Conformational Studies by Dynamic Nuclear Magnetic Resonance. Part 20.[1] Internal Motion in Hydrazones and Related Derivatives

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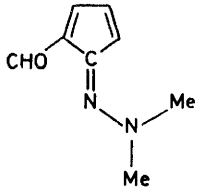
Restricted rotation about the N–N bond in unhindered, non-conjugated hydrazones (*e.g.* $Me_2N–N=CH_2$) has been detected by ^{13}C n.m.r. below −150 °C. The results indicate that the N=C plane is coplanar with the dynamically averaged plane of the sp^3 nitrogen, in contrast with hindered hydrazones (containing the 2,2,6,6-tetramethylpiperidinyl ring, TMP) where the N=C moiety adopts a perpendicular conformation. Effects due to the slowing of ring reversal were not observed in hydrazones containing the TMP ring, but were detected in other hindered derivatives such as TMP–NH_2 and TMP–NO. A most interesting feature becomes apparent in two hydrazones with the 2,6-*cis*-dimethylpiperidinyl (DMP) ring, DMP–$N=CH_2$ and DMP—N=CHPh. In the same molecule the N=C moiety is coplanar with the averaged sp^3 nitrogen plane when the methyls are axial, but perpendicular when the methyls are equatorial.

BROADENING of the linewidth due to internal motion was first reported in hydrazones by Mannschreck *et al.*[2] who detected anisochronous methyl signals in derivative (1) at low temperature. This was attributed to restricted NN rotation ($\Delta G^{\ddagger}$ 11.8 kcal mol^{-1}) due to the contributions of conjugated forms of types B and C. When



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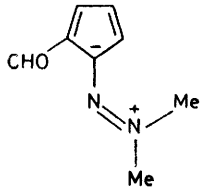

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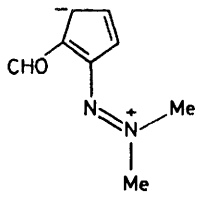

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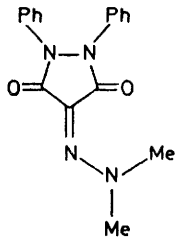
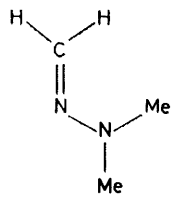


(2)

the negative charge is delocalized even more, the methyls become anisochronous at room temperature,[3] as in (2). The activation free energy for rotation thus increases[3] to 17.7 kcal mol^{-1}. On the other hand, in simple, non-conjugated hydrazones such as methylideneamino-(dimethyl)amine (3) restricted NN rotation has not, so far, been detected; it was inferred[4] that its $\Delta G^{\ddagger}$ value was probably lower than 6 kcal mol^{-1}. A number of hindered, non-conjugated hydrazones containing the 2,2,6,6-tetramethylpiperidinyl (TMP) ring, for instance 2,2,6,6-tetramethyl-1-(1-methylethylideneamino)-piperidine (4), do show, however, two pairs of diastereotopic ring methyls, in some cases even at room temperature.

This phenomenon was found[4,5] to depend on restricted rotation about the NN bond in *perpendicular* conformers (the C=N plane being orthogonal to the dynamically averaged plane of the sp^3 nitrogen) and should not be confused with restricted rotation in *coplanar* hydrazones. The results so far available on the stereodynamics of hydrazones can be summarized as follows: (i) conjugated hydrazones have coplanar conformations and restricted rotation has been reported;[2,3] (ii) hindered, non-conjugated hydrazones, have perpendicular conformations: NN rotation has been also detected;[4,5] (iii) non-conjugated, unhindered hydrazones are likely to have planar conformations but this cannot be unambiguously



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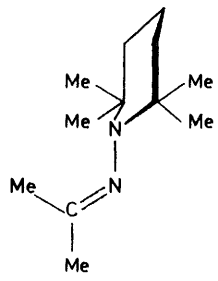

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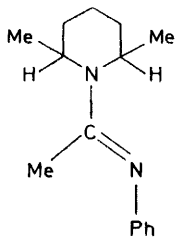

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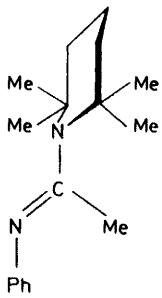


(6)

ascertained since direct evidence for restricted motion is still lacking.

