compound 6 ($\Delta F^* \leq 10$ kcal/mole) as compared to compound 2 ($\Delta F^* = 14.5$ kcal/mole). In the bicycloheptane derivative 5,

endo-CH₃-endo-H-1,3 interactions are expected to raise the energy of the ground state more than the energy of the transition state and lower the barrier to inversion with respect to 2, as is observed ($\delta\Delta F^* = 1.3$ kcal/mole).

As estimated from CH₃-H distances on molecular models, the nonbonded CH₃-H interactions in 8 are presumably weaker than in 5 and stronger than in 2 in the ground state. Assuming that in the transition state these interactions do not differ vastly for 2, 5, and 8, the decrease in strain on going from the bicycloheptane to the bicyclooctane series is reflected in a decrease of 0.8-2.1 kcal/mole in the activation energy for nitrogen inversion (see ΔF^* values of Table III). We then may estimate the height of the potential barrier to nitrogen inversion in compound 2 from the contributions of the different terms. The trimethylamine nitrogen inversion barrier (*ca.* 10 kcal/mole²⁹) corrected for reduced mass effects²⁹ (*ca.* 10%) gives a contribution of 11 kcal/mole. Adding to this 1-2 kcal/mole for nonbonded interactions in the transition state (see diagram of Figure 3) and 1-2 kcal/mole strain effects, a barrier of *ca.* 13-15 kcal/mole is obtained.

Replacing CH₃ by CD₃ in compound 2 does not lead to any noticeable isotope effect (see compound 2 and 3 in Table II). This is not unexpected since isotope effects on activation energies are often very small, as shown by the change $\delta\Delta F^*$ of *ca.* 0.1 kcal/mole observed in the racemization of bridged biphenyls, when the two interacting CH₃ groups are replaced by CD₃ groups.³⁵ Such small effects are within the experimental error of the nmr method (see Experimental Section).

Solvent Effects. Hydrogen bonding to the lone pair of nitrogen substantially decreases the rate of nitrogen inversion in the aziridines^{3b} by stabilization of the ground state. In the present case, the ΔF^* values for pentane solutions are about 0.5 kcal/mole lower than those for solutions in deuteriochloroform, which may form weak hydrogen bonds to the nitrogen lone pair. Because of the temperature dependence of such solvent effects the results for pentane solutions are considered to be more accurate. Furthermore, a solution of compound 2 in deuterium oxide displays at 27° a spectrum similar to the low-temperature spectrum of 2 in CDCl₃ (Figure 1B). The coalescence temperature is +47°, giving $\Delta F_c^* = 16.1 \pm 0.2$ kcal/mole (with $\Delta\nu(\text{N-CH}_3) = 15.5$ Hz). This value is 2.3 kcal/mole higher than that found in pentane solution ($\Delta F_{17^\circ}^* = 13.8$ kcal/mole), showing an appreciable ground-state stabilization in D₂O solution.

Experimental Section

Melting points were obtained on a Koffler block and are uncorrected. Infrared spectra were measured with a Beckman IR-5A spectrometer and ultraviolet spectra with a Beckman DK-2 spectrometer. Only characteristic features of these spectra will be described. Refractive indices were measured with an Abbe refractometer. Analyses were performed at the Strasbourg Division of the microanalytical laboratory of the Centre National de la Recherche Scientifique.

Nmr Spectra. Nmr spectra were measured with a Varian A-60 spectrometer equipped with the variable-temperature accessory. The temperatures were measured by means of the Varian methanol and glycol samples and shift-temperature correlation charts:

(30) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p 207.

(31) W. M. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **42**, 2253 (1965).

(32) ΔH^* is neither equal to ΔE^* nor to the Arrhenius activation energy E_a . The relations between these quantities are

$$E_a = \Delta H^* + RT$$

$$\Delta H^* = \Delta E^* + RT^2[d \ln (f^*/f_i)/dT]$$

where f^* and f_i are the partition functions for the transition state and for the ground state, respectively. The variation of the logarithm of the partition function ratio with temperature is presumably very small.³³

(33) R. Daudel, R. Lefèbre, and C. Moser "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 11.

(34) A. Allerhand, F. M. Chen, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3040 (1965).

