$>\mathrm{CHC}H_3$), 1.80 (d, $J = 7.0$ Hz, 3 H, $=\mathrm{CHC}H_3$), 1.99 and 2.15 (s, 3 H each, $=\mathrm{C(C}H_3)_2$), 4.91 (q, $J = 6.5$ Hz, 1 H, $>\mathrm{C}H\mathrm{CH_3}$), 5.77 (q, $J = 7.0$ Hz, 1 H, $=\mathrm{C}H\mathrm{CH_3}$), and 7.32 (m, 5 H, aromatic H).

2:1 Adduct 21 (derived as a mixture with **20**): nmr ($CDCl_3$) δ 1.50 (d, $J = 6.4$ Hz, 3 H, $>\mathrm{CHC}H_3$), 1.63 (d, $J = 6.4$ Hz, 3 H, $=\mathrm{CHC}H_3$), 1.92 and 2.11 (s, 3 H each, $=\mathrm{C(C}H_3)_2$), 4.64 (q, $J = 6.4$ Hz, 1 H, $>\mathrm{C}H\mathrm{CH_3}$), 5.07 (q, $J = 6.4$, 1 H, $=\mathrm{C}H\mathrm{CH_3}$), and 7.40 (m, 5 H, aromatic H).

2,2,3-Trimethylisobutenylidenecyclopropane (22) with PTAD. Adduct 23: mp 127–128° (ether); nmr ($CDCl_3$) 1.60 (s, 6 H), $>\mathrm{C(C}H_3)_2$), 1.70 (d, $J = 7.0$ Hz, 3 H, $=\mathrm{CHC}H_3$), 1.88 and 2.17 (s, 3 H each, $=\mathrm{C(C}H_3)_2$), 5.55 (q, $J = 7.0$ Hz, 1 H, $=\mathrm{C}H\mathrm{CH_3}$), and 7.35 (m, 5 H, aromatic H); mass spectrum *m/e* calcd for $C_{18}H_{21}N_3O_2$ 311.164, found 311.165.

Adduct 24: nmr ($CDCl_3$) δ 1.38 (d, $J = 6.7$ Hz, 3 H, $>\mathrm{CHC}H_3$), 1.75 (s, 3 H, $-\mathrm{C}H_3$), 1.80 (s, 6 H, 2 $-CH_3$'s), 2.13 (s, 3 H, "outside" methyl of $=\mathrm{C(CH_3)_2}$), 4.85 (q, $J = 6.7$ Hz, 1 H, $>\mathrm{C}H\mathrm{CH_3}$), and 7.35 (m, 5 H, aromatic H).

2:1 Adduct 25: 249–250° dec (ethyl acetate); nmr ($CDCl_3$) δ 1.47 (d, $J = 6.2$ Hz, 3 H, $>\mathrm{CHC}H_3$), 1.79 (s, 9 H, 3 $-CH_3$'s), 2.20 (s, 3 H, $-\mathrm{CC}H_3$), 4.69 (q, $J = 6.2$, 1 H, $>\mathrm{CHC}H_3$), and 7.40 (m, 10 H, aromatic H); mass spectrum *m/e* calcd for $C_{26}H_{26}N_6O_4$ 486.21, found 486.19.

2,2,3,3-Tetramethylisobutenylidenecyclopropane (26) with PTAD. Adduct 27: mp 184–185° (ether); uv max (95% ethanol)222 nm (log ϵ 4.31) and 255 (3.77); nmr ($CDCl_3$) δ 1.76 (s, 12 H, 4 $-\mathrm{C}H_3$'s), 1.87 (s, 3 H, $-CH_3$), and 2.13 (s, 3 H, "outside" methyl of $=\mathrm{C(CH_3)_2}$); mass spectrum *m/e* calcd for $C_{19}H_{23}N_3O_2$ 325.179, found 325.178.

Conformational Interchange in Acyclic Hydrazines[1,2]

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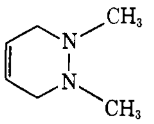
Abstract: Conformational isomerization in some acyclic hydrazines has been studied by dynamic nmr spectroscopy. The barriers to nitrogen inversion in 1,1-dibenzylhydrazine and tetrabenzylhydrazine are ($\Delta G^{\ddagger}$) 8.0 kcal/mol at −105°. Larger barriers in hydrazines with *E* substituents are attributed to hindered rotation about the NN bond. Barriers to rotation about CN bonds were observed in acetylhydrazines and picrylhydrazines.

The conformational stereochemistry of hydrazines and the barriers in them to inversion of nitrogen and rotation about the NN bond have recently attracted considerable interest.[4,5] Studies by microwave spectroscopy and electron diffraction of hydrazine[6] and some substituted hydrazines[7] have shown that the preferred configuration is one with the nitrogen lone pairs gauche to one another, and the barriers to inversion of nitrogen in tetrafluorohydrazine[8] and in cyclic hydrazines such as *N*,*N*-dimethyltetrahydropyrazine (**1**) and *N*-aminoaziridine[9] (**2**) have recently been measured. The barriers in **1** and **2** are considerably larger than those in the corresponding amines, piperidine[10] and aziridine,[11,12] a result which seems to throw doubt on the claim[6] that the barrier in hydrazine itself is much less than that in ammonia or methylamine.



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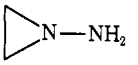

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When we began the present investigation, no barriers to nitrogen inversion seemed to have been measured by nmr spectroscopy in acyclic hydrazines. Griffith and Roberts[13] had found that the nmr spectrum of 1-benzyl-1,2,2-trimethylhydrazine remained unchanged down to −80°, implying that nitrogen inversion was still fast on the nmr time scale at this temperature.[14]

Several groups of workers[15] had shown that large NN rotational barriers exist in some di- and tetraacylhydrazines, but no barriers had been measured in other types of hydrazines.

Recent work has shown that the barriers to rotation about σ bonds connecting atoms of group V or VI elements with lone pairs of electrons can be quite large and amenable to study by the nmr method. Compounds of this type where torsional barriers have been measured include the N–S bond in sulfenamides[16] and

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sulfinamides,[17] the N–O bond in hydroxylamines,[18] the N–P bond in aminophosphines,[19] the N–As bond in aminoarsines [19e,20] and the N–Sb bond in aminostibines.[20]

Our object here was to study the preferred conformations of some simple acyclic hydrazines and to see if the rates of nitrogen inversion and NN rotation were slow enough to be measured by the dynamic nmr method.[21] Since our preliminary account[2] of this work was submitted, NN rotational barriers have been measured for some tetraalkyl and alkyl–aryl hydrazines[22] and N-silylated hydrazines.[23]

Experimental Section

Elemental analyses were carried out by Galbraith Laboratories. Melting points were determined using a Thomas–Hoover apparatus.

