into the reaction vessel. Oxygen bubbling was resumed for 15–30 min. $BaCO_3$ was collected as before. The reaction mixture was then heated at 88 °C for the specified time. Extraction with CH_2Cl_2 gave benzoic acid and nitrobenzene which were separated by extraction with NaOH. The aqueous hydrolysate was neutralized with NaOH and more ammonia and dimethylamine were trapped in acetic anhydride. The final aqueous solution was neutralized with dilute HCl and calcium oxalate was precipitated with $CaCl_2$ solution as described above.

Preparation of DL-Alanine Dimethylamide. The L form of this compound had been prepared earlier by Freudenberg and Nickolai.[15] The DL derivative was prepared by a procedure very similar to the one described above for the phenylalanine case. The *N*-carbobenzoxy precursor was a crystalline solid: mp 80.5–82.5 °C from ether–hexane; ^1H NMR ($CDCl_3$) δ 1.25–1.35 (d, 3 H), 2.95–3.05 (d, 6 H), 4.7 (m, 1 H), 5.15 (s, 2 H), 5.9 (br, 1 H), 7.4 (s, 5 H).

Anal. Calcd for $C_{13}H_{18}N_2O_3$: C, 62.38; H, 7.25; N, 11.19. Found: C, 62.61; H, 7.27; N, 11.45.

DL-Alanine dimethylamide was prepared from this material by hydrogenation in essentially quantitative yield: ^1H NMR δ 1.2–1.3 (d, 3 H), 2.3 (br, 2 H), 2.95–3.05 (2 s, 6 H), 3.85 (m, 1 H).

Anaerobic Reaction of DL-Alanine Dimethylamide with Nitrobenzene and Potassium *tert*-Butoxide in *tert*-Butyl Alcohol. The amino amide (186 mg, 1.60 mmol) was treated with nitrobenzene (438 mg, 3.55 mmol) and 5.0 mL of 0.52 N potassium *tert*-butoxide in *tert*-butyl alcohol in a septum-covered centrifuge tube at 50 °C for 44 h as described above. The precipitated solids were washed with ether and weighed, 242 mg. Extraction with degassed Me_2SO left 157 mg of solids after washing with ether. The Me_2SO solution gave a strong nitrobenzenide ESR spectrum. The residual solids showed no significant NMR absorption except for that due to formate. Analysis of these solids for formate (by NMR—adding known amounts of HCO_2Na) indicated a 20% yield of potassium formate. Gravimetric analysis for carbonate showed a 28% yield of this material as potassium carbonate. The balance of the solids may have been potassium oxalate but an analysis for this product was not carried out. Workup of the reaction solution showed no NMR evidence for organic compounds other than starting materials.

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Acknowledgment. We express our gratitude to National Science Foundation for a grant (GP-42837-X) supporting this work.

Registry No. DL-1, 3705-50-8; L-1, 29618-17-5; DL-*N*-carbobenzoxyphenylalanine dimethylamide, 75768-06-8; DL-*N*-(carbobenzoxy)phenylalanine *p*-nitrophenyl ester, 2578-86-1; L-*N*-(carbobenzoxy)phenylalanine *p*-nitrophenyl ester, 2578-84-9; potassium nitrobenzenide, 34480-35-8; DL-*N*-carbobenzoxyalanine dimethylamide, 75801-52-4; DL-alanine dimethylamide, 75768-07-9; potassium formate, 590-29-4; $PhNO_2$, 98-95-3; KO-*t*-Bu, 865-47-4; K_2CO_3, 584-08-7; $K_2C_2O_4$, 583-52-8; $PhCO_2K$, 582-25-2; NH_3, 7664-41-7; Me_2NH, 124-40-3.

Conformational Analysis of Fused-Ring 1,2-Diazetidines by Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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A series of 1,2-diazetidines with alkyl and carbonyl substituents on nitrogen has been synthesized, and conformational changes observed for these compounds have been examined by variable-temperature ^{13}C NMR spectroscopy. All compounds exhibit conformational changes involving nitrogen inversion, and those with carbonyl substituents have barriers to inversion 2–3 kcal/mol lower than those of alkylated analogues. Differences in activation parameters are discussed in terms of steric and electronic effects.

