Conformational Studies by Dynamic NMR. V.[1] The Stereodynamics of Hindered Aliphatic Hydrazones

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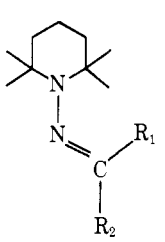
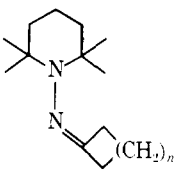
Abstract: A number of *N*-ketiminyl-2,2,6,6-tetramethylpiperidines (TMP—N=CR_2) have been synthesized and investigated by ^{1}H NMR spectroscopy. The piperidyl methyls are either nonequivalent in pairs at room temperature or become nonequivalent in pairs at low temperatures. This is shown to be due to restricted rotation about the N–N bond, a phenomenon that is not observed in less hindered hydrazones even at very low temperatures. The free energies of activation for rotation in TMP—N=CR_2 were determined by line shape analysis. They increase from a low of 7.6 kcal/mol for $R_2 = H_2$ through 11.6, 14.3$_5$, and 18.0 kcal/mol for $R_2 = (CH_2)_4$, $(CH_2)_5$, and $(CH_2)_6$, respectively. This trend is rationalized in terms of a conformation in which the plane of the N=CR_2 moiety is perpendicular to the dynamically averaged plane of the tetramethylpiperidine ring. This conclusion is supported by an x-ray diffraction determination of the structure and conformation of TMP—N=C-$(CH_3)C_6H_5$. The rotational barriers of some *N*-nitrosoamines are also reported.

The occurrence of restricted rotation around the nitrogen–nitrogen single bond of *N*-nitrosoamines, $R_2'N—N=O$, is well documented.[3-8] At room temperature the proton NMR signals due to R′ are usually nonequivalent but they coalesce into averaged signals at higher temperatures. In contrast, a similar nonequivalence of the R′ protons is not observed in the corresponding hydrazones,[9,10] $R_2'N—N=CR_2$, presumably because there is much less (or no) N–N double bond character in these compounds. We recently discovered[11] a class of sterically hindered hydrazones which show restricted motion on the NMR time scale at ambient temperatures. The present paper presents our experimental data on these compounds and discusses their unanticipated stereodynamical behavior.

Results and Discussion

All the hydrazones that show evidence of restricted motion in their ^{1}H NMR spectra contain the 2,2,6,6-tetramethylpiperidyl (TMP) group. As a typical example, we shall first discuss, in some detail, compound **1** (*N*-acetoneimineTMP).





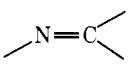
1, $R_1 = R_2 = CH_3$
2, $R_1 = R_2 = H$
3, $R_1 = H$; $R_2 = CH_3$
4, $R_1 = CH_3$; $R_2 = C_6H_5$

5, $n = 1$
6, $n = 2$
7, $n = 3$
8, $n = 4$
9, $n = 5$
10, $n = 9$

At room temperature the ^{1}H NMR spectrum (60 MHz) shows two sharp signals due to the ketimino methyls and two broader signals due to the four piperidyl methyls (see Figure 1). On raising the temperature, the ketimino methyl signals remain sharp and nonequivalent, but the piperidyl methyl signals at first broaden and then coalesce into a single line at 54 °C. The thermodynamic parameters for the process which makes the piperidyl methyls equivalent are given in Table I.

There are two possible ground state conformations:

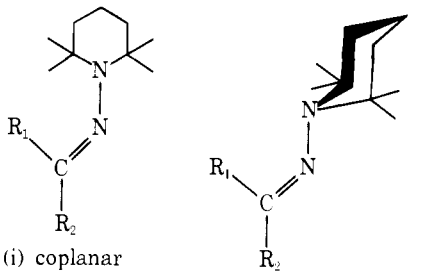
(i) **The coplanar conformation** in which the



A

moiety is coplanar with the "virtual" plane dynamically created in the TMP ring by fast motions 2 and 3 (see below).

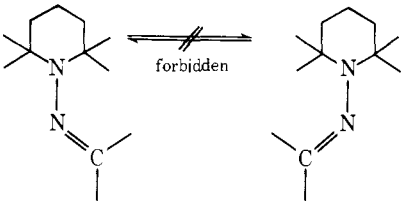
(ii) **The perpendicular conformation** in which the moiety A is perpendicular to this plane.



(i) coplanar (ii) perpendicular

There are four stereodynamical processes which require consideration:

1. Inversion of the iminyl (sp^2) nitrogen in the coplanar conformation can be ruled out since it would make the two ketimino methyls also equivalent at high temperatures. However, it is found experimentally that these methyls give sharp NMR signals even at 150 °C (in tolan).