Materials. Trichlorofluoromethane (Freon 11) and dichlorofluoromethane (Genetron 21) were obtained from Matheson and had purities of 99.9 and 99.0%, respectively. 1,1-Dibenzyl-2-(2,4,6-trinitrophenyl)hydrazine (**3b**) (mp 174–175°, lit.[24] 176°), 2-benzoyl-1,1-dibenzylhydrazine (**3e**) (mp 167–168°, lit.[25] 166–168°), and 1,1-dibenzyl-2-(*p*-toluenesulfonyl)hydrazine (**3g**) (mp 123–124°, lit.[26] 124°) were prepared by literature procedures.[24–27]

1,1-Dibenzylhydrazine (3i). The procedure of Biel, *et al.*,[28] was improved by the following modifications. A solution of benzyl chloride (120 g, 0.97 mol) in methanol (500 ml) was slowly added (3 hr) to a stirred refluxing solution of 95–100% hydrazine hydrate (100 g, 2.0 mol) and water (10 ml) in methanol (1 l.). The solution was refluxed for a further 3 hr and then allowed to stand overnight. The precipitated needles of hydrazine hydrochloride were filtered off and the filtrate was concentrated, diluted with ether, and washed twice with water (to remove water soluble hydrazine and monobenzylhydrazine). The dried ($MgSO_4$) ether layer was concentrated and the residue was distilled *in vacuo* to afford dibenzylhydrazine (37 g, 35%), bp 128–130° (0.5 mm), as an oil which solidified in the receiver. Recrystallization from pentane gave colorless crystals of pure dibenzylhydrazine, mp 56–57° (lit.[28] 55°).

1,1-Dibenzyl-2-(2,4-dinitrophenyl)hydrazine (3a). A mixture of 2,4-dinitrofluorobenzene (0.75 g), 1,1-dibenzylhydrazine (0.85 g), and sodium bicarbonate (0.7 g) was heated for 2 hr in boiling ethanol (15 ml). The filtered solution deposited yellow crystals on standing, which after recrystallization from chloroform–carbon tetrachloride had mp 160.5–161.5° (1 g, 65%).

Anal. Calcd for $C_{20}H_{18}N_4O_4$: C, 63.49; H, 4.79; N, 14.81. Found: C, 63.64; H, 4.59; N, 15.05.

1,1-Dibenzyl-2-(2-pyrimidyl)hydrazine (3c). A mixture of 2-chloropyrimidine (0.46 g), 1,1-dibenzylhydrazine (0.85 g), and sodium bicarbonate (0.7 g) was heated with stirring in boiling diethylene glycol dimethyl ether (2 ml) for 3 hr. The cooled mixture was diluted with benzene, washed four times with water to remove the ether, and dried ($MgSO_4$). The benzene was removed and the resulting dark oil was dissolved in hexane. The crude product was obtained as straw-colored needles (0.11 g, 10%) after standing in a refrigerator. Recrystallization from hexane gave an analytical sample, mp 119–120°.

Anal. Calcd for $C_{18}H_{18}N_4$: C, 74.46; H, 6.25; N, 19.29. Found: C, 74.44; H, 6.25; N, 19.15.

2-Acetyl-1,1-dibenzylhydrazine (3d). 1,1-Dibenzylhydrazine (1.0 g) and acetic anhydride (0.5 g) were refluxed in dry ether (10 ml) for 0.5 hr. The ether solution was washed with water and dried ($MgSO_4$) and the solvent removed. Recrystallization of the residue from hexane gave colorless crystals (0.8 g, 67%), mp 82–84°.

Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.13; N, 11.01. Found: C, 75.70; H, 7.20; N, 11.00.

1,1-Dibenzyl-2-ethylhydrazine (3f). 2-Acetyl-1,1-dibenzylhydrazine (5.1 g) was reduced with lithium aluminum hydride (1.6 g) in dry methylal (35 ml) under nitrogen according to the general procedure of Kratzl and Berger.[29] After work-up, the crude hydrazine (oil) was immediately dissolved in ether and the hydrochloride (5.1 g) precipitated with gasous hydrogen chloride, mp 140–145°. Recrystallization (twice) from ether–chloroform (with filtration to remove a small quantity of insoluble material) afforded an analytical sample of 1,1-dibenzyl-2-ethylhydrazine hydrochloride (1.7 g, 30%), mp 146–148°.

Anal. Calcd for $C_{16}H_{21}ClN_2$: C, 69.43; H, 7.65; N, 10.12. Found: C, 69.33; H, 7.58; N, 10.25.

The free base was liberated as required by shaking a pentane solution of the hydrochloride with a solution of sodium bicarbonate. The hydrazine was fairly rapidly oxidized in air to the hydrazone, $(PhCH_2)_2NH{=}CHCH_3$.

1,1-Dibenzyl-2-(*p*-bromobenzenesulfonyl)hydrazine (3h). The compound was prepared in an analogous manner to the *p*-toluenesulfonyl derivative.[26] The product was obtained as colorless plates, mp 125–126° dec from methanol.

Anal. Calcd for $C_{20}H_{19}BrN_2O_2S$: C, 55.68; H, 4.45; Br, 18.52; N, 6.51. Found: C, 55.76; H, 4.44; Br, 18.64; N, 6.48.

Tetrabenzylhydrazine (3j). A solution of benzyl chloride (30 g) in ethanol (25 ml) was slowly added to a stirred mixture of hydrazine hydrate (99%, 12 g) in water (12 ml) and ethanol (25 ml) with intermittent cooling. The mixture was stirred vigorously, refluxed for 2 hr, and then allowed to stand overnight. Tetrabenzylhydrazine separated as colorless needles (3.3 g), mp 137–140°, raised to 139–140° by recrystallization from ethanol (lit.[30] 139°).

Anal. Calcd for $C_{28}H_{28}N_2$: C, 85.67; H, 7.19; N, 7.14. Found: C, 85.69; H, 6.91; N, 7.08.

***N*-(Dibenzylamino)succinimide (15).** A mixture of 1,1-dibenzylhydrazine (1.06 g) and succinic anhydride (0.50 g) was heated at 160–170° under nitrogen for 3 hr and the resulting semisolid residue recrystallized from ethanol to give colorless crystals (0.92 g, 62%), mp 113–116°, raised by recrystallization to 115–116°.

Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.60; H, 6.16; N, 9.57.