Introduction

Three processes have been described[1] to explain conformational changes observed by dynamic nuclear magnetic resonance spectroscopy for cyclic hydrazines of various ring sizes: (1) ring reversal, (2) nitrogen inversion, and (3) rotations about amide bonds. In many examples, more than one of these processes can occur, rendering the unambiguous assignment of the conformational change difficult. This problem is nowhere more apparent than in the study of four-membered-ring hydrazines, 1,2-diazetidines. For example, temperature-dependent ^1H NMR spectral changes observed for N,N-dialkylated 1,2-diazetidines have been interpreted as involving nitrogen inversion.[2] Spectral changes exhibited by diethyl tetramethoxy-1,2-diazetidine-1,2-dicarboxylate are consistent with a conformational change involving rotations about amide bonds.[3] Temperature-dependent ^{19}F spectra of 1,2-bis(trifluoromethyl)tetrafluoro-1,2-diazetidine[4] and diethyl tetrafluoro-1,2-diazetidine-1,2-dicarboxylate[5] have been interpreted as involving either ring reversal[6] or nitrogen inversion.[4,5]

We have prepared a series of 1,2-diazetidines in which ring torsion has been minimized in order to study "torsion-free" nitrogen inversion and/or amide rotations in 1,2-diazetidines. We now report conformational changes and corresponding activation energies as a function of nitrogen substituent in a series of fused-ring 1,2-diazetidines.

(1) For reviews, see: (a) S. F. Nelsen, *Acc. Chem. Res.*, **11**, 14 (1978); (b) Y. Shvo, "Chemistry of Hydrazo, Azo, and Azoxy Groups", S. Patai, Ed., Wiley, New York, 1975, Part 2, pp 1017–1095; (c) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1971).
(2) J. H. Hall and W. S. Bigard, *J. Org. Chem.*, **43**, 2785 (1978).
(3) H. Carlson, A. P. Schaap, and M. Raban, *J. Org. Chem.*, **38**, 1605 (1973).
(4) P. Ogden, *J. Chem. Soc. D*, 1084 (1969).
(5) W. D. Phillips, "Determination of Organic Structures by Physical Methods", F. C. Nachod and W. D. Phillips, Eds., Academic Press, New York, 1962, p 455.
(6) B. Price, I. O. Sutherland, and F. G. Williamson, *Tetrahedron Lett.*, 1603 (1967).

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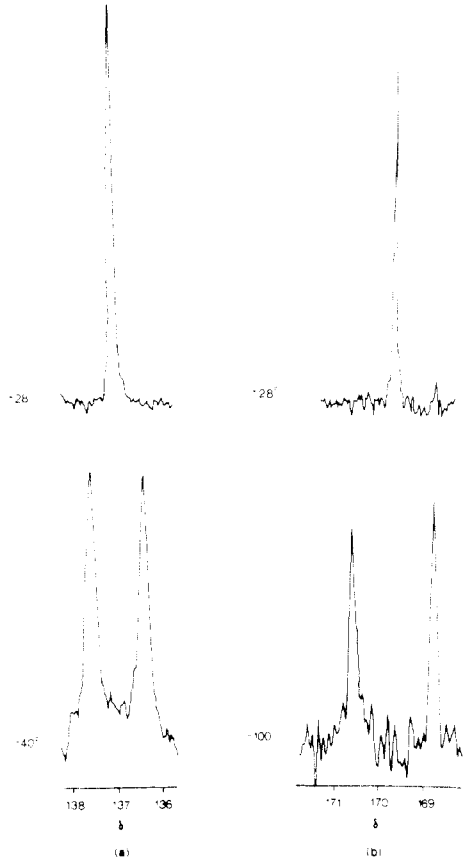


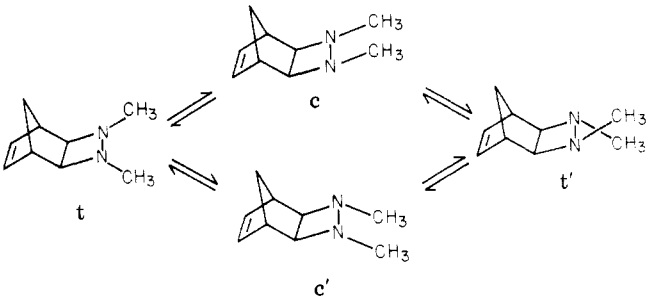
Figure 1. Temperature-dependent ^{13}C NMR spectra for (a) alkene carbons (C-7, C-8) of **3b** and (b) carbonyl carbons of **2b**.

