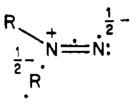
J. Org. Chem. **1980**, *45*, 3609-3613

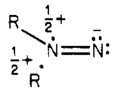
L-strain simultaneously increases from 0 to 55° (both remaining unchanged in the radical R′NN·); (2) the NNR angle changes little during reaction, the N–R bond simply lengthening; (3) the more advanced leaving group (sp_3 carbon in the GS) planarizes at the MPRC with concomitant increase of internal bond angles from 109.5° to 120° (see **18** and eq 8) but moves partially back in the product radical **17**; (4) this leaving group acquires a transient partial negative charge, and the β-nitrogen a partial positive charge, at the MPRC.

For cases not yet studied, it can therefore be predicted that the reaction will be facilitated by anything that favors these changes, and vice versa. Examples have been given of retardation arising from resistance to planarization, R′NN angle increase and R′N L-strain, and of charge effects. One predicts further that resistance to increase of internal bond angles in the leaving group, e.g., if it is a small ring (including a two-membered ring, i.e., a double bond), will retard reaction.

The above principles should also apply to other homolyses in which the atom β to the primary leaving group is a heteroatom, such as the decomposition of 1,1-diazenes,[48] in which the best MPRC is **22** rather than **23**.

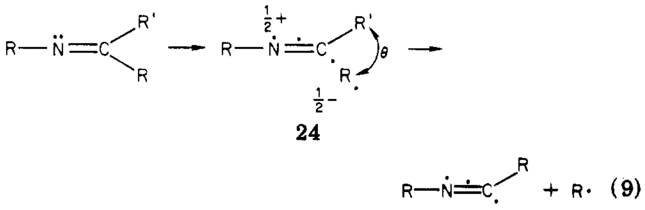


22



23

Although the β-situated atom must have unshared electrons in order to have MPRC's like **15** and **22** be favored, the α atom need not. Thus the above principles should also apply to reaction 9, with the added feature that angle θ shrinks from about 120° in the GS to about 90° at the MPRC, offering an additional opportunity for testing. Although this reaction should have an E_a ca. 23 kcal/mol higher than that for the correspondingly substituted azo compound,[49] it might be observable.



24

(9)

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(48) W. D. Hinsberg III and P. B. Dervan, *J. Am. Chem. Soc.*, 101, 6142 (1979); P. G. Schultz and P. B. Dervan, *ibid.*, 102, 878 (1980).

(49) Comparing **20** with **24**, which has the same array of electrons around the five-electron bond: Δ(bond E) for N═N → N≐N exceeds that for N═C → N≐C by 13 kcal/mol;[50] C–R′ in **24** has 55° L-strain, 6 kcal/mol (including secondary L-strain);[19] Δ(bond E) for C–C → C·C minus N–C → N·C, 4 kcal/mol,[50] assuming that a one-electron bond equals half a bond.

(50) R. A. Firestone, *J. Chem. Soc. A*, 1570 (1970), Table 2.

Conformational Effects on Tetraalkylhydrazine Nitrogen-15 Nuclear Magnetic Resonance Chemical Shifts

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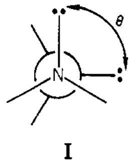
^{15}N NMR chemical shifts are reported for 22 tetraalkylhydrazines. For seven acyclic compounds, a plot of δ_N vs. δ_C (^{13}C NMR shift at CH for the hydrocarbon analogue of the hydrazine, with N replaced by CH) is a fairly good straight line: $\delta_N = 1.98_5\delta_C - 67.5_8$ ($r = 0.99$, average deviation 0.8 ppm). Cyclic hydrazines, especially those which have the lone pair–lone pair dihedral angle held near 180 or 0°, show considerable deviations from this line. It is suggested that the amount of flattening at nitrogen has a significant effect on δ_N.