Nmr Spectra. The spectra were determined using a Varian Associates HA-100 spectrometer equipped with a modified variable-temperature accessory (−150 to 200°). Samples were generally 10–15% w/v and were degassed and sealed *in vacuo* with a few per cent of tetramethylsilane or hexamethyldisilane (obtained from NMR Specialties Ltd. for use as a reference above 40°) as internal lock. Probe temperatures were measured by inserting a copper–constantan thermocouple into a sample tube containing 0.5 ml of a toluene solution or an isohexane mixture (for temperature below −100°).[31] In several experiments, temperatures were also measured using the standard methanol or ethylene glycol samples. The temperatures are believed to be accurate to ±2°. Many of the hydrazines were observed to deteriorate on standing in solution; therefore, spectra were determined on freshly prepared samples.

Line-Shape Calculations. Theoretical spectra were calculated using the University of Texas CDC 6600 digital computer and plotted on microfilm. Spectra which involved the collapse of an

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Table I. Spectral Data and Free Energy of Activation ($\Delta G^{\ddagger}$) for Conformational Interchange in $(PhCH_2)_2NNXY$, Determined at the Coalescence Temperature (T_C)

Compd	X	Y	Solvent	$\Delta\nu_{AB}$,[a] Hz	J_{AB}, Hz	T_C, °C	Exchange rate at T_C, sec^{-1}	$\Delta G^{\ddagger}$, kcal/mol
3a	H	2,4-Dinitrophenyl	$CDCl_3$	26.4	13.0	59	78	16.6
3b	H	2,4,6-Trinitrophenyl	$CDCl_3$	12.3	12.8	50	54	16.4
3c	H	2-Pyrimidyl	$CHCl_2F$	29.6	13.2	−34	91	11.7
3d	H	CH_3CO (*E* isomer)[b]	$CDCl_3$	23.1	12.7	39	89	15.5
	H	CH_3CO (*Z* isomer)[b]	$CHCl_2F$	*c*		<−100		
3e	H	PhCO	$CDCl_3$	*c*		<−60		
3f	H	CH_3CH_2	$CHCl_2F$	*c*		<−130		
3g	H	*p*-$CH_3C_6H_4SO_2$	$CHCl_2F$	~11[d]	13.7	(−80)[d]	(20)[e]	(10.0)[e]
3h	H	*p*-$BrC_6H_4SO_4$	$CHCl_2F$	*c*		<−100		
3i	H	H	$CHCl_2F-CCl_2F_2$	57.0	12.0	−106	144	8.0
3j	$PhCH_2$	$PhCH_2$	$CHCl_2F$	~105	~12	~−105	~150[f]	8.2[g]
15	*N*-(Dibenzylamino)succinimide		$CHCl_2F$	*c*		<−130		

[a] Chemical shift nonequivalence of the benzyl methylene protons (in Hz at 100 MHz) at low temperature. [b] The isomers result from slow rotation around the N–CO bond. [c] The benzyl methylene signal broadened considerably at low temperature, but remained a singlet. [d] Approximate data only as $\Delta\nu_{AB}$ was small and very temperature dependent. [e] The agreement between the experimental and computed spectrum was very poor as $\Delta\nu_{AB}$ appeared to have decreased considerably near coalescence. [f] The approximate rate of exchange between two sites of unequal population was obtained from the graph of A. Jaescke, H. Muensch, H. G. Schmid, H. Friebolin, and A. Mannschreck, *J. Mol. Spectrosc.*, **31**, 14 (1969) (see Discussion). [g] The rate of inversion at a single nitrogen is half the exchange rate (see Discussion).

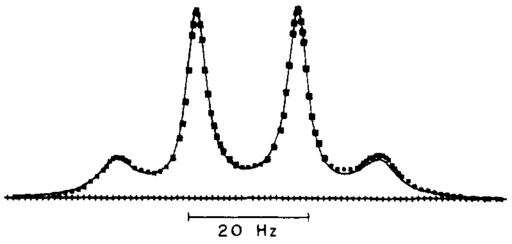

Figure 1. The 100-MHz proton nmr spectrum of the methylene protons of 1,1-dibenzyl-2-(2,4-dinitrophenyl)hydrazine (**3a**) in $CDCl_3$ at 35°. The curve is the "best fit" computed spectrum (k = 12.8 sec^{-1}) to the digitized experimental spectrum.

AB quartet to a singlet were calculated using a program (CURVE 1) devised by Jonas, Allerhand, and Gutowsky.[32] The program iterates the exchange rate to afford the best least-squares fit of the theoretical spectra to the digitized experimental spectrum (Figure 1). The temperature dependence of the chemical shift nonequivalence ($\Delta\nu_{AB}$) and the coupling constant (J_{AB}) were investigated in the slow exchange region. In all cases except 1,1-dibenzyl-2-(*p*-toluenesulfonyl)hydrazine (see Table I), the values of $\Delta\nu_{AB}$ and J_{AB} were found to be essentially constant over a 30–50° temperature range. The agreement between the calculated and experimental spectra (as judged by the standard deviation) was very good in the region of collapse and was not improved by changing the values of $\Delta\nu_{AB}$ and J_{AB} estimated from the preexchange region. According to normal procedure, the spin–spin relaxation time (T_2) was replaced by an effective T_2 which included inhomogeneity broadening and unresolved coupling of the methylene protons to the aromatic protons. This approach is justified as the half-height line width was at least an order of magnitude less than $\Delta\nu_{AB}$. In the case of line-shape calculations at the coalescence temperature alone (Table I), the natural line width employed was that measured in the fast or slow exchange limits. In cases where the calculations were carried out at a series of temperatures (see Results section) to estimate all the activation parameters, a small quantity of toluene was added to the sample to serve as a line-width reference. The line width of the toluene methyl signal (1.5 Hz) was similar to that of the benzyl methylene signals of the hydrazines in the absence of exchange broadening.