Compounds Studied. Cycloadditions of diethyl azodicarboxylate[7] and of diaroyl azo compounds[8] to quadricyclane **1** afford 1,2-diazetidines **2**. Reductive saturation[9,10] of carbamate **2a** and hydrazides **2b–d** with $LiAlH_4$ affords saturated hydrazines **3**. The bicyclo ring fusion in **2** and **3** prevents significant torsion in the four-membered ring, and any conformational processes observed for these compounds should involve rotations about carbon–nitrogen bonds or inversion at nitrogen.

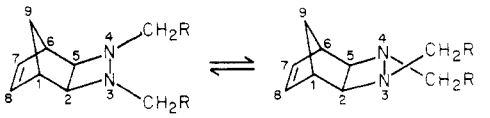
2a, R = C_2H_5O
b, R = C_6H_5
c, R = p-$CH_3OC_6H_4$
d, R = p-$CF_3C_6H_4$

3a, R = H
b, R = C_6H_5
c, R = p-$CH_3OC_6H_4$
d, R = p-$CF_3C_6H_4$

Scheme I



Conformations of 2a–d and 3a–d. Low-temperature ^1H NMR spectra of **3a** display two equal-intensity singlets for *N*-methyl protons that equilibrate on warming. Equilibration of enantiomeric conformations t and t′ by consecutive nitrogen inversions[11] via c and c′ (Scheme I) adequately explain this observation. The use of ^1H NMR spectroscopy for observing changes in **2a–d** and **3b–d**, however, is impossible as a result of extensive coupling and overlap of resonances. Proton-decoupled ^{13}C NMR eliminates this problem. For example, low-temperature ^{13}C NMR spectra of saturated 1,2-diazetidines **3b–d** exhibit two well-resolved, equal-intensity absorptions for each inequivalent carbon pair C-1 and C-6, C-2 and C-5, C-7 and C-8, and the two benzylic carbons. Upon being warmed, these pairs coalesce, attributable to equilibration of enantiomers **3** and **3′** via consecutive nitrogen inversions.

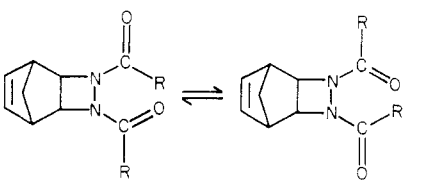


3 **3′**

Intermediate conformations with eclipsed benzylic substituents should be less stable[12] than **3** and **3′** and are not observed in the low-temperature spectra. Figure 1a shows the ^{13}C NMR spectra for alkene carbons C-7 and C-8 for **3b** as a function of temperature.

Carbamate **2a** and hydrazides **2b,c** can exhibit conformational changes involving either nitrogen inversion or rotations about amide bonds. ^{13}C NMR spectra of **2b–d** at −90 °C show two equal-intensity absorptions for carbonyl resonances that equilibrate on warming. Further cooling to −100 °C or below causes no other spectral change. Figure 1b shows the ^{13}C NMR spectra for the carbonyl resonances of **2b** as a function of temperature.

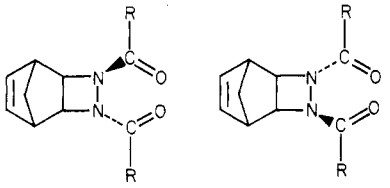
Three explanations for this coalescence phenomenon are conceivable: (1) compounds **2** exist as a pair of rotational isomers with planar nitrogen atoms, e.g., **2e** and **2e′**, that



2e **2e′**

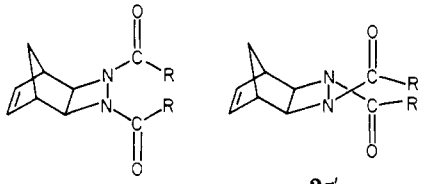
equilibrate by rotations about amide bonds; (2) compounds **2** exist as inversional isomers with a singular rotational conformation, e.g., **2f** and **2f′**, that equilibrate via nitrogen

(7) N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *J. Am. Chem. Soc.*, **91**, 5668 (1969).
(8) M. E. Landis and J. C. Mitchell, *J. Org. Chem.*, **44**, 2288 (1979).
(9) S. F. Nelsen, V. E. Peacock, G. R. Weisman, M. E. Landis, and J. A. Spencer, *J. Am. Chem. Soc.*, **100**, 2806 (1978).
(10) M. E. Landis and J. C. Mitchell, *J. Heterocycl. Chem.*, **16**, 1637 (1979).
(11) J. E. Anderson and J. M. Lehn, *J. Am. Chem. Soc.*, **89**, 81 (1967).
(12) A. Y. Jones, A. R. Katritzky, A. R. Martin, D. L. Ostercamp, A. C. Richards, and J. A. Sullivan, *J. Am. Chem. Soc.*, **96**, 578 (1974).