We report the ^{15}N NMR chemical shifts (δ_N values) of several tetraalkylhydrazines in this paper. Lichter and Roberts[1] have previously discussed δ_N values for tetramethylhydrazine and several less alkylated hydrazines, but we were interested in determining whether δ_N is sensitive to the lone pair–lone pair dihedral angle θ (see I). Acyclic hydrazines electronically prefer, and exist in, $\theta \approx 90°$ conformations,[2] but the steric effects accompanying incorporation of the hydrazine unit into cyclic structures cause cyclic tetraalkylhydrazines to assume conformations with θ varying between 0 and 180°, as has been demonstrated by studies employing photoelectron spectroscopy (PES),[3,4] low-temperature ^{13}C NMR[5] spectroscopy, and X-ray crystallography.[6] The compounds studied here were



I

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(1) Lichter, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 4904.

(2) Shvo, Y. "The Chemistry of Hydrazo, Azo, and Azoxy Groups"; Patai, S., Ed.; Wiley: New York, 1975; Part 2, p 1017.

(3) (a) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1973**, *95*, 2011. (b) Nelsen, S. F.; Buschek, J. M.; Hintz, P. J. *Ibid.* **1973**, *95*, 2013. (c) Nelsen, S. F.; Buschek, J. M. *Ibid.* **1974**, *96*, 2392. (d) Nelsen, S. F.; Buschek, J. M. *Ibid.* **1974**, *96*, 6982. (e) Nelsen, S. F.; Buschek, J. M. *Ibid.* **1974**, *96*, 6987. (f) Nelsen, S. F.; Peacock, V. E.; Weisman, G. R. *Ibid.* **1976**, *98*, 5269. (g) Nelsen, S. F.; Peacock, V. E.; Kessel, C. R. *Ibid.* **1978**, *100*, 7017.

(4) (a) Rademacher, P. *Angew. Chem.* **1973**, *85*, 410. (b) Rademacher, P. *Tetrahedron Lett.* **1974**, 83. (c) Rademacher, P. *Chem. Ber.* **1975**, *108*, 1548. (d) Rademacher, P.; Koopman, H. *Ibid.* **1975**, *108*, 1557.

(5) (a) Nelsen, S. F.; Weisman, G. R. *J. Am. Chem. Soc.* **1976**, *98*, 1842. (b) Nelsen, S. F.; Weisman, G. R. *Ibid.* **1976**, *98*, 3281. (c) Weisman, G. R.; Nelsen, S. F.; *Ibid.* **1976**, *98*, 7007.

(6) Nelsen, S. F.; Hollinsed, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4461.

0022-3263/80/1945-3609$01.00/0

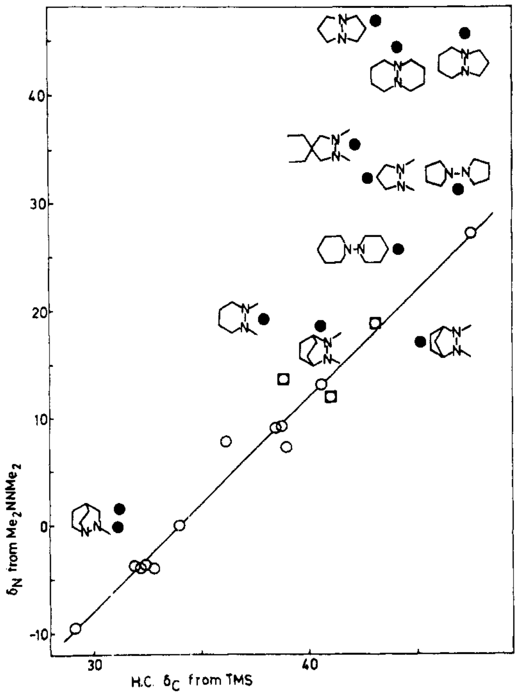

Figure 1. δ_N vs. δ_C for the hydrocarbon with N replaced by CH for the tetraalkylhydrazines of Table I: open circles, acyclics for which δ_C has been experimentally measured (entries 1–7); open squares, acyclics for which δ_C was estimated; solid circles, cyclic compounds.

chosen to include examples with a range of θ values.