The rate of rotation around the N–CO bond in **3d** was determined near the coalescence of the methylene signals for the *E* and *Z* isomers by visual comparison of the spectrum with spectra calculated for exchange between two unequally populated sites using a multisite program devised by Saunders.[33]

Results

The nmr spectra of most of the substituted benzylhydrazines investigated in this study showed the benzyl methylene protons as an AB quartet at low temperatures. At higher temperatures the quartet collapsed reversibly to a singlet, rapid conformational interchange making the diastereotopic methylene protons enantiotopic[34] on the nmr time scale. The exchange rates were determined at the coalescence temperature by computer matching of experimental and calculated spectra. The free energies of activation for the rate-determining stereochemical process (nitrogen inversion or NN bond rotation) were calculated from the Eyring equation assuming a transmission coefficient of unity. The results are presented in Table I. The entropy of activation for a torsional process such as NN bond rotation should be small so the free energies of activation listed in Table I should approximate closely to the enthalpies of activation. This assumption can be checked by determining the exchange rates at a series of temperatures, although it is now well established that the complete line-shape method can lead to large errors in $\Delta S^{\ddagger}$ if the chemical shift difference is small or significantly temperature dependent. Fortunately 1,1-dibenzyl-2-(2,4-dinitrophenyl)hydrazine proved to be well suited for such a study because the chemical shift nonequivalence of the geminal methylene protons (in $CDCl_3$) was found to be constant (within 1%) over the temperature range −40 to 20°. Furthermore, the use of this value for the chemical shift nonequivalence led to excellent agreement between the computed and experimental spectra in the region of collapse (see Figure 1). The results for a solution of 1,1-dibenzyl-2-(2,4-dinitrophenylhydrazine) in $CDCl_3$ were as follows [T, °K (k, sec)]: 303 (7.5), 308 (12.8), 313 (22.5), 318 (34.8), 324 (43.0), 328 (54.4), 332 (78.0), 336 (136.0), 341 (136.0), 341 (192.0), 347 (240.0), 353 (360.0). A plot of log (k/T) *vs.* $1/T$ by the method of least squares

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gave $\Delta H^{\ddagger} = 15.6$ kcal/mol, $\Delta S^{\ddagger} = -3$ eu. An Arrhenius plot gave $E_a = 16.2$ kcal/mol, $\log A = 12.6$ sec^{-1}.

The value for $\Delta S^{\ddagger}$ is considered to be zero within the limits of experimental error, though a small negative value might be expected since the transition state for NN bond rotation is probably more hindered than the ground state.

The entropy of activation for pyramidal inversion of nitrogen should also be small unless solvation is strongly affected by changes in conformation. To check this assumption, the rates of nitrogen inversion in 1,1-dibenzylhydrazine were determined at a series of temperatures in the range −112° to −80° using the complete line-shape method. In this case, however, the experimental difficulties were greater than in the previous one because the benzyl methylene signal was broadened at low temperatures by processes other than site exchange. Thus the benzyl methylene signal collapsed at −100° and split into a broad AB quartet at −120°. The quartet broadened again on further cooling, and below −130° the signals could barely be seen. The line width of the methyl signal of a small amount of toluene added as a reference remained essentially unchanged over the temperature range −80 to −130°. The broadening of the benzyl signals made it difficult to measure the coupling constant (J_{AB}) and the chemical shift separation ($\Delta\nu_{AB}$) accurately, and also prevented us from studying the temperature dependence of these parameters. However, the use of the values of $\Delta\nu_{AB}$ and J_{AB} at −120°, together with natural line width of the toluene reference, gave very good agreement between the experimental and calculated spectra around the coalescence temperature. Increasing or decreasing $\Delta\nu_{AB}$ or J_{AB} from the preexchange values led to a less satisfactory agreement, suggesting that these parameters did not depend significantly on temperature over the temperature range studied. The results for a solution of 1,1-dibenzylhydrazine in $CHCl_2F-CCl_2F_2$ (1:1) using these parameters were as follows [(T, °K k, sec^{-1})]: 161.5 (76), 167 (144), 170 (195), 175 (396), 179 (590), 185 (1200), 191 (2080). A plot of log (k/T) *vs.* $1/T$ by the method of least squares gave $\Delta H^{\ddagger} = 6.7$ kcal/mol, $\Delta S^{\ddagger} = -7$ eu. An Arrhenius plot gave $E_a = 7.0$ kcal/mol, $\log A = 11.3$ sec^{-1}. The $\Delta S^{\ddagger}$ value may reflect the lower accuracy of these results.

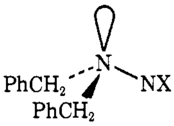
Discussion

(a) **The Rotation–Inversion Dichotomy.** The three pertinent intramolecular processes in a substituted hydrazine **3** are (i) inversion at N-1, (ii) inversion at N-2, (iii) rotation around the N–N bond.

$$(PhCH_2)_2N^{1-2}NXY$$

3

In order to observe these processes by nmr, the prochiral[35] benzyl group was selected as a probe. In a hydrazine of type **3**, the chemical shifts of the four benzylic methylene protons are rendered equivalent by rapid inversion at *both* nitrogen atoms together with rapid rotation around the N–N and N–CH$_2$ bonds. Throughout this discussion, it is assumed that rotation around the N–CH$_2$ bonds is always fast on the nmr time scale over the temperature range considered (above −130°).[36–38] If, however, the rate of inversion at either nitrogen atom in **3** becomes slow on the nmr time scale, the geminal methylene protons of each benzyl moiety become diastereotopic and can exhibit different chemical shifts in the nmr spectrum. This can be seen by considering **4** and **5**



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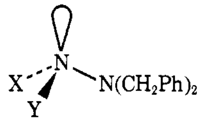

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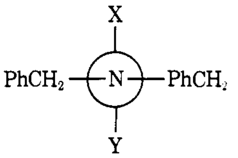

6

which indicate the molecular dissymmetry introduced by slow inversion at N-1 or N-2, respectively. Since neither **4** nor **5** possesses a plane of symmetry (σ plane) containing the prochiral methylene carbon atoms, the methylene protons are diastereotopic. Slow rotation around the NN bond (with rapid inversion at both nitrogen atoms) will also render the methylene protons diastereotopic *provided that the gauche conformation is adopted.* The molecular dissymmetry introduced by restricted rotation around the NN bond is depicted in **6**. The nitrogen atoms are drawn planar to represent rapid inversion which interconverts the gauche conformations. This libration is shown more fully in Scheme I, where the conformations **8** and **8′** interconvert by successive nitrogen inversions, but where NN bond rotation through greater than 90° is forbidden. Interconversion of the "true" gauche conformations **7** and **7′** by "inversion" also involves torsion through 60°.[39]

Restricted NN rotation in conformations **9** or **10**, with the lone pairs of electrons syn or anti, would result in separate signals for the two benzyl groups together with nonequivalence of the geminal methylene protons within each benzyl group. Therefore, the observation of a *single* AB quartet for the methylene protons of a hydrazine of type **3** (X = Y) implies either slow inversion at N-1, or slow inversion at N-2, or slow rotation around the NN bond, provided that the ground-state conformation has the lone-pair electrons gauche or orthogonal (Scheme I). *A priori*, no decision can be made between these alternatives. However, in a 1,1-dibenzylhydrazine with identical substituents on N-2, the barrier to inversion at N-1 can be independently studied since in a hydrazine of this type the geminal methylene protons can be diastereotopic only if inversion at N-1 is slow.[40] It is easily seen by comparing **5** (X = Y) with **6** (X = Y) that neither slow inversion at N-2 nor slow rotation can make the geminal methyl-

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(35) K. R. Hanson, *J. Amer. Chem. Soc.*, **88**, 2731 (1966).