Recently we showed that some amidines can adopt either a planar (5) or a perpendicular (6) conform-

ation, in the sense previously described, depending on the extent of the steric effect (see ref. 3).

The aim of this work is to show that non-conjugated hydrazones can also be driven to adopt either a planar or a perpendicular conformation by modifying the extent of the steric hindrance. An even more interesting and novel feature has been also pursued in this work, the direct observation of planar and perpendicular arrangements not only, as in amidines (5) and (6), in two different *molecules* of the *same class*, but also in two different *conformers* of the *same molecule*.

TABLE 1

^{13}C Chemical shifts (p.p.m. from Me_4Si) of compounds (3), (4), (7), and (9)—(16) at various temperatures

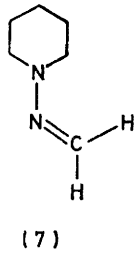
Compound	Solvent	t/°C	C-2, -6	C-3, -5	C-4	2-, 6-Me	Other	C=N
(3)	CHF_2Cl–$CHFCl_2$	−145					43.2	127.8
		−156					39.4, 47.0	127.8
(7)	CHF_2Cl	−100	52.1	25.9	24.6			126.4
		−163	48.3, 55.5	25.5	23.7			127.6
	C_6D_6	+25	56.9	40.3	18.0	19.9, 32.9	19.5, 24.6	171.6
(4)	CHF_2Cl	−100	57.3	40.7	18.0	20.9, 32.7	20.65, 24.8	176.4
(9)	CHF_2Cl	−100	57.0	40.2	17.5	27.0		155.8
		−130	57.2	40.0	17.9	20.7, 33.7		157.5
(10)	CHF_2Cl	−40	50.7	39.0	18.7	31.4		
		−130	50.3	38.4	18.3	27.1, 34.8		
(11)	Me_2O	−60	57.3	41.1	18.1	26.0		
		−120	57.4	40.8	18.2	18.2, 33.3		
(12)	CHF_2Cl	−115	64.3, 62.7	42.6, 39.6	17.0	26.4 (2 Me), 32.1 (2 Me)		
		−157	65.0, 63.2	42.4, 39.2	16.9	22.1 (1 Me), 31.3 (3 Me)		
(13)	CHF_2–$CHFCl_2$	−90	56.1	33.0	20.3	19.4		141.0
		−138 60% [a]	59.7	34.1	24.5	22.2		156.4
		−138 40% [a]	45.5, 57.3	30.4, 31.0	14.7	12.2, 19.7		121.3
	Me_2O	−80	54.3	32.4	19.0	18.5		132.0
		−135 35% [a]	Under solvent	34.0	25.0	22.2		156.7
		−135 65% [a]	45.0, 56.9	30.6, 31.0	15.0	12.0, 19.8		118.5
(14)	CHF_2Cl	−80	57.6	33.3	20.8	20.1		150.1
		−135 63% [a]	60.6	34.3	24.6	22.4		164.9
		−135 37% [a]	47.2, 58.0	30.9, 30.9	14.7	13.7, 20.7		126.9
(15)	CHF_2Cl	−140	59.6	33.4	23.7	21.3	18.1	164.8
	Me_2O	−138	59.4	34.1	24.6	22.1	18.1	163.9
(16)	CHF_2Cl	−140	60.3	33.8	24.5	21.6	20.9, 25.6	173.3

[a] See text.