Results

The δ_N values for 22 tetraalkylhydrazines studied here are given in Table I. By analogy with the work of Roberts and co-workers[7] on alkylamines, we also report the ^{13}C NMR chemical shifts for the CH carbons of the hydrocarbon analogues which have N replaced by CH (δ_C values). Roberts and co-workers found that an excellent straight line was produced by plotting δ_N vs. δ_C for primary amines ($r > 0.99$), implying that the same structural factors influence δ_N as δ_C and establishing that the hydrocarbon analogues are valuable models for the amines. They found roughly linear δ_N vs. δ_C correlations for acyclic tertiary amines, but more scatter was observed ($r = 0.91$–0.95).[7c] Alkylated piperidines and protonated amines gave similar plots.[7d]

As for amines, δ_N for hydrazines is more sensitive to structural changes than is δ_C. The δ_N range in Table I is 56.2 ppm, and the δ_C range is 18.3 ppm. The δ_N vs. δ_C plot for tetraalkylhydrazines, however, is decidedly nonlinear (see Figure 1). The rest of this paper is devoted to attempting to understand why such extensive scatter is observed.

Discussion

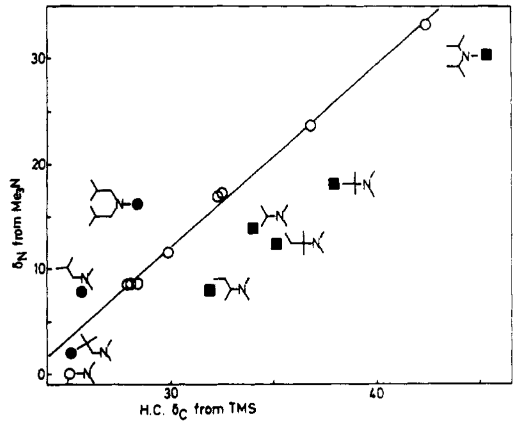

Figure 2. δ_N vs. δ_C plot for acyclic tertiary amines, from the data of Duthaler and Roberts:[7c] the open circles are α- and β-unbranched compounds.

The 12 points for seven acyclic hydrazines (entries 1–7 in Table I, open circles in Figure 1) give a good straight line in Figure 2 (the least-squares line shown is $\delta_N = 1.98_5\delta_C - 67.5_8$ ($r = 0.99$, average vertical deviation 0.8 ppm). Compounds **8**–**10** are acyclic hydrazines for which δ_C values are not experimentally available. They have been placed on the plot (as open squares) by use of estimated[8–10] values and fall close to the line through the points for **1**–**7**. In contrast to the acyclic compounds, cyclic hydrazines (solid circles) show a great deal of deviation from the line in Figure 1.

We wish to point out that the lone pair–lone pair dihedral angle θ appears to have a definite influence upon the size of the deviation observed from the acyclic line in Figure 1. It has been known since the 1930's that acyclic hydrazines have the electronically preferred gauche (actually, near $\theta = 90°$) orientation of their lone pairs.[2] PES has been shown to be a convenient experimental method for study of the lone pair–lone pair dihedral angle in hydrazines,[2,3] because the separation of the lone pair combination orbital ionization potentials, Δ, is sensitive to θ when θ is far from 90°. There is a broad minimum in a Δ vs. θ plot between about $\theta = 75$ and $100°$, where values of $\Delta = 0.53 \pm 0.2$ eV are observed,[3f] but Δ follows a rough cos θ dependence outside of this range, rising to about 2.3 eV at $\theta = 0$ and $\theta = 180°$. The Δ values for hydrazines **1**–**22** are included in Table I, along with estimates for θ taken from the literature.[3,5,6]