(36) The barrier to rotation around the N–CH$_2$ Ph bond would be expected to lie between that for rotation around the N–CH$_3$ bond in trimethylamine ($V = 4.4$ kcal mol),[37] and the N–C(CH$_3$)$_3$ bond in *tert*-butyldimethylamine ($\Delta H^{\ddagger} = 6.2$ kcal mol,[38] *i.e.*, considerably lower than the barriers reported in the present study.

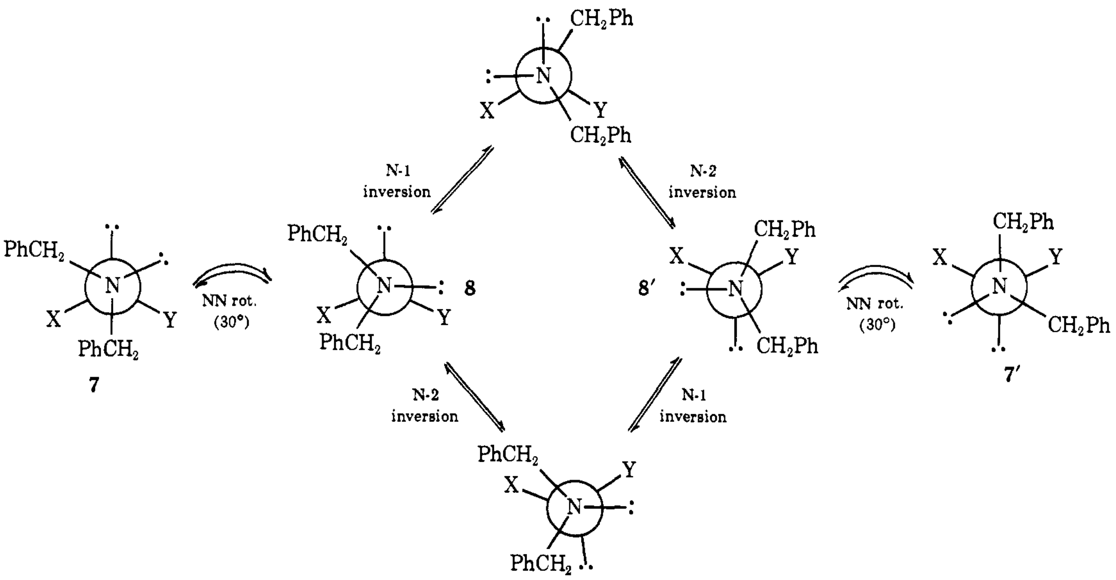
(37) J. P. Lowe, *Progr. Phys. Org. Chem.*, 6, 1 (1968), and references therein.

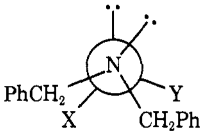
(38) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *J. Amer. Chem. Soc.*, **92**, 6349 (1970).

(39) A process that changes the dihedral angle between the lone pairs by greater or less than 180° involves some torsional libration around the NN bond.

(40) This statement is not *strictly* correct as the geminal methylene protons would also be diastereotopic if the ground state conformation was **9** or **10** (X = Y) and *both* NN bond rotation and inversion at N-2 were slow on the nmr time scale, even though inversion at N-1 was rapid. This explanation can be rejected as it would require two different benzyl signals to be observed in the spectra of the unsymmetrical hydrazines where X = Y, or else a conformational inconsistency between the two types of compound.

Scheme I





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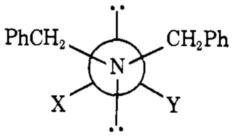
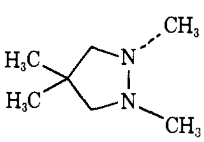


10

ene protons diastereotopic in a hydrazine of this type. This follows since **5** and **6** possess a symmetry plane containing the methylene carbon atoms when X = Y.

(b) The Rate-Determining Stereochemical Process. The free energy barriers ($\Delta C^{\ddagger}$) corresponding to the topomerization[41] of the geminal methylene protons are given in Table I. In some cases, the methylene protons remained a singlet down to the lowest temperature at which the solubility was sufficient to allow spectra to be recorded, and no information could be obtained regarding the dynamic stereochemistry of the molecule. The barriers measured in compounds **3a–h**, where X = Y, may be assigned to inversion at N-1 or N-2, or to rotation around the NN bond. However, slow inversion at N-2 can be excluded on the grounds that the barriers are highest in compounds **3a**, **3b**, and **3d** where the nitrogen atom is of the amide type and so must have a very low barrier to inversion. In any case, this nitrogen atom is secondary and could invert rapidly by proton exchange or possibly by tunnelling. Barriers of 15 kcal/mol also seem too large to be due to inversion at N-1. The inversion barriers in acyclic amines are only 6 to 7 kcal/mol,[42] though the effect of the NXY moiety is admittedly difficult to estimate. However, as discussed in section a, the barriers to inversion at N-1 may be independently studied in hydrazines with identical 2 substituents. Thus the activation parameters for the topomerization of the methylene protons in 1,1-dibenzylhydrazine (**3i**) and tetrabenzylhydrazine (**3j**) refer to inversion at N-1 (for a full discussion of the latter case, see section d). The barrier to inversion in **3i** may be compared with that recently measured in dibenzylmethylamine ($\Delta G^{\ddagger} = 6.7$ kcal/mol at −135°).[42b] It is not strictly correct to compare $\Delta G^{\ddagger}$ values obtained at different temperatures. We therefore calculated $\Delta G^{\ddagger}$ for **3i** at −135° (7.7 kcal/mol) using the activation parameters in the Results section. Replacement of the methyl group by the approximately isosteric amino group evidently increases the barrier to inversion by 1 kcal/mol. This effect is probably due to enhanced repulsion between vicinal lone pairs of electrons in the transition state for pyramidal inversion. However, it has recently been suggested that electronegativity effects may also be largely responsible for the enhanced barriers to nitrogen inversion in compounds where the nitrogen atom is bonded to another heteroatom.[43] It is interesting in this connection that the barrier to nitrogen inversion in the cyclic hydrazine **11** is ~3.5 kcal/mol higher than in the corresponding amine **12**, whereas the barrier in the hydrazine **13** with an exocyclic NN bond is only increased by ~1 kcal/mol.[44] This difference can be explained in terms of repulsion between nonbonding electrons. Both 1,1-dibenzylhydrazine and **13** undergo inversion *via* the conformation **14** which minimizes repulsion between adjacent nonbonding p orbitals. The cyclic hydrazine **11** is presumably constrained to a conformation in which the lone-pair orbitals are nearly eclipsed, the resulting repulsions leading to an enhanced barrier. It is difficult to explain these observations in terms of electronegativity effects.