RESULTS AND DISCUSSION

The ^{13}C n.m.r. spectrum of hydrazone (7), 1-methylideneaminopiperidine, shows, at −162 °C, two signals (Table 1) of equal intensity for the carbons in positions 2 and 6 of the piperidinyl ring: they coalesce into a single line above −160 °C (Figure 1). The chemical shift difference for C-3 and -5 in the ring is too small to be detected under these experimental conditions. At the coalescence point (−160 °C) a $\Delta G^{\ddagger}$ value of 5.0 kcal mol^{-1} has been determined (Table 2). A slightly higher free energy of activation has been measured for the acyclic hydrazone Me_2N–N=CH_2 (3), whose methyl signals become anisochronous below −152 °C. These experiments indicate that non-hindered hydrazones adopt a conformation with the N=C plane coplanar with the dynamically averaged plane of the sp^3 nitrogen.

As expected [4] the barriers are quite low: in some hydrazones they are even lower than 5 kcal mol^{-1}. For instance in 1-methylethylideneamino(dimethyl)-amine (8), which is the methyl analogue of (3), the *N*-methyl signals broaden more than the others, but even at −155 °C are well above the coalescence point. The method [6] of estimating the N–N rotational barriers by



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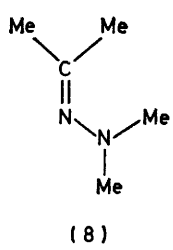

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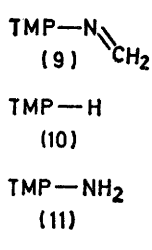


means of ^{15}N shifts turns out to overestimate the real values by 40%, thus confirming [7,8] that, at least for hydrazones, this approach is not a reliable substitute for direct observation. Our results also show that the double-bond character of the NN bond in hydrazones

is extremely sensitive to conjugation, since the rotational barriers may vary from 5 to 17.7 kcal mol^{-1} in derivatives (7) and (2), respectively.

When the hydrazone (7) is compared with its crowded analogue TMP–N=CMe$_2$ (4), where six methyl groups

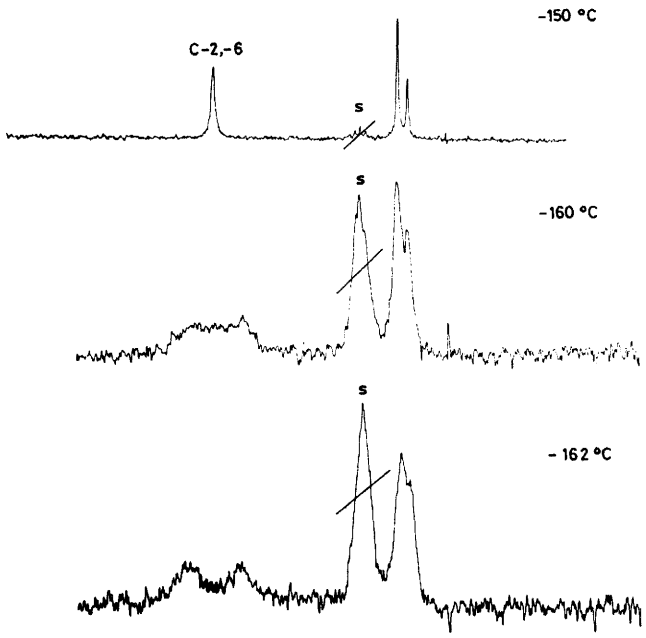
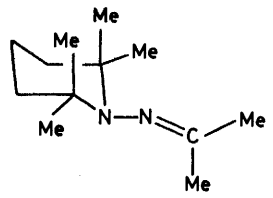