Compounds **14** and **15** are indicated to exist exclusively in anti-fused conformations ($\theta = 180°$)[6] by both PES[3e] and ^{13}C NMR[5] data. They show large vertical deviations from the line in Figure 1 (Dev values) of +24.2 and +18.9 ppm, respectively. These large Dev values seem to be associated with the $\theta = 180°$ conformation. **13**, which shares the structural feature of a hexahydropyridazine ring with **14** and **15** but has been shown to exist as a mixture of about 60% $\theta \approx 180°$ and 40% $\theta \approx 60°$ conformations,[5b] has a considerably lower Dev value of +11.3 ppm. The other compounds which show large Dev values also occupy

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[7] (a) Lichter, R. L.; Roberts, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 2495. (b) Duthaler, R. O.; Williamson, K. L.; Giannini, D. D.; Bearden, W. H.; Roberts, J. D. *Ibid.* **1977**, *99*, 8406. (c) Duthaler, R. O.; Roberts, J. D. *Ibid.* **1978**, *100*, 3889. (d) Duthaler R. O.; Roberts, J. D. *Ibid.* **1978**, *100*, 3882.

[8] Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245.

[9] Values of 38.5 and 39.5 ppm are reported[8] for the two diastereomers of the hydrocarbon.

[10] Estimated from additive parameters.[8] We subtracted δ 0.6 from the values calculated, as the values thus calculated were consistently high, averaging δ 0.6 for 16 examples in their paper.[8]

[11] Dalling, D. K.; Grant, D. M. *J. Am. Chem. Soc.* **1967**, *89*, 6612. This value was calculated from the shifts of these authors for *trans*- and *cis*-1,2-dimethylcyclohexanes by using the 58% equatorial–equatorial, 42% axial–equatorial conformational mixture determined by the ^{13}C NMR for the hydrazine at room temperature in ref 5b.

[12] For *trans*-decalin: Dalling, D. K.; Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1973**, *95*, 3718. A value of 44.9 ppm has also been reported: Lippmaa, E.; Pekh, T. *Eesti NSV Tead. Akad. Toim., Keem, Geol.* **1968**, *17*, 287; *Chem. Abstr.* **1969**, *69*, 15795.

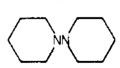
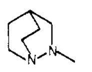
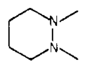
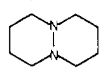
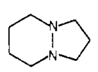
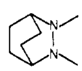
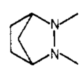
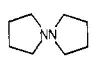
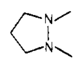
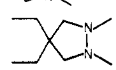
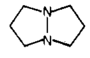
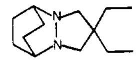
[13] Lippmaa, E.; Pekh, T.; Paasivirta, J.; Belikova, N.; Plate, A. *Org. Magn. Reson.* **1970**, *2*, 581.

[14] Christl, M.; Reich, H. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 3463.

[15] Estimated by using the upfield shift of 0.6 ppm at C_3 of 1,1-dimethylcyclopentane relative to that of cyclopentane.[14]

[16] Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* **1977**, *42*, 3878.

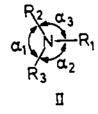
Table I. Comparison of Hydrazine ^{15}N Shifts with ^{13}C Shifts for Their Hydrocarbon Analogues (N → CH)

no.	compd	δ_N,[a] ppm	δ_C,[b] ppm	Dev,[c] ppm	Δ,[d] eV	estim θ, deg
1	Me_2NNMe_2	0	34.0[e]	0.1	0.55	~90
2	$Me_2NNMeEt$	−3.8 13.1	31.9[e] 40.6[e]	0.5 0.1	0.53	~90
3	EtMeNNMeEt	7.3	39.0[e,f]	−2.5	0.51	~90
4	Me_2NNEt_2	−9.5 27.2	29.1[e] 47.6[e]	0.3 0.3	0.52	~90
5	Me_2NNMe-*n*-Pr	−4.0 9.1	32.8[e] 38.5[e]	−1.5 0.3	0.51	~90
6	Me_2NNMe-*n*-Bu	−3.9 9.2	32.2[e] 38.8[e]	−0.2 −0.2	0.54	~90
7	Me_2NNMe-*i*-Bu	−3.7 7.8	32.4[e] 36.2[e]	−0.4 3.5	0.55	~90
8	Et_2NNEt_2	18.8	[43.1][g]	0.8	0.51	~90
9	*n*-Pr_2NN-*n*-Pr_2	13.6	[38.9][g]	4.0	0.60	~90
10	*i*-PrMeNNMe-*i*-Pr	12.0	[41.0][g]	−1.8	0.52	~90
		25.7	44.2[h]	5.5	0.52	~90
12		−0.1 1.6	31.1[i] 31.2[i]	5.7 7.2	0.51	~75
13		19.2	38.0[j]	11.3	mixture	mixture
14		+44.4	44.2[k]	24.2	2.32	180
15		+45.4	47.4[l]	18.9	2.31	180
16		18.5	40.6[i]	5.5	1.82	~140
17		17.0	45.2[m]	−5.1	1.78	>120
18		31.2	47.0	5.5	0.56	~90
19		32.3	42.8[n]	14.9	mixture	mixture
20		33.5	42.2[o]	19.3	2.38	large
21		46.7	43.2[p]	28.5	1.57	~30
22		25.8			2.32	~0