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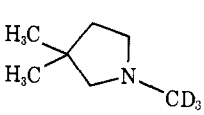

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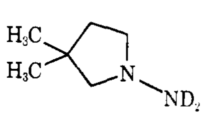

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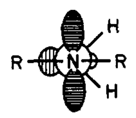

14

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(41) G. Binsch, E. L. Eliel, and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 10, 570 (1971).

(42) (a) C. H. Bushweller and J. W. O'Neil, *J. Amer. Chem. Soc.*, 92, 2159 (1970); (b) M. J. S. Dewar and W. B. Jennings, *ibid.*, 93, 401 (1971).

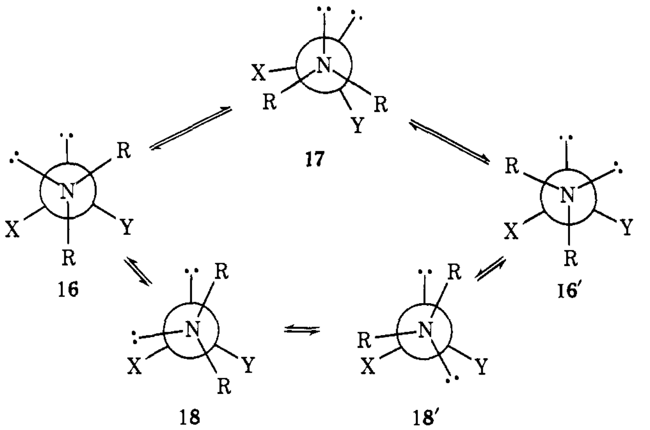
(43) K. Muller and A. Eschenmoser, *Helv. Chim. Acta*, 52, 1823 (1969).

(44) J. M. Lehn and J. Wagner, *Tetrahedron*, 26, 4227 (1970).

Returning to the barriers listed in Table I, we next have to explain the very large values (10–17 kcal/mol) for compounds carrying certain substituents at the second nitrogen (N-2). It is extremely difficult to believe that substitution at N-2 could lead to so great an increase in the barrier to inversion at N-1. The barriers measured in **3a–d** must therefore almost certainly refer to restricted rotation about the NN bond, the molecules being confined to the conformation **6** with the lone pairs gauche. This would account for our failure to observe any splitting of the signal for **15**, since a high NN torsional barrier would not lead to spectral changes in this compound (see section a), whereas a high barrier to inversion at N-1 would make the methylene protons of the benzyl groups diastereotopic.

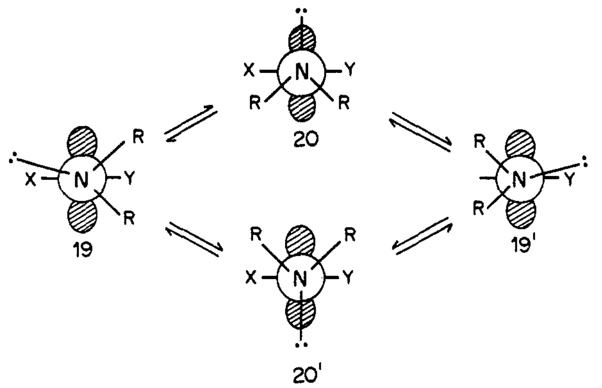
The magnitude of the NN torsional barriers seems to increase with an increase in the ability of the substituent to delocalize the nitrogen lone pair. An attractive explanation is that vicinal lone-pair repulsions and nonbonded interactions augment $\Delta G^{\ddagger}$ and that these effects depend on the hybridization of the nitrogen atoms. Consider, for example, an alkylhydrazine where both nitrogen atoms are approximately sp^3 hybridized. The ground state conformations **16** and **16′** depicted in Scheme II can be interconverted by rotation through 120° (*via* **17**) or through 240° (*via* **18** and **18′**). Taking a rather simple view of electron repulsions, the energy might be expected to increase in the order **16** $\ll$ **18** $<$ **17**. Interconversion of **16** and **16′** by rotation could then occur fairly readily *via* **18**, thus avoiding the unfavorable interactions in **17**. The barriers to interconversion of the gauche conformations by rotation do indeed seem to be fairly low, though possibly somewhat higher than in the analogous ethanes.[45] However, in a hydrazine where one of the nitrogen lone pairs participates in a π system, that nitrogen atom will become more planar in the ground state and the lone pair will tend to occupy an orbital with a high degree of *p* character.[46]

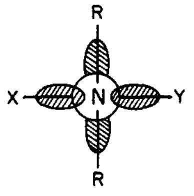
Scheme II



Interconversion of the ground state conformations **19** and **19′** by rotation through 180° (Scheme III) involves a transition state (**20** or **20′**) in which both the lone-pair repulsions and the nonbonded interactions between the substituents are at a maximum. This could account for the large NN torsional barriers in **3a**, **3b**, and **3d**, the interactions between the lone-pair orbital on N-1 and the π system at N-2 being repulsive. The intermediate barrier heights shown by **3c** and **3g** can also be explained in this way because in them the π interactions at N-2 (p_π–p_π and p_π–d_π, respectively) would be expected to be weaker than in **3a** or **3d**. One might also expect the transition state to be still further destabilized relative to the ground state if both nitrogen atoms participate in separate π systems, the change in the p_π–p_π repulsions and nonbonded interactions on going from **21** to **22** being even greater than on going from **19** to **20**. This indeed seems to be the case, the barriers to NN rotation in 1,2-diacylhydrazines and in tetracylhydrazines ($\Delta G^{\ddagger}$ = 20–25 kcal/mol[15]) being much greater than in **3d**.