(35) K. Mislow, R. Graev, A. J. Gordon, and G. H. Wahl Jr., *J. Am. Chem. Soc.*, **86**, 1733 (1964).

their absolute values are correct to within $\pm 2^\circ$. However within a series of measurements temperature differences of 0.5° are significant. Spectra calibration was effected at every temperature with a Hewlett-Packard 200CD wide-range oscillator and a Hewlett-Packard 5212A frequency counter. During the recording of the spectra a low enough radiofrequency field was used so as to avoid differential saturation effects especially at low temperatures. The products were distilled from sodium and the samples (concentration *ca.* 0.5 M in CDCl_3 or pentane) were stored in the cold over molecular sieves (3 A); the N-Me amines are quite hygroscopic and the rate of inversion is sensitive to traces of water. The solutions remained liquid down to -75° .

Chemical shifts are in ppm downfield from internal tetramethylsilane (TMS). Coupling constants are in Hertz (Hz).

Determination of the Rate Constants. Above the coalescence temperature the line width, W , of the N- CH_3 signal (except in the case of compound **3**; see text) was measured; W was then corrected: (1) for "natural" line width by subtracting from it W_0 , the line width of the TMS signal at the same temperature; (2) for other non-exchange broadening W_n (unresolved long-range coupling^{36,37}). W_n is taken as the difference between the N- CH_3 line width and the TMS line width at temperatures where exchange is very fast. The rate constant k is calculated from the equation

$$k = \frac{\pi (\Delta\nu)^2}{2B} \quad (\text{i})$$

where the exchange broadening $B = W - W_0 - W_n$ (this is a modified form of eq 10.22 in ref 21).

Below the coalescence temperature line widths of both N- CH_3 signals were measured when these signals did not overlap. k was calculated from

$$k = \pi B \quad (\text{ii})$$

(see eq 10.17 in ref 21). The different terms of B were obtained as in the case of the high-temperature spectra. Now, W_n is the difference in line width between the N- CH_3 signals and the TMS signal at very slow exchange rates. The values of W_n for the two N- CH_3 signals are different (see text and Figure 1B). In the case of **2** in CDCl_3 (though not in pentane) where it was clear that $\Delta\nu$ of the N- CH_3 signals changed with temperature, allowance was made for this by extrapolating $\Delta\nu = f(T)$. The values of k obtained from eq i and ii were used for plotting $\log(k/T) = f(1/T)$ (see Figure 2). From this plot and from eq 3 ΔH^* and ΔS^* values were calculated (Table III). For a valid comparison, values of ΔF^* for **2**, **5**, and **8** at 264°K (in CDCl_3) and 268°K (in pentane) were obtained using eq 2 and values of k measured at these temperatures (Table III). Errors in the determination of ΔH^* and ΔS^* were estimated by drawing lines of maximum and minimum slope containing in between them all the experimental points. The values ΔH^* and ΔS^* quoted are the means of the values obtained from these lines, and the error quoted is half the difference between them. The error in ΔF^* is obtained from the errors in $T(\pm 2^\circ)$ and in k (generally less than 15% as estimated from reproducibility of line widths).³⁸

2,3-Diazabicyclo[2.2.1]-5-heptene-2,3-dicarboxylic acid-diethyl ester (1) was prepared according to the literature;¹² bp 120° (0.55 mm) [lit.¹² bp 123.5° (0.75 mm)]. It showed an infrared spectrum (CCl_4): $\nu(\text{C}=\text{O})$ 1710 (s) and 1750 (s) cm^{-1} .

2,3-Diazabicyclo[2.2.1]heptane-2,3-dicarboxylic Acid Diethyl Ester (4). A solution of **1** (5 g) in methanol (50 ml) is shaken under hydrogen (3 atm) in the presence of 5% palladium on car-

bon, for 12 hr at room temperature. The catalyst is filtered off, and the solvent is evaporated. The residue is distilled under reduced pressure. Compound **4** distills at $139\text{--}141^\circ$ (1 mm) (4.3 g; 85%) (lit.¹³ bp 131° [0.4 mm]).

2,3-Diazabicyclo[2.2.2]-5-octene-2,3-dicarboxylic acid diethyl ester (7) was prepared according to the method of Askani¹⁵ and had the following properties: bp $138\text{--}139^\circ$ (0.35 mm) (lit.¹⁵ bp $111\text{--}112^\circ$ [0.05 mm]); infrared spectrum (CCl_4), $\nu(\text{C}=\text{O})$ 1705 (s) and 1750 (s) cm^{-1} .

2,3-Diazabicyclo[2.2.2]octane-2,3-dicarboxylic acid diethyl ester (9) was prepared according to the method of Askani,¹⁵ and it showed bp 125° (0.28 mm) (lit.¹⁵ bp 103° [0.01 mm]).