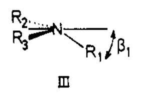
[a] Reported in parts per million downfield from tetramethylhydrazine (**1**) which appears 303.6 ppm upfield from internal nitromethane (see Experimental Section). For **2** and **4–7**, the top δ_C refers to the CH replacing the first nitrogen in the structure written and the bottom one the second nitrogen. The nitrogen shifts were assigned to correspond. [b] Reported in parts per million downfield from internal tetramethylsilane. [c] Dev = $\delta_N - 1.98_5\delta_C + 67.58$, the downfield shift of δ_N from the line through the values for **1–7**. [d] Reference 2, reproducibility estimated at +0.03 eV. [e] Reference 8. [f] Reference 9. [g] Estimated value, see reference 10. [h] Determined in this work. [i] Reference 4a. [j] Reference 11. [k] Reference 12. [l] Reference 4c. [m] Reference 13. [n] Reference 14. [o] Reference 15. [p] Reference 16.

conformations which have large lone pair–lone pair interactions, as shown by their photoelectron spectra. The only detected conformation for pyrazolidine derivative **20** (Dev = +19.3 ppm) has pseudo-axial lone pairs,[3e] as does the major conformation for pyrazolidine **19** (Dev = 14.9 ppm). 1,5-Diazabicyclo[3.3.0]octane (**21**) has the largest Dev value observed (+28.5 ppm), and is known to cis fused in solution;[17] its θ value was estimated to be 30° from its photoelectron spectrum.[3e] Cyclic tetraalkylhydrazines which have gauche lone pairs, **11**, **12**, and **18**, show smaller positive Dev values ranging from +5.5 to +7.2 ppm.

We believe that these data establish empirically that when structural constraints of cyclic hydrazines force them into conformations with large lone pair–lone pair interactions (θ far from 90°, resulting in PES Δ values much larger than the 0.5 eV observed for the $\theta \approx 90°$ tetraalkylhydrazines), large positive Dev values are observed. We wish to suggest that the change in hybridization at nitrogen which is known to accompany rotation about the NN bond to θ = 180° is principally responsible for the large Dev value. Hybridization changes at amino nitrogen atoms are reflected in the degree of pyramidality of the nitrogen. For asymmetrically substituted nitrogen atoms, such as those of hydrazines, it is convenient to discuss pyramidality at nitrogen in terms of the average RNR′ bond angle, α_{av}, or the average angle between the R′NR″ plane and the RN line, β_{av}. For definitions of α and β, see II and III. α_{av}



II



III

is $^1/_3\,(\alpha_1 + \alpha_2 + \alpha_3)$, and $\beta_{av} = {}^1/_3\,(\beta_1 + \beta_2 + \beta_3)$. To an excellent approximation, $\cos\beta_{av} = [\cos(180 - \alpha_{av})]/[\cos(\alpha_{av}/2)]$. The sizes of α_{av} and β_{av} are significantly different for gauche and anti hydrazines, as shown by the X-ray