2f 2f′

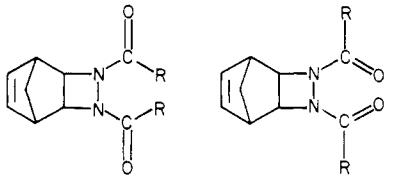
inversion; or (3) hydrazides **2** exist as inversional enantiomers **2g** and **2g′** that equilibrate via consecutive nitrogen



2g 2g′

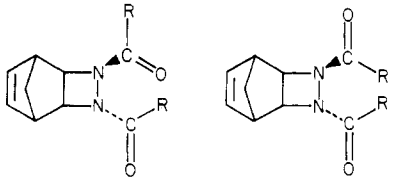
inversions coupled with rapid rotation about amide bonds even at −100 °C.

Explanation 1 seems unreasonable since other rotational isomers are possible, e.g., **2e″** and **2e‴**, and should give rise



2e″ 2e‴

to additional carbonyl resonances in low-temperature spectra. Indeed, for 1,2-dibenzoylpyrazolidine, a mixture of all possible diasteriomeric rotational isomers is observed in low-temperature NMR spectra,[13] and a similar set of diasteriomers would be anticipated for compounds **2**. Interpretation 2 also requires the existence of a sole symmetrical rotational isomer. Other isomers, e.g., **2f″**, **2f‴**,



2f″ 2f‴

and their inversional isomers, are possible and should be observed in low-temperature spectra. As a result, we believe the coalescence phenomenon observed for **2** involve nitrogen inversion with barriers to amide rotations being small.

The temperature-dependent ^{13}C NMR spectra for the carbonyl resonances of carbamate **2a** are provided in Figure 2. The sharp singlet observed at 28 °C broadens and resolves into two absorptions at −65 °C, attributable to freezing nitrogen inversion with rotation about amide bonds still rapid. As the temperature is lowered, rotation about amide bonds slows and eight absorptions are observed at −109 °C. This coalescence phenomenon can be understood in terms of the eight equilibrating conformers shown in Scheme II. In this scheme, **4**, **4′**, **5**, **5′**, **6**, **6′**, and **7**, **7′** are enantiomeric pairs and k_r and k_i represent rates

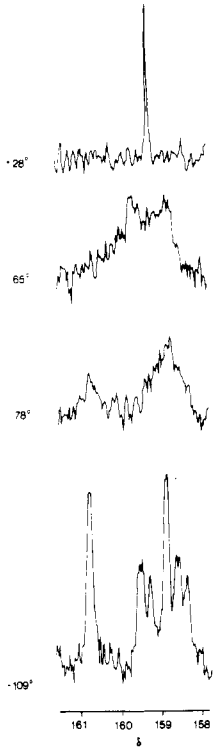


Figure 2. Temperature-dependent ^{13}C NMR spectra for carbonyl carbons of **2a**.

of rotation about amide bonds and rates of inversion, respectively. At 28 °C, k_i and k_r are large and one carbonyl resonance is observed. At −65 °C, k_i is slowed relative to k_r and two absorptions are observed. At −109 °C, both k_r and k_i are slow and eight unique carbonyl resonances can be detected. It is also possible that these spectral changes are associated with rotational isomerism associated with the ethoxy substituent; however, this is unlikely since simple aliphatic esters[14] and N,N-disubstituted carbamates[15] exist as a sole conformer and/or show very low barriers to rotation about the C–O bond.