FIGURE 1 ^{13}C Spectrum of (7) in CHF_2Cl at various temperatures. The signal for C-2 and -6 is split in two at −162 °C. Line S is that for [$^2H_6$]acetone added as lock

have been added, the ^{13}C spectrum changes, in that even at room temperature there are two different ^{13}C signals for the two pairs of methyls in the TMP ring (Table 1). On the other hand, C-2 and -6 and C-3 and -5 remain isochronous, thus proving that the N=C group is not coplanar.[4,9] In fact the existence of a perpendicular conformation (where the N=CMe$_2$ plane is orthogonal to the average plane of the sp^3 nitrogen) accompanied by slow N–N rotation, makes the molecule intrinsically prochiral,[10,11] *i.e.* without a σ-plane of symmetry through the pairs of methyls[11] bonded to C-2 and -6. In consequence, even in the presence of fast ring reversal and nitrogen inversion, these methyl groups are diastereotopic, as it has been discussed in more detail elsewhere.[4,9,12] In addition to NN rotation, *also* ring



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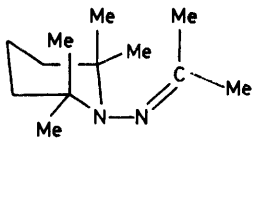


(4b)

reversal could also, in principle, be 'frozen' at an appropriate low temperature, so that two conformers (4a and b) with different shifts and intensities for all the carbons should be detectable.

The sp^3 nitrogen inversion is known[13] to be faster than ring reversal; accordingly only the equatorial conformers[13] have been considered, for the sake of simplicity. However, even at −150 °C no indication was found for the two conformers of (4). This behaviour was also observed in the case of TMP–N=CH$_2$ (9), the only difference being the temperature at which the two pairs of ring methyls become diastereotopic (−130 °C). The lowering of the NN rotational barrier (7.3 kcal mol^{-1}) with respect to (4) depends, obviously, on the smaller steric hindrance experienced, in the perpendicular arrangement, by the N=CH$_2$ group in (9) with respect to the bulkier N=CMe$_2$ in (4). These results are in agreement with those obtained by a previous ^{1}H n.m.r. study.[4]

There are two possible reasons to account for the absence of two conformers in (4) and (9), even at very

TABLE 2

Free energy of activation ($\Delta G^{\ddagger}$) of internal motions and conformational preferences for hydrazones and related derivatives. The values were taken at the coalescence point: the uncertainty is mainly due to errors in determining the temperatures

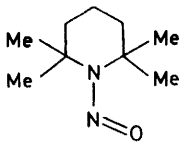
Compound	$\Delta G^{\ddagger}$/kcal mol^{-1} (±0.1)	Motion	Conformation
(3)	5.4	NN rotation	Coplanar
(7)	5.0	NN rotation	Coplanar
(4)	15.6$_4$	NN rotation	Perpendicular
(9)	7.3	NN rotation	Perpendicular
(10)	8.0	Ring reversal	
(11)	8.8	Ring reversal	
(12)	19.6$_4$	NN rotation	Coplanar
	5.8	Ring reversal	
(13)	7.1	Ring reversal	Axial, coplanar
	7.0	NN rotation	Equatorial, perpendicular
(14)	7.15	Ring reversal	Axial, coplanar
	7.0	NN rotation	Equatorial, perpendicular
(15)	Not observed		Axial, perpendicular
(16)	Not observed		Axial, perpendicular

low temperature: either the reversal of the 2,2,6,6-tetramethylpiperidinyl (TMP) ring has a very low $\Delta G^{\ddagger}$, or one of the two possible conformers (4a or b) is largely predominant. To decide between these two, ring reversal in TMP-H (10) and TMP-NH$_2$ (11) was studied. No data are in fact available for such a process in hindered piperidines and attempts of detecting it by ^{1}H n.m.r. were inconclusive.[4]