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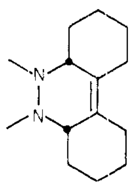
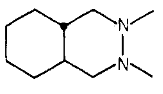
(17) Lehn, J. M. *Fortschr. Chem. Forsch.* **1970**, *10*, 311.

structures of **23** and **24**,[6] for which pertinent data are



23

$\theta = 70\text{–}74°$
$\alpha_{av} = 110.9°$ (NMe_{ax}), 112.2° (NMe_{eq})
$\beta_{av} = 51.0°$ (NMe_{ax}), 47.4° (NMe_{eq})
$d_{NN} = 1.45_0$ Å



24

$\theta = 178\text{–}179°$
$\alpha_{av} = 107.7, 107.4°$
$\beta_{av} = 59.0, 59.6°$
$d_{NN} = 1.48_6$ Å

summarized below the structures. Compound **24** has the electronically disfavored anti ($\theta \approx 180°$) lone-pair conformation, and the result is an NN bond length increase and significantly more pyramidal nitrogen atoms (β_{av} increases by about 10°). These changes minimize lone pair–lone pair overlap in the $\theta \approx 180°$ conformation (or maximize lone pair–θ^*_{CN} overlap in the $\theta \approx 70°$ conformation[18]) and are predicted by MO calculations[19] to occur when conformations far from $\theta = 90°$ are assumed. Changes in the degree of pyrimidality at nitrogen are, of course, changes in the hybridization at nitrogen, and δ_N is expected to be sensitive to such changes. MINDO/3 calculations[19] suggest that the nitrogen charge density is sensitive to β_{av}, the calculated ρ_N decreasing as β_{av} increases for trimethylamine, aniline, and hydrazine. MINDO/3 calculations are not accurate enough for correlation with NMR chemical shifts, but we believe that the direction of the change predicted, an increase in δ_N as β is increased, is significant.

A significant hybridization effect on δ_N has not been discussed, despite considerable previous work on the ^{15}N NMR of amino nitrogen compounds, but because of the substantial lack of knowledge about the degree of pyramidality at nitrogen in such compounds, this does not seem particularly surprising. The extensive alkylamine data reported by Roberts and co-workers[7] can also be construed as supporting the idea of a significant effect of amino nitrogen hybridization upon ρ_N. Their δ_N vs. δ_C plot for 14 primary alkylamines shows a good fit ($r = 0.998$) to the line δ_N(from Me_3N) $= 2.06\delta_C - 10.53$, but considerably more scatter was seen for 17 acyclic tertiary amines, for r was only 0.906. These tertiary amine data (in cyclohexane as solvent) are replotted in Figure 2 with δ_N in parts per million downfield from Me_3N to correspond with the hydrazine plot of Figure 1. The open circles in Figure 2 represent eight α- and β-unbranched compounds, which lie on a good straight line [$r = 0.998$ for δ_N(from Me_3N) $= 1.74\delta_C - 40.22$]. Trimethylamine lies significantly below this line (see below) and was not used in its calculation. We note that the five α-branched amines (squares in Figure 2) show significant negative vertical deviations from the line (average Dev = −7.4 ppm). The strain introduced by having α branching might well be expected to introduce flattening at nitrogen. Although α branching did not cause negative deviations in the δ_N vs. δ_C plot for primary amines, they are significantly less sterically hindered and would be expected to show less flattening. Flattening at nitrogen is clearly not the only factor causing the δ_N vs. δ_C plot not to be linear. The β-branched compounds (solid circles in Figure 2) illustrate this. The isobutyl-substituted compounds show significant positive deviations (Dev = 3.3 and 6.9). β branching surely affects the distribution of $lpN,C_\alpha C_\beta$ rotamers and thus the degree of lone pair–σ system interaction. As Roberts and co-workers suggested,[7] such conformational differences are expected to affect ρ_N. In another spectroscopic measurement, isobutyl-substituted hydrazines and 2-tetrazenes show detectable effects on their lone-pair ionization potentials compared to the less conformationally restricted n-alkyl compounds.[3g] The negative Dev for trimethylamine, which lacks $C_\alpha C_\beta$ bonds, could involve such factors. The direction of the $C_\alpha C_\beta$ rotamer effect and the sterically induced flattening at nitrogen effect on δ_N are opposite in sign. In this context, the N-alkylpiperidine data[7d] make an interesting comparison with the acyclic amine data. Twelve alkylpiperidines give a δ_N vs. δ_C line ($r = 0.991$) of the form δ_N (from Me_3N) $= 1.65_6\delta_C - 30.20$ (average deviation 1.0 ppm). These data lie nearly parallel with the acyclic trialkylamine line but an average of 7.4 ppm above it. In piperidines, two $C_\alpha C_\beta$ bonds are held by the ring in a gauche arrangement with the nitrogen lone pair. Positive deviations are observed for the isobutyl compounds, where such conformations are sterically favored relative to β-unbranched compounds. In our hydrazine data, inclusion of rings in the structure, even when θ remains gauche as for **11**, **12**, and **18**, resulted in positive Dev values of similar magnitude.