9,10-Dihydroanthracene-9,10-bisimino-11,12-dicarboxylic acid dimethyl ester (11) was prepared according to the literature,¹⁸ mp $191.5\text{--}192.5^\circ$ (lit.¹⁶ mp 192°).

N,N'-Dimethyl-2,3-diazabicyclo[2.2.1]-5-heptene (2) was prepared according to the general method of Snyder and Michels¹⁴ by reduction of adduct **1** with LAH. The product was distilled from sodium and stored in the cold over molecular sieves, yield 70%; bp 84° (100 mm), n_{D}^{25} 1.4740. *Anal.* Calcd for $\text{C}_7\text{H}_{12}\text{N}_2$: C, 67.70; H, 9.74; N, 22.56. Found: C, 67.77; H, 9.90; N, 22.43. The infrared spectrum (CCl_4) showed: 3050 (w), 2980 (s), 2950 (s), 2850 (s), 2750 (w), 1460 (m), 1330 (m), 1030 (m), 910 (m), 890 (s), and 870 (m) cm^{-1} . The ultraviolet spectrum (cyclohexane) showed: λ_{max} 267 $\text{m}\mu$ (ϵ 680). The origin of this band will be discussed in a forthcoming communication.²⁰

The N,N'-di(trideuteriomethyl) compound **3** was prepared from **1** in the same way as **2** using lithium aluminum deuteride, yield 62%. It contained over 98% deuterium (d_6) in the N- CD_3 groups as judged from the nmr spectrum; n_{D}^{20} 1.4713. The infrared spectrum (CCl_4) shows two different CD_3 parallel bands at 2200 and 2050 cm^{-1} .

N,N'-Dimethyl-2,3-diazabicyclo[2.2.1]heptane (5) was prepared from **4** according to the literature¹⁴ and showed: bp $48\text{--}49^\circ$ (29 mm) (lit.¹⁴ bp $45\text{--}45.5^\circ$ [24 mm]); n_{D}^{25} 1.46518 (lit.¹⁴ n_{D}^{25} 1.46518).

N,N'-Dimethyl-2,3-diazabicyclo[2.2.2]-5-octene (8) was prepared from adduct **7** according to the literature method.¹⁴ The product was distilled from sodium and stored in the cold over molecular sieves, yield 52%; bp 97° (75 mm); n_{D}^{25} 1.4862. *Anal.* Calcd for $\text{C}_8\text{H}_{14}\text{N}_2$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.37; H, 10.35; N, 20.25. The infrared spectrum (CCl_4) showed: 3050 (w), 2950 (s), 2850 (s), 2750 (w), 1550 (m), 970 (s), 895 (s), and 850 (m) cm^{-1} . The ultraviolet spectrum (cyclohexane) showed an inflection point at 270 $\text{m}\mu$.

N,N'-Dimethyl-2,3-diazabicyclo[2.2.2]octane (10) was prepared from compound **9** the same way as **8**,¹⁴ distilled from sodium, and stored in the cold over molecular sieves, yield 77%; bp 102° (70 mm); n_{D}^{25} 1.4791. *Anal.* Calcd for $\text{C}_8\text{H}_{16}\text{N}_2$: C, 68.52; H, 11.50; N, 19.98. Found: C, 68.44; H, 11.62; N, 19.93.

N,N'-Dimethyl-9,10-dihydroanthracene-9,10-bisimino (12) was prepared from compound **11** the same way as compound **8**,¹⁴ yield 45%. Compound **12** sublimed at 60° (bath temperature) under 1-mm pressure, mp $81\text{--}82^\circ$. *Anal.* Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2$: C, 81.32; H, 6.83; N, 11.86. Found: C, 81.42; H, 6.77; N, 12.36.

2,3-Diazabicyclo[2.2.1]heptane (6) was prepared according to the literature.^{13,39} The product was sublimed (60° [20 mm]) giving a white solid. It is very rapidly oxidized on contact with air and is highly hygroscopic; no accurate melting point was obtained. The product was merely characterized by its nmr spectrum. The nmr measurements were done on a sample containing $\sim 20\%$ of the oxidation product. The results for this compound should therefore be treated with reserve.

(36) J. E. Anderson and J. C. D. Brand, *Trans. Faraday Soc.*, **62**, 39 (1966).

(37) H. G. Schmid, H. Friebolin, S. Kabuss, and R. Mecke, *Spectrochim. Acta*, **22**, 623 (1966).

(38) For a detailed discussion see A. Allerhand, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Am. Chem. Soc.*, **88**, 3185 (1966).

(39) J. Pirsch and J. Jörgl, *Ber.*, **68B**, 1324 (1935).