In contrast to hydrazones such as (4) or (9) ring reversal is the only motion that can generate two signals of equal intensity in TMP-H (10) or TMP-NH$_2$ (11), for the two pairs of methyl groups. All the other carbons are not affected by ring reversal, whereas slow sp^3 nitrogen inversion would produce, if observed, signals of unequal intensity for *all* the carbons.[13,14] Below −100 °C for (10) and −80 °C for (11), two ^{13}C signals were detected for the two pairs of axial and equatorial methyl groups: although smaller than in unsubstituted piperidine[13,15] (whose $\Delta G^{\ddagger}$ is 10.4 kcal mol^{-1}) the barrier to ring reversal of (10) and (11) are easily accessible to ^{13}C n.m.r. ($\Delta G^{\ddagger}$ 8.0 and 8.8 kcal mol^{-1}, respectively). This demonstrated that (4) and (9) exist solely in one of

the two conformations, most likely the less hindered (4a), as indicated by an *X*-ray study of an analogous hydrazone.[4] The amidine (6) thus remains the only TMP derivative where two such conformers have so far been observed.[9]

On the other hand if we investigate a TMP derivative which, as opposite to the above mentioned molecules,



(12)

adopts a planar conformation we are bound to observe, at a suitable temperature, axial and equatorial methyl groups, since the two conformers are now identical (topomers) owing to symmetry. Let us consider, therefore, *N*-nitroso-2,2,6,6-tetramethylpiperidine (12). From room temperature down to −120 °C each carbon (except C-4) displays two signals, owing to slow N–N rotation and to the existence of a planar conformation.[4,16,17]

Below −130°, however, the signal for the methyl

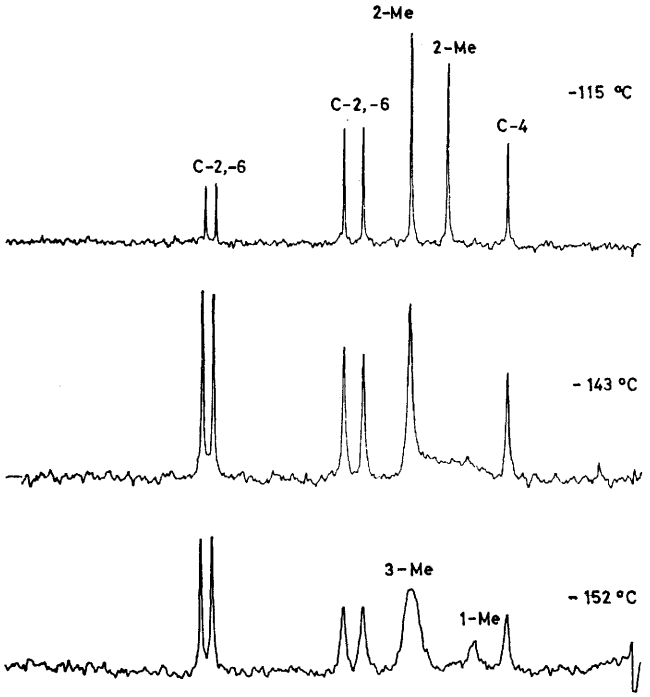
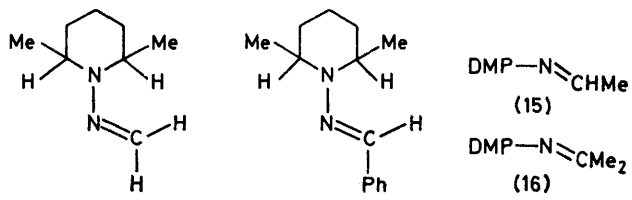


FIGURE 2 Temperature dependence of the ^{13}C spectrum of (12). The signal for 2- and 6-Me upfield (*syn* to NO) broaden at −143 °C and is split at −152 °C into two signals corresponding to one methyl each. That upfield (axial) is detectable whereas that downfield (equatorial) is superimposed on the pair of methyls *anti* to NO

groups *syn* to NO (assigned according to ref. 17) broadens considerably and splits in two at −152 °C (Figure 2). One of these two signals (corresponding to one methyl) is visible, whereas its companion is superimposed on those of the pair of methyls *anti* to NO (this signal corresponds now to three methyls). Whereas the *syn*-methyls have difference between the equatorial (downfield) [18] and axial (upfield) [18] shifts large enough to be observed at −152 °C, the *anti*-methyls have a difference smaller than the linewidths.