Activation Parameters. Rate constants (k) for nitrogen inversion in **2b–d** and **3b–d** were determined by simulation of the experimental ^{13}C NMR spectra as a function of temperature (T) using the DNMR/3 program of Binsch and Kleier.[16] Eyring plots of ln (k/T) vs. $1/T$ gave straight lines from which activation enthalpies ($\Delta H^{\ddagger}$), entropies ($\Delta S^{\ddagger}$), and free energies ($\Delta G^{\ddagger}$) were determined. Table I lists these parameters together with coalescence temperatures (T_c) and differences in frequency ($\Delta\nu$) for equilibrating resonances at temperatures where exchange is slow. Corrections in T_2*, the effective transverse relaxation time, were made as a function of temperature.[17] Analyses were performed on resonances where overlap was insignificant. The solvent systems in this study were chosen on the basis of their ability to solubilize the appropriate 1,2-diazetidines at low temperature. The listed errors in the activation parameters represent 95% confidence limits in slope and intercept. Comparing the data for distinct carbons in one compound, e.g., **3b**, we believe the actual error in the activation parameters is larger than those listed (as previously noted by Binsch[18] and Nelsen

(13) S. Caccamese, P. Finocchiaro, P. Maravigno, and G. Montando, *Gazz. Chim. Ital.*, 107, 415 (1977).

(14) M. Oki and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, 44, 3144 (1971).
(15) M. Oki and H. Nakanishi, *Bull. Chem. Soc. Jpn.*, 44, 3148 (1971).
(16) DNMR/3 by G. Binsch and D. A. Kleier available from Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.
(17) O. Yamamoto, M. Yanaglasawa, K. Hayamizer, and G. Kotowycz, *J. Magn. Reson.*, 9, 216 (1973).