Scheme III





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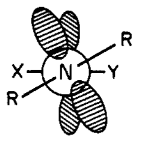

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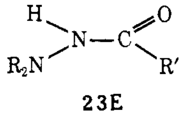
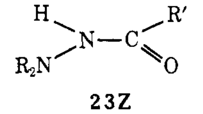
(c) Restricted Rotation Around the CN Bond in 3b and 3d. The spectrum of 2-acetyl-1,1-dibenzylhydrazine (**3d**) at 0° showed in addition to the AB system for the diastereotopic methylene protons (τ_A 6.19, τ_B 6.45, J_{AB} = 12.5 HZ) another methylene signal at τ 6.03 (Figure 2). These separate methylene signals (ratio 3.35:1 by integration) were assigned to the *E* and *Z* isomers (**23E** and **23Z**, R = CH_2Ph, R′ = CH_3) arising from slow rotation around the amide bond. On raising the probe temperature to 30°, the AB quartet collapsed, indicating the onset of fast rotation around the NN bond in the major isomer, and at 85° the methylene signals of the *E* and *Z* isomers collapsed to a singlet as rotation around the N–CO bond became rapid on the nmr time scale (Figure 2). The rate of rotation around the N–CO bond in 1,1,2,2-tetrachloroethane solution was determined to be 50 sec^{-1} (minor to major isomer) and 15 sec^{-1} (major to minor isomer) at 84° by the total line-shape method, corresponding to $\Delta G^{\ddagger}$ = 18.2



23E



23Z

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(45) (a) For an alternative view of the origin of torsional barriers between atoms possessing lone pairs of electrons, see S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972). (b) The barrier to torsion through the conformation **17** could be quite large. However, this barrier would not normally be detectable by nmr since it can be bypassed by a lower energy path (*via* **18**).

(46) Strong conjugation would be required in order to make the nitrogen atom completely sp^2 hybridized; see M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 406.

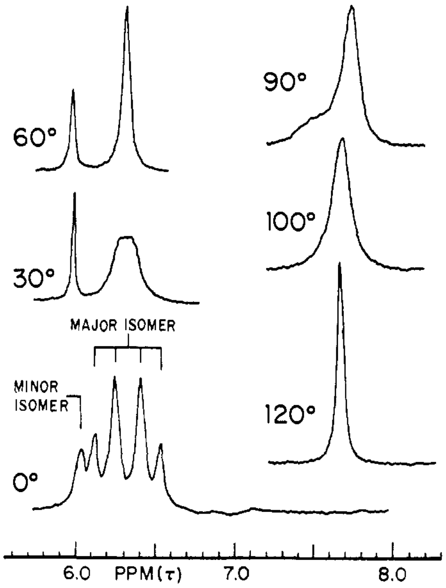


Figure 2. The 100-MHz proton nmr spectrum of the methylene protons of 2-acetyl-1,1-dibenzylhydrazine (**3d**) in $CHCl_2$–$CHCl_2$ solution at various temperatures.

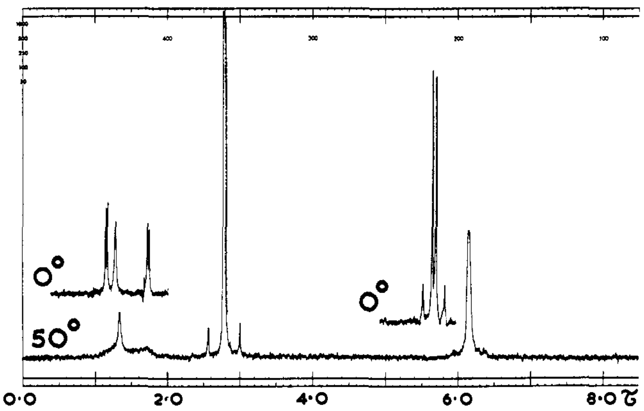
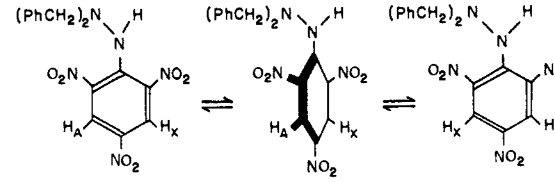


Figure 3. The 100-MHz proton nmr spectrum of 1,1-dibenzyl-2-(2,4,6-trinitrophenyl)hydrazine (**3b**) in $CDCl_3$.

and 19.1 kcal/mol, respectively. This barrier is of similar magnitude to the barriers reported in other acetamides.[21,47] The spectrum of **3d** was investigated down to −100° in $CHCl_2F$ solution. Although the methylene signal of the minor isomer broadened considerably, it failed to split into an AB quartet. This indicates either that the barrier to rotation around the NN bond in the minor isomer is very low (<10 kcal/mol) or that the methylene protons are diastereotopic but accidentally equivalent in chemical shift. Two groups of investigators[48,49] have independently reported similar observations in the nmr spectra of some related acylhydrazines. They observed that the methylene protons in the *E* isomer (**23E**) showed an AB quartet, whereas they remained a singlet in the *Z* isomer. The configuration of the isomers was assigned on the basis that the proportion of the *Z* isomer (**23Z**) increased with increasing steric bulk of R and R′. The NN torsional barriers therefore seem to be much lower in the *Z* isomers than in the *E* isomers given that a variety of compounds show similar spectral behavior in several solvents. The fact that the methylene protons in **3e** gave only a single signal (Table I) may then indicate that this compound exists mainly in the *Z* configuration (**23Z**, R = CH_2Ph; R′ = Ph).

Anthoni, *et al.*,[48] believed the process responsible for the collapse of the AB quartet in the *E* isomers to be slow nitrogen inversion. However, for reasons discussed above (section b), we consider this unlikely and agree with Walter and Reubke[49] that NN torsion is the rate-determining step.

The spectrum of 1,1-dibenzyl-2-(2,4,6-trinitrophenyl)hydrazine (**3b**) also shows additional temperature effects that arise from hindered rotation around the CN bond. At 0°, the two protons on the trinitrophenyl ring are anisochronous and occur as an AX system (τ_A 1.15, τ_X 1.72, J_{AX} = 2.7 Hz) (Figure 3). These signals collapse to an A_2 singlet above 50° as the interconversion of **24** and **24′** becomes rapid on the nmr time scale. The overlapping NH signal at τ 1.33 was removed by exchange with deuterium oxide and the rate of rotation around the N–Ar bond was computed for the collapse of a coupled AX system near coalescence: k = 114 sec^{-1} at 56° in deuteriochloroform solution, $\Delta G^{\ddagger}$ = 16.2 kcal/mol. The magnitude of the barrier is similar to that previously reported for rotation around the N–Ar bond in 1,1-diphenyl-2-(2,4,6-trinitrophenyl)hydrazine.[50] It is interesting to note that the barrier to rotation around the N–Ar bond in **3b** is equal to that proposed for rotation around the NN bond ($\Delta G^{\ddagger}$ = 16.4 kcal/mol at 50° in $CDCl_3$) within the accuracy of the measurements. This could be a coincidence, but it is possible that there is a common transition state on the potential energy surface for rotation around both the N–Ar and N–N bonds.[51]



24 **25** **24′**

Thus as the trinitrophenyl ring rotates further out of the coplanar conformation **24**, the steric hindrance to rotation around the NN bond will be reduced and the vicinal lone-pair repulsions in the transition state **18** for rotation around the NN bond will also be diminished since N-2 will become more pyramidal owing to the loss in conjugation with the trinitrophenyl moiety. The converse is also true in that torsion around the NN bond will render N–Ar rotation more facile, thereby making a common transition state an attractive possibility.