The activation energy ($\Delta G^{\ddagger}$ 5.8 kcal mol^{-1}) for ring reversal in (12) was found to be much smaller than in TMP–H (10) or TMP–NH_2 (11); this is due to the importance of the mesomeric forms such as $\overset{+}{N}{=}N{-}\bar{O}$, which reduce the sp^3 character of the piperidinyl nitrogen. Ring reversal in six-membered ring is known [19] to be favoured when the hybridisation of the atoms is sp^2: compare, for instance, the barrier of cyclohexene [20] or methylenecyclohexane [21] (5.4 and 7.7 kcal mol^{-1}, respectively) with that of cyclohexane [22] (10.2 kcal mol^{-1}).

The observation that hydrazones with unsubstituted



(13) (14)

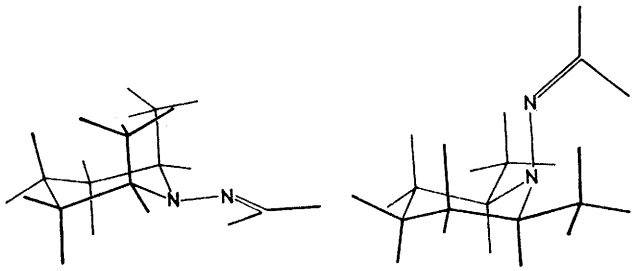
SCHEME

piperidinyl ring, *e.g.* (7), have a coplanar arrangement, whereas those with a TMP ring, *e.g.* (4), are perpendicular, raises the problem of the conformation adopted by hydrazones with intermediate steric effects such as, for instance, dimethylpiperidinyl (DMP) derivatives.

If the two methyl groups are *cis*, they can be either equatorial or axial, situations which, as we have just seen, can be ' frozen ' by ^{13}C n.m.r. If the two methyls are axial the steric effect experienced by the N=C group of a DMP hydrazone should be similar to those of the unsubstituted derivative (7); on the other hand, if the methyl groups are equatorial the steric effect will be very close to that of a TMP hydrazone such as (4). This argument allows us to understand the complex spectral patterns observed at low temperature in the spectra of 2,6-*cis*-dimethyl-1-methylideneamino- (13) and 2,6-*cis*-dimethyl-1-benzylideneammino-piperidine (14).

As shown for the case of (13) in Figure 3, either in Me_2O or in Freon (CHF_2Cl–$CHFCl_2$), below −130 °C there are a larger number of lines than expected. In both spectra only two lines for N=CH_2 and C-4 are observed (see Table 1). On the other hand C-2 and -6 as well as C-3 and -5 and the pair of methyls give three lines, two of them of equal intensity and the third of different intensity. This feature means that there are two conformers of different stability, one with the methyls axial and one with them equatorial. However, whereas in the equatorial conformer the N=CH_2 group adopts a perpendicular arrangement (as happens in TMP–N=CMe_2) in the axial N=CH_2 is coplanar, as in derivative (7). In the perpendicular arrangement