Evidence for a negative Dev accompanying flattening at nitrogen is also apparent in the N-alkylpiperidine data. N-Isopropylpiperidine has a Dev (from the N-alkylpiperidine line) of −3.8 ppm, compared to +0.5 ppm for N-ethylpiperidine, and 2-methyl-2-azaadamantane, which is forced to have an axial N-methyl group, has a Dev = −10.4 ppm.

Conclusions

Our data suggest strongly that nitrogen-flattening (hybridization) effects are an important factor in determining δ_N. The interplay between sterically induced flattening, the bending induced by the large lone pair–lone pair interaction in hydrazines with θ values far from 90° and shifts caused by lone pair–σ_{CC} interactions, is obviously complex. We are certainly in no position to understand why **16** shows a positive Dev value and **17** a negative one, for example.

Consideration of δ_N vs. δ_C plots can only give information about hybridization changes at nitrogen relative to those which occur at carbon in the related hydrocarbon. The degree of flattening at carbon is more sensitive to substitution charges than might once have been thought, as is becoming clear from recent work by the groups of Ingold,[20], Rüchardt,[21] Mislow,[22] Lüttke,[23] and Ritter.[24] There is even enough flattening in a 2,3-dimethylbutane to cause the gauche HC_2–C_3H conformation to be present in higher concentration than the anti conformation, which would predominate in the absence of such flattening. Empirical force field calculations are an excellent way of quantitating

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sterically induced flattening in hydrocarbons.[21,22]

The data reported here indicated that hybridization at nitrogen is an important factor in determining δ_N, a hypothesis which ought to be tested on other amino compounds. Because the amount of pyrimidality at nitrogen is quite difficult to measure experimentally (a complete structure determination is now required), better understanding of the various factors influencing δ_N could ultimately promote a spectroscopic way of estimating the hybridization at nitrogen, which we expect to be important in determining the reactivity of amino compounds.

Experimental Section

Natural-abundance ^{15}N Fourier transform NMR spectra were obtained on a Varian XL-100-15 spectrometer equipped with a V4412 (12 mm) probe and a Varian FT data system using the GyroObserve option. Spectra were recorded at a spectral width of 5120 Hz, and 4096 data points (1.25 Hz/point) were obtained. A pulse width corresponding to a 30° flip angle was used at a 1.6–2.0-s repetition rate. Sample concentration was typically 1.5–3.0 M in 1/1 (v/v) acetone-d_6/nitromethane. This solvent mixture provided both the internal deuterium lock and nitromethane reference.[25] The solutions were approximately 0.085 M in Cr(acac)$_3$ to shorten relaxation times. Sample volumes of 2–3 mL were employed. Adequate signal-to-noise ratios were observed for 3 M hydrazine samples having two equivalent nitrogens in 4 h; more dilute samples required up to 16 h of data acquisition.