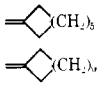


2. Inversion of the amino (sp^3) nitrogen in the perpendicular conformation is likely to be extremely fast at room temperature. Barriers to nitrogen inversion are known to be quite low[12] even in strained rings.[13] It is therefore improbable that inversion of this nitrogen could be responsible for the observed nonequivalence in a six-membered ring at room temperature.[14]

3. Chair-to-chair reversal of the piperidyl ring in the perpendicular conformation is also likely to be very fast at room temperature. It is known that with piperidine itself this motion can be observed on the NMR time scale only at −85 °C.[14,15] Since the four methyl groups on the ring should *reduce* the barrier for this process we must rule out this motion as the source of our nonequivalence.

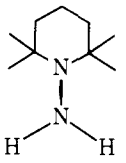
Further evidence that neither motion 2 nor 3 could produce the observed nonequivalence in the hydrazone comes from

Table 1. Thermodynamic Parameters for Motional Averaging in Hydrazones of General Formula TMP—N=CR_2 (Unless Otherwise Indicated all Data were Obtained at 60 MHz)

=CR_2		$\Delta G^{\neq a}$	$E_a{}^a$	$\Delta H^{\neq a}$	$\Delta S^{\neq b}$	T_c, °C	Solvent	$\Delta\nu$, Hz
	(1)	16.7 ± 0.05 16.5 ± 0.05	17.8 ± 0.4 17.6 ± 0.4	17.2 ± 0.4 17.0 ± 0.4	1.5 ± 1.1 1.4 ± 1.2	54.5 53	C_2Cl_4 $C_6H_5NO_2$	23.1 24.0
	(2)	7.6 ± 0.1 7.5[c] ± 0.1				−122 −121[c]	CHF_2Cl CHF_2Cl	15.4 26.0[c]
	(3)	8.9 ± 0.1				−91.5[c]	CHF_2Cl	30.5[c]
	(4)	15.6 ± 0.1				36	$CDCl_3$	25.2
	(5)	11.6 ± 0.06	12.0 ± 0.8	11.5 ± 0.8	−0.2 ± 3.7	−47	CS_2	13.5
	(6)	14.3_5 ± 0.05	14.3 ± 0.3	13.7_5 ± 0.3	−2.1 ± 1.0	5.5	$CDCl_3$	17.4
	(7)	18.0 ± 0.1	18.6 ± 0.6	17.9 ± 0.6	−0.4 ± 1.8	79	C_2Cl_4	23.1
	(8)	17.5 ± 0.1	18.4 ± 0.4	17.7 ± 0.4	0.6 ± 1.2	67	C_2Cl_4	21.1
	(9)	17.2 ± 0.05	18.0 ± 0.2	17.4 ± 0.2	0.5 ± 0.5	62	C_2Cl_4	20.0
	(10)	18.2 ± 0.1				83	C_2Cl_4	22.4

[a] kcal mol^{-1}. [b] cal (mol^{-1} deg^{-1}). [c] At 100 MHz.

low-temperature studies on two compounds which lack the ketimino moiety. Both TMP at −150 °C (in CHF_2Cl) and *N*-aminoTMP, **11**, at −80 °C (in toluene-d_8, because it reacted with CHF_2Cl) were found to display four equivalent methyl groups.



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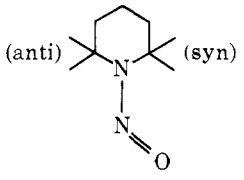
4. Restricted rotation about the N–N bond remains as the only likely cause for the nonequivalent piperidyl methyls.

The coplanar conformation is, of course, similar to the preferred conformation of the analogous *N*-nitrosoTMP, **12**.[4,5,8] It is immediately apparent that in this conformation



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the two syn methyls are different from the two antimethyls and that these four methyls will become equivalent if rotation about the N–N bond is faster than the nuclear spin lifetime.

It is not so immediately obvious that restricted rotation about the N–N bond in a hydrazone in the perpendicular conformation can also generate two pairs of nonequivalent methyls. Scheme I shows, on its left-hand side, the four possible conformations (I–IV) that could arise because of inversion at the sp^3 nitrogen and chair-to-chair ring reversal. In each structure the N—N=C group has not been allowed to rotate. On the right-hand side, the same conformations have been drawn with a 180° rotation about the N–N bond. These conformers, I′, etc., are topomers of those labeled I, etc., equal numbers indicating identical structures.