Another explanation of the spectral changes might be that steric hindrance prevents the trinitrophenyl ring from adopting the coplanar conformation **24**. The molecule could then be chiral on the nmr time scale in which case the prochiral methylene protons would be

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[47] W. J. Deloughry and I. O. Sutherland, *Chem. Commun.*, 1104 (1971).

[48] U. Anthoni, C. Larsen, and P. H. Nielsen, *Acta Chem. Scand.*, 23, 3513 (1969).

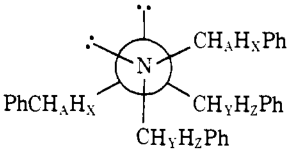
[49] W. Walter and K. J. Reubke, *Chem. Ber.*, 103, 2197 (1970).

[50] J. Heidberg, J. A. Weil, G. A. Janusonis, and J. K. Anderson, *J. Chem. Phys.*, 41, 1033 (1964).

[51] Another example of two conformational processes that may share a common transition state has been discussed by C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *J. Amer. Chem. Soc.*, 93, 542 (1971).

diastereotopic, if rotation through *both* the coplanar conformation **24** and the bisected conformation **25** were slow. Rapid rotation through **25** would simultaneously interconvert the methylene protons (assuming rapid nitrogen inversion and NN bond rotation) and the aromatic protons H_A and H_X. This explanation could hold only if the barrier to rotation through the coplanar conformation **24** were greater than 16.2 kcal/mol because this process alone would make the methylene protons equivalent in chemical shift. It seems very unlikely that the steric interactions in **24** could be sufficient to overcome the strong conjugative stabilization by greater than 16 kcal/mol. Indeed, the barrier to rotation around the N–Ar bond in the less hindered *N*-methyl-2,4,6-trinitroaniline is only E_A = 14.5 kcal/mol,[50] contrary to the effect expected for a very large steric destabilization of the coplanar conformation **24** in **3b**.

(d) **Tetrabenzylhydrazine (3j).** The nmr spectrum of tetrabenzylhydrazine showed unusual changes with temperature. The methylene singlet separated at around −120° into a broad doublet at τ 5.47 (2 H) and a broad signal at τ 6.52 (6 H) (Figure 4).[52] This behavior, in contrast to the single AB system shown by other hydrazines at low temperatures, suggests that both nitrogen inversion and NN bond rotation are slow on the nmr time scale at −120°, the molecules being locked in the gauche conformation **26**. The doublet at τ 5.47 can be assigned to one of the four types of diastereotopic protons in **26**, arbitrarily labeled H_A.



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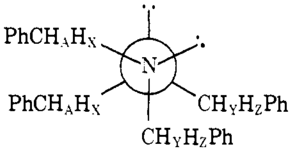

26′

The unresolved peak at higher field would then correspond to H_X, H_Y, and H_Z which are presumed to be approximately isochronous. In support of this assignment, irradiation at τ 6.52 (presumed to correspond to H_X) collapsed H_A to a broad singlet (Figure 4). The two equivalent sets of four diastereotopic methylene protons in **26** are rendered equivalent in chemical shift by rapid inversion at both nitrogen atoms which generates four equivalent sets of enantiotopic protons. Rapid rotation around the NN bond (with slow inversion) would result in four equivalent sets of diastereotopic protons and a single AB quartet in the spectrum. Since the complex pattern observed at −120° collapsed directly to a singlet on raising the temperature to −100°,

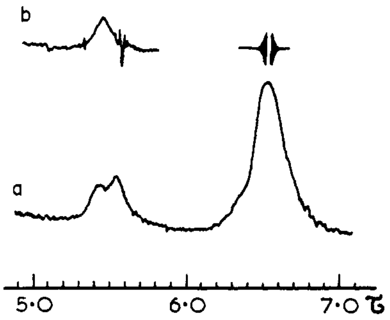

Figure 4. The 100-MHz proton nmr spectrum of the methylene protons of tetrabenzylhydrazine (**3j**) at −120° in $CHCl_2F$ solution: (a) single resonance; (b) with irradiation at τ 6.52 (reduced spectrum amplitude).

the barrier to rotation cannot be measured but must be greater than (or approximately equal to) the barrier to nitrogen inversion.

Owing to the complexity of the spectrum the barrier to inversion could not be calculated exactly; the rate of site exchange was, however, estimated by neglecting the coupling J_{AX}. This is a reasonable approximation as the chemical shift separation of H_A from H_{XYZ} is an order of magnitude larger than J_{AX} and, in any case, the latter is only slightly greater than the line width. It is then necessary to establish how the rate of inversion relates to the site exchange process. Inversion at a nitrogen atom (**26** $\rightleftharpoons$ **26′**) converts *both* H_A protons into the isochronous H_X, H_Y, H_Z set (one $H_A \rightarrow H_X$; other $H_A \rightarrow H_Y$ or H_Z). Therefore, the rate of transfer of magnetization from the site at τ 5.47 to the site at τ 6.52 (relative intensity 3) is equal to the rate of nitrogen inversion. This rate was determined to be 150 sec^{-1} at the coalescence temperature (−105°) from the nomograph of Jaeschke, *et al.*[53] Allowing for the presence of two identical nitrogen atoms in **3j**, the rate of inversion at given nitrogen atom is 75 sec^{-1}, corresponding to $\Delta G^{\ddagger}$ = 8.2 kcal/mol at −105°. The inversion barrier is similar to that observed in 1,1-dibenzylhydrazine and 1-benzyl-1,2,2-trimethylhydrazine.[14] Provided that our assignment is correct, the barrier to rotation around the NN bond in **3j** must be greater than or equal to 8 kcal/mol. Fletcher and Sutherland[22a] have reported that the torsional barrier in 1,1,2-tribenzyl-2-ethylhydrazine is $\Delta G^{\ddagger}$ = 10.8 kcal/mol at −53°. As these two compounds are virtually isosteric, it is evident that the barrier to rotation around the NN bond in **3j** is indeed greater than the barrier to nitrogen inversion and that the two processes do not share a common transition state.

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(52) The spectrum of this compound has been discussed in a preliminary publication: M. J. S. Dewar and W. B. Jennings, *Tetrahedron Lett.*, 339 (1970).

(53) A. Jaeschke, H. Muensch, H. G. Schmid, H. Friebolin, and A. Mannschreck, *J. Mol. Spectrosc.*, **31**, 14 (1969).