The observed ^{15}N chemical shifts are internally consistent to ±0.2 ppm relative to CH_3NO_2. While we recognize the deficiencies of internal standards for accurate and reproducible absolute chemical shift determination,[26] we feel that for compounds of similar structural type run under similar conditions these conditions provide the most consistent and convenient means of obtaining relative shifts. A study of chemical shift changes with substrate concentration was undertaken for 1,2-dimethyl-1,2-diethylhydrazine, in which a 0.2-ppm downfield shift was observed when the hydrazine concentration was increased from 1.3 to 2.7 M at a constant Cr(acac)$_3$ concentration of 0.087 M. Almost all of our hydrazine samples fall in this concentration range. The effect of paramagnetic relaxation reagents on ^{15}N shifts has been noted.[25] The circumvention of such effects by using internal referencing has been found to be quite adequate. Varying the concentration of Cr(acac)$_3$ from 0.05 to 0.10 M resulted in less than a 0.1-ppm change in the chemical shift for both nitrogens of isobutyltrimethylhydrazine relative to internal nitromethane, but a 0.6_6-ppm upfield shift relative to external $D^{15}NO_3$ [the hydrazine chemical shift was 294.1_8 ppm upfield from external $D^{15}NO_3$, 1.0 M in D_2O, which is 4.3_3 ppm upfield from neat external nitromethane, and the hydrazine shift was 295.7_0 ppm upfield from internal nitromethane, all experiments quoted being at 0.10 M Cr(acac)$_3$].

^{13}C NMR spectra were obtained at 15.9 MHz on a JEOL FX-60 spectrometer.

The tetraalkylhydrazines were prepared by previously reported methods.[3,5] Purification and drying was performed by distillation and/or allowing the sample to stand over NaOH pellets. Solids were crystallized or sublimed, as appropriate.

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Registry No. **1**, 6415-12-9; **2**, 50599-41-2; **3**, 23337-93-1; **4**, 21849-74-1; **5**, 60678-65-1; **6**, 52598-10-4; **7**, 68970-04-7; **8**, 4267-00-9; **9**, 60678-69-5; **10**, 60678-71-9; **11**, 6130-94-5; **12**, 6523-29-1; **13**, 26163-37-1; **14**, 3661-15-2; **15**, 5721-43-7; **16**, 14287-92-4; **17**, 14287-89-9; **18**, 18389-95-2; **19**, 38704-89-1; **20**, 74096-71-2; **21**, 5397-67-1; **22**, 23211-28-1; **23**, 60387-16-8; **24**, 63892-83-1.

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Molecular Asymmetry in *trans*-Thiacycloalkenes. 2. Barriers to Interconversion of Diastereomeric Conformers of 2-Substituted Nine- to Eleven-Membered (*E*)-Thiacycloalk-4-enes[1]

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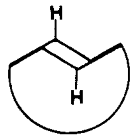
trans-Thiacycloalk-4-enes of ring size 9 to 11 carrying a substituent (CH_3 or $COOCH_3$) at C_2 were synthetized. These species have two elements of chirality (a plane and a center) and exist as diastereomeric pairs which may interconvert via a conformational process (180° revolution of the π plane inside out the ring). The energy barrier for this process has been measured by dynamic ^{13}C NMR and found to be 16.4, 10.7, and 8.3 (or 7.0) kcal/mol for the 9-, 10-, and 11-membered-ring compound, respectively, lower than those for their carbocyclic analogues. The lower barriers may arise from the heteroatom across the ring, which, unlike the corresponding carbon in the homocyclic counterpart, carries no ligand and allows for less steric compression in the transition state.

Eight-membered and larger rings may accommodate a double bond of *E* configuration. Rings having this feature are chiral enantiomeric pairs[2] whose interconversion occurs through configurational inversion of a chiral plane. This process requires a 180° rotation of the sp^2 plane around the σ bonds adjacent to the π bond and involves the passage of one of the olefinic hydrogens inside out the ring via a transition state in which the olefinic H was moved against the atoms across the ring and the ligands thereon.



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