Scheme II

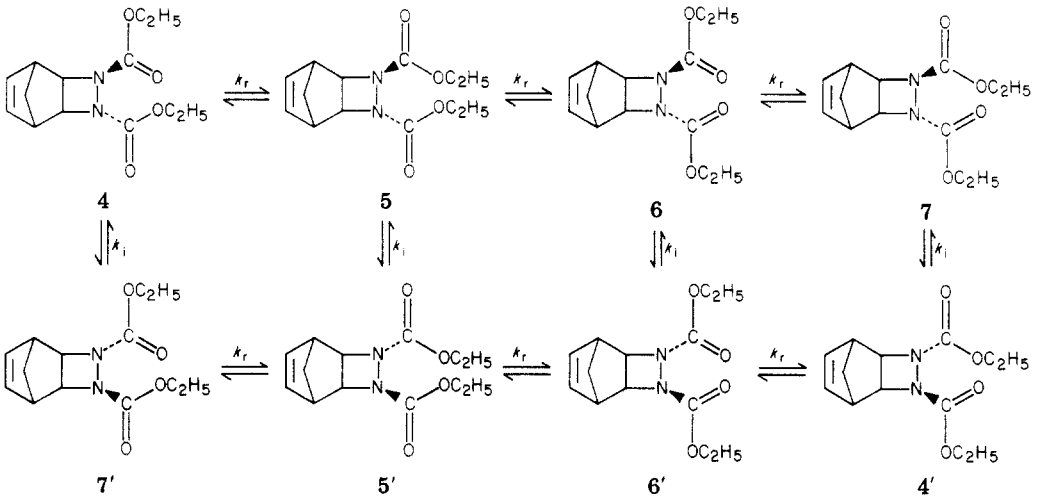


Table I. Activation Parameters for Nitrogen Inversion in 2b–d and 3b–d

compd	resonance analyzed	T_c, °C	$\Delta\nu$	solvent[a]	$\Delta H^{\ddagger}$, kcal/mol[b]	$\Delta S^{\ddagger}$, eu[b]	$\Delta G^{\ddagger}_{298}$, kcal/mol[b]
2b	C-1, C-6	−80	18.4	A	9.7 ± 0.2	−0.3 ± 1.1	9.8
	carbonyl	−70	27.1	A	10.9 ± 0.1	5.0 ± 0.7	9.4
	average			A	10.3 ± 0.2	2.4 ± 0.9	9.6
2c	C-1, C-6	−68	18.0	A	10.7 ± 0.4	0.96 ± 1.9	10.6
	carbonyl	−55	27.9	A	10.8 ± 0.3	0.25 ± 1.8	10.6
	average			A	10.8 ± 0.4	0.63 ± 1.7	10.6
2d	C-1, C-6	−78	14.0	A	10.6 ± 0.4	2.6 ± 2.1	9.8
	carbonyl	−71	27.1	A	11.3 ± 0.3	6.8 ± 1.4	9.3
	average			A	10.9 ± 0.4	4.7 ± 1.4	9.5
3a	NCH_3			B	13.8 ± 0.5	6.7 ± 2.3	11.8
3b	C-2, C-5	−7	74.4	C	14.6 ± 0.8	7.1 ± 2.3	12.5
	C-7, C-8	−18	18.5	C	12.9 ± 0.6	1.1 ± 0.8	12.6
		−15	19.1	A	14.4 ± 0.2	6.3 ± 0.7	12.5
	benzylic	+5	159.4	C	13.7 ± 0.4	4.0 ± 1.4	12.5
		+8	159.8	A	13.3 ± 0.5	2.7 ± 1.8	12.5
	average			C	13.7 ± 0.6	4.1 ± 1.9	12.5
	average			A	13.8 ± 0.5	4.5 ± 1.8	12.5
3c	C-2, C-5	−10	71.0	C	14.9 ± 0.3	9.3 ± 1.3	12.2
	C-7, C-8	−23	17.0	C	13.4 ± 0.3	3.8 ± 1.2	12.2
	average			C	14.2 ± 0.3	6.6 ± 1.3	12.2
3d	C-2, C-5	−10	70.7	C	12.7 ± 0.2	0.6 ± 0.7	12.5
	C-7, C-8	−20	14.7	C	12.0 ± 0.5	−2.1 ± 1.3	12.6
	benzylic	+6	154.0	C	13.4 ± 0.7	2.7 ± 1.5	12.6
	average			C	12.7 ± 0.5	0.4 ± 1.2	12.6

[a] Solvent A is tetrahydrofuran-d_8/dimethylformamide-d_7 (5:1); B is $CFCl_3$; C is toluene-d_8. [b] 95% confidence limits in slope and intercept. [c] By ^1H NMR, from ref 9.

and Weisman[19]). On the basis of the data for **2b** and **3b**, a more realistic estimate of the errors in $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}_{298}$ is ±0.9 kcal/mol, ±3 eu, and ±0.2 kcal/mol, respectively. Systematic errors[18] affect $\Delta S^{\ddagger}$ to the greatest extent and $\Delta G^{\ddagger}$ to the least. As a result, comparisons in $\Delta G^{\ddagger}_{298}$ will be discussed.

Free energies of activation for alkylated diazetidines **3b–d** (12.2–12.6 kcal/mol) are essentially independent of para substituent, indicating the unimportance of inductive effects. Replacement of the benzylic methylene group with a carbonyl (e.g., **2b–d**) causes a significant decrease in the activation barrier (2–3 kcal/mol). This observation is consistent with a planar transition state for the first, rate-determining inversion of nitrogen, stabilized by increased delocalization of the lone pair into the carbonyl moiety. The effect of a para substituent is also small for the series of hydrazides **2b–d**, possibly indicating that the carbonyl is not appreciably delocalized into the aromatic ring at the transition state for the inversion.

The observation that hydrazides **2b–d** undergo nitrogen inversion while **2a** undergoes conformational changes involving inversion coupled with rotation may be a result of steric interactions. The large size[20] of the aromatic substituents in **2b–d** provides significant electrostatic repulsion and imparts increased tetrahedral character to these diazetidine nitrogen atoms relative to other unhindered acyclic amides.[21] The smaller ethoxy substituents[20] in **2a** allow for increased planar character for each nitrogen, and both rotational and inversional changes are observed. Presumably, 1,2-diazetidines with even smaller carbonyl

(18) G. Binsch, "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Eds., Academic Press, New York, 1975, p 76.
(19) S. F. Nelsen and G. R. Weisman, *J. Am. Chem. Soc.*, **98**, 1842 (1976).
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(21) M. B. Robin, F. A. Bovey, and H. Basch, "Chemistry of Amides", S. Patai, Ed., Wiley, New York, 1970, pp 1–72.