(corresponding to the equatorial conformer) only one signal is expected for all the carbons, since there is a symmetry plane containing C-4 and the N–N=C moiety.* On the contrary, in the planar arrangement (corresponding to the axial conformer) only C-4 and N=CH_2 are singlets, whereas all the other ring carbons must give doublets of equal intensity. In Freon the perpendicular is favoured with respect to the coplanar arrangement (60 : 40): in fact, within the group of three signals corresponding to the pair of methyls, the single peak (60%) is at lower field than the doublet, as expected for equatorial methyls.[18] In dimethyl ether the ratio is reversed (as is clearly visible in Figure 3 for the N=CH_2 signals). The conformer with the methyl groups axial (*i.e.* with a planar arrangement) is now preferred and accordingly the signals of C-2 and -6, C-3 and -5, and the methyls have singlets less intense then the corresponding doublets (35 : 65) The fact that the two lines of these doublets keep their relative 1 : 1 ratio even when the conformational ratio is reversed, proves that the three signals for each carbon *cannot* be interpreted as due to three different conformers. In the Scheme the two arrangements (perpendicular on the right and planar on the left hand side) are reported for the case of DMP–N=CH_2 (13):



It has thus been demonstrated that a switch from a planar to a perpendicular arrangement may occur not only in two molecules of the same class [such as hydrazones (2) and (4) or amidines (5) and (6)] but even within the very same molecule: the axial and equatorial conformers of (13) and (14) have sufficient steric difference to accomplish such a change.

By monitoring the two lines for C=N in (13) we could determine the barrier to ring reversal ($\Delta G^{\ddagger}$ 7.1 kcal mol^{-1}); the shape of these lines is not affected, in fact, by NN rotation. The knowledge of the rate constants for ring reversal would allow us, in principle, to obtain those for NN rotation in the coplanar (axial) conformer, by monitoring the lines of C-2 and -6 whose shape depends on both motions. However, the rotational process in (13) has rate constants of the same order of magnitude as ring reversal and the line shape of the three signals of C-2 and -6 was insensitive to the introduction of this second rate constant. The same behaviour was observed, in both solvents, also for DMP–N=CHPh (14). The barrier to ring reversal in (13) and (14) is smaller than in piperidine or in TMP–H (10) and TMP–NH_2 (11), although not as low as in TMP–NO (12) (see Table 2). Again this can be explained by the partial sp^2 character acquired by the piperidinyl nitrogens of (13) and (14), owing to conjugation with the N=C moiety in the planar arrangement: the conjugation, however, is not as strong as with NO (N–NO rotation is slow even at room temperature) and therefore the $\Delta G^{\ddagger}$ for ring reversal in (13) and (14) has an intermediate value.

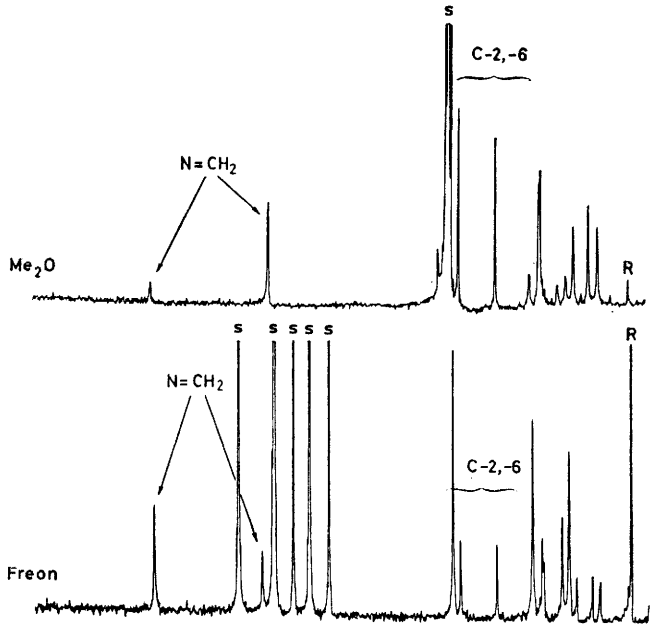


FIGURE 3 Spectra of (13) at −138 °C in Me_2O and Freon (CHF_2Cl–$CHFCl_2$). The lines of the solvent are marked with S, that of Me_4Si with R. The inversion of the axial : equatorial ratio is clearly shown by the relative intensity of the two lines for N=CH_2. In Freon the three lines of C-2 and -6 are clearly detectable, whereas in Me_2O one line is under the peak of the solvent