Table II. ^{13}C NMR Assignments (δ) for Diazetidines 2a–d and 3b–d

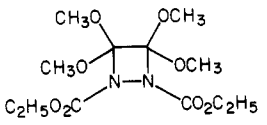
compd	$C_{1,6}$	$C_{2,5}$	$C_{7,8}$	C_9	benzylic	carbonyl	aromatic	other
2a[a]	44.6	62.2	136.1	40.9		159.3		65.3 (OCH_2), 14.8 (CH_3)
2b[b]	46.1	67.2	136.4	41.1		170.9	128.9 129.1 132.2 135.1	
2c[b]	45.9	76.2	136.4	41.0		170.7	114.1 125.8 130.7 163.3	55.7 (OCH_3)
2d[b]	45.9	67.6	136.4	40.9		169.6	126.4 (q, J = 2.7 Hz) 129.7 133.6 (q, J = 35.7 Hz) 137.3	124.9 (q, J = 272 Hz, CF_3)
3b[a]	44.2	64.0	137.0	44.5	60.9		128.1 129.5 130.4 139.8	
3c[c]	43.8	63.4	136.3	44.1	59.7		114.1 130.9 131.0 159.7	54.8 (OCH_3)
3d[c]	43.9	64.2	136.6	44.3	60.5		125.0 (q, J = 4.0 Hz) 129.2 129.4 (q, J = 32.3 Hz) 142.5	124.8 (q, J = 271 Hz, CF_3)

[a] In CF_2Cl_2–acetone-d_6 (1:1). [b] In tetrahydrofuran-d_8/dimethylformamide-d_7 (5:1). [c] In toluene-d_8.

substituents may exhibit rotational isomerism as the highest energy conformational change.

That rotational barriers are apparently higher for **2a** than for **2b–d** cannot be attributed to the ability of the carbonyl to delocalize the nitrogen lone pair of electrons, since the rotational barrier for *N,N*-dimethylbenzamide[22] is larger than that for ethyl *N,N*-dimethylcarbamate.[23] Unfortunately, activation parameters for both processes in **2a** could not be determined since the coalescence temperatures for both changes were similar (between –65 and –80 °C).

Perhaps the difference in conformational changes observed for diethyl tetramethoxy-1,2-diazetidine-1,2-dicarboxylate[3] (**8**; rotational isomerism) and diethyl tetrafluoro-1,2-diazetidine-1,2-dicarboxylate[5] (**9**; inversional isomerism) can be explained on a similar basis. Steric



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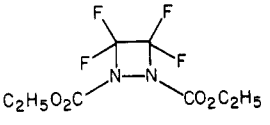

9

interactions between *N*-carboethoxy and ring-methoxy substituents in **8** should be larger than those between ring-fluoro and *N*-carboethoxy substituents in **9**, resulting in increased planar character for nitrogen atoms in **8** relative to those **9**. As a result, the highest energy barriers are rotational in **8** as opposed to inversional in **9**.

(22) See, for example: (a) P. K. Korver, P. J. Van der Haak, Th. J. DeBoer, *Org. Mag. Reson.*, **3**, 605 (1971); (b) K. C. Ramey, D. J. Louick, P. W. Whitehurst, W. B. Wise, R. Rabindranath, R. M. Moriarty, *ibid.*, **3**, 201 (1971).

(23) P. Stilbs, *Tetrahedron*, **29**, 2269 (1973).

Experimental Section

Hydrazides **2a–d**[7,8] and hydrazines **3a–d**[9,10] were prepared as previously described. All ^{13}C NMR spectra were recorded on a JEOL FX-60Q NMR spectrometer at 15 MHz.

^{13}C NMR Studies. Carbon NMR assignments for **2a–d** and **3b–d** were made by using decoupled and off-resonance decoupled spectra (Table II). All variable-temperature work was done with a JEOL NM 5471 variable-temperature controller with a copper-constatan thermocouple and digital readout to ±1 °C. Solutions of diazetidines **2b–d** in tetrahydrofuran-d_8/dimethylformamide-d_7 (5:1 v/v) were 0.2 M, and solutions of **3b–d** in toluene-d_8 were 0.33 M. All spectra were obtained on samples contained in tightly capped 10-mm (o.d.) NMR tubes. The spectral resolution was never less than 0.5 Hz per point. Typically, suitable spectra were obtained after 300–500 accumulations with pulse repetitions of 3-s and 5-μs pulse width.

Rate constants were determined by spectral simulation using the DNMR/3 program of Binsch and Kleier[16] adapted for a CDC-Cyber 72 computer and Hewlett-Packard 7200A plotter. Simulated spectra were compared visually with experimental spectra with resonances where overlap was insignificant. Linear least-squares analyses of the plots of ln (k/T) vs. $1/T$ were used to determine ΔH^* and ΔS^*. Correction for T_2^* was made as a function of temperature,[17] and a transmission coefficient[11] of $^1/_2$ was used for all compounds.

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