Also there is no doubt that the N–N rotational barrier in the planar arrangement of the axial conformer of both (13) and (14) is larger (although we could not measure it) than in the analogous piperidinylhydrazone (7). For, in the case of (13) and (14) NN rotation is slow on the n.m.r. time scale at −130 °C whereas in (7) this happens only below −160 °C, despite the fact that some of the shift differences in (13) or (14) are smaller than in (7) [compare for instance, in Table 1, C-3 and -5 of (13) with C-2 and -6 of (7)]. This fact agrees well with the interpretation of the spectra in Figure 3: in (13) or (14) the coplanar conformer has two methyl groups axial, which are expected to hinder N–N rotation relative to the case of (7), where there are no methyl groups on the piperidinyl ring.

Time-dependent phenomena were not observed in the analogous hydrazones DMP–N=CHMe (15) and DMP–N=CMe_2 (16), even below −150 °C. As often happens in 2,6-*cis*-dimethylpiperidinyl derivatives, the conformational equilibrium is completely biased toward the equatorial conformer (in DMP–H itself, we could not see

* As observed for (4), of the two possible rotational conformers of a perpendicular hydrazone only the less hindered is appreciably populated.

line broadening effects). According to our interpretation, if (15) and (16) have the two methyl groups equatorial, the N=C moiety must adopt a perpendicular arrangement, where a single signal is expected for all the carbons. Had the axial conformer been preferred, two lines, with the expected broadening effects, should have been observed for C-2 and -6, for C-3 and -5, and for the pair of methyl groups. The lack of this feature indicates that hydrazones (15) and (16) are only in the perpendicular, equatorial conformation, thus exhibiting different behaviour to (13) and (14).

It is not yet clear why molecules so similar display different conformational preferences. It must be kept in mind, however, that in (13) and (14) we could reverse the ratio of the conformers by a simple change of solvent. No wonder, therefore, that the introduction of different substituents leads to a substantial change in the conformational equilibrium of (15) and (16) with respect to (13) and (14).

EXPERIMENTAL

Preparation of Compounds.—The hydrazones were prepared by condensation of 1,1-dialkylhydrazines with the appropriate carbonyl compounds.[4,23] Hydrazines were either commercially available or prepared by reduction of the corresponding *N*-nitroso-derivatives with $LiAlH_4$.[4,23,24]

The b.p.s of the compounds are as follows: (3), 66° at 760 mmHg; (4), 100—102° at 20 mmHg; (7), 81° at 50 mmHg; (9), 68° at 13 mmHg; (11), 78° at 25 mmHg; (12), 92° at 9 mmHg; (13), 40° at 70 mmHg; (14), 98—99° at 4 mmHg; (15), 50° at 10 mmHg; (16), 35° at 7 mmHg.

The synthesis of 2,6-*cis*-dimethyl-1-benzylideneaminopiperidine (14) is typical. To 2,6-*cis*-dimethyl-1-aminopiperidine [4] (2 g, 0.015 6 mol) was added benzaldehyde (1.65 g, 0.015 6 mol) with stirring. The temperature increases and after 30 min the reaction is complete. The mixture is dissolved in ether, dried ($MgSO_4$), and filtered. The residue obtained after elimination of ether *in vacuo* is distilled (yield 2.25 g).

N.m.r. Spectra.—^{13}C Spectra were obtained in the Fourier transform mode on a Varian XL-100 spectrometer operating at 25.16 MHz. The temperatures were measured by a thermocouple inserted in a dummy tube before or after each spectral determination. The samples were prepared by condensing in the 10 mm n.m.r. tubes, connected to a vacuum line, the gaseous solvents with liquid nitrogen. In addition to the products some $[^2H_6]$acetone or $[^2H_{12}]$-tetramethylsilane was added, for locking the instrument at the deuteron frequency.

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