If the perpendicular conformation is to be a realistic possibility, it is necessary that, when N–N rotation is slow, the averaging of the four structures on the left (I–IV) should yield two pairs of nonequivalent methyls. Inspection of these

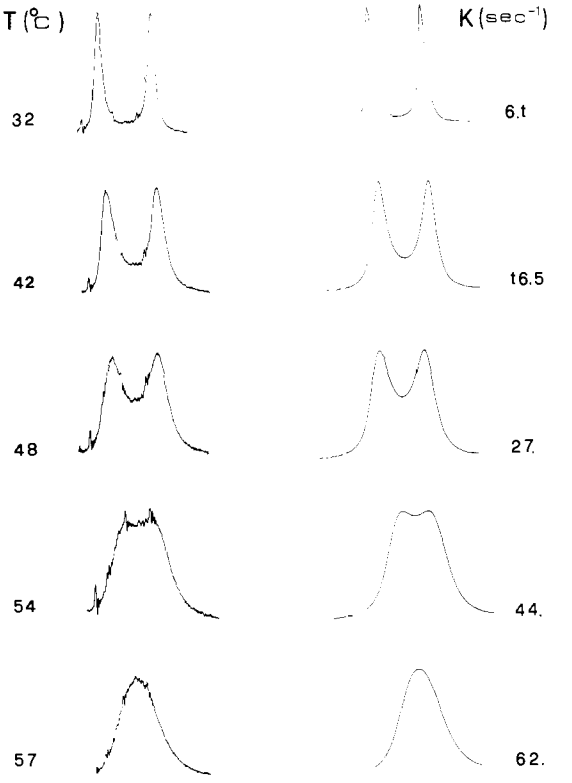
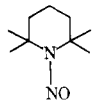
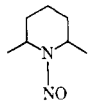


Figure 1. Example of nonequivalence in hydrazones at high temperature. Experimental (left) and computed (right) NMR signals of piperidyl methyls of TMP—N=CMe_2 (**1**) as a function of temperature. The separation of the peaks is 23.1 Hz (at 60 MHz), the solvent is C_2Cl_4.

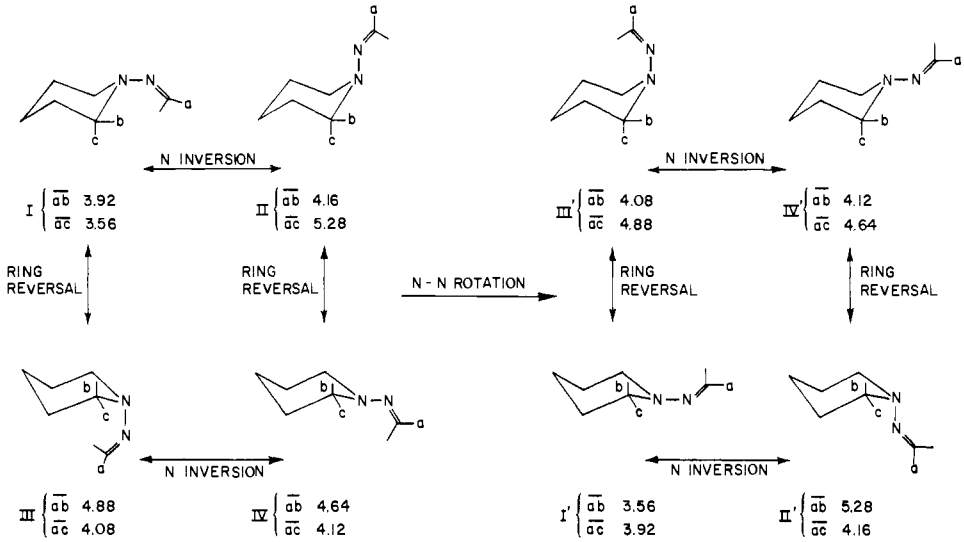
structures shows that they are all different and that in each structure the methyl labeled b is always different from that labeled c. The chemical shift of b can, therefore, never be equal to that of c unless there is an "accidental" coincidence. As a probe of the difference between b and c we have taken the distances between methyl a and methyls b and c. These distances were measured between the carbons using Dreiding molecular models and are given in ångstroms in Scheme I. It can be seen that the distance $\overline{ab}$ is not the same as the distance $\overline{ac}$ in any structure. Accordingly, whatever the relative popu-

Table II. Thermodynamic Parameters for Motional Averaging in *N*-Nitrosamines (Unless Otherwise Indicated all Data were Obtained at 60 MHz)

		$\Delta G^{\ddagger}$ [a]	E_a [a]	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	Solvent
	(12)	19.6 ± 0.1	19.3 ± 0.2	18.5 ± 0.2	−2.9 ± 0.7	C_2Cl_4
	(13)	19.6 ± 0.1	18.7 ± 0.9	17.9 ± 0.9	−4.5 ± 2.5	$C_6H_5NO_2$
	(14)	22.7[c] ± 0.1	24.0 ± 0.4[c]	23.4 ± 0.4[c]	−1.8 ± 0.9	Neat
$(i\text{-Pr})_2N-NO$	(15)	23.5 ± 0.1	24.4 ± 0.6	23.5 ± 0.6	0.15 ± 1.3	$C_6H_5NO_2$
Et_2N-NO	(16)	23.2 ± 0.1	23.9 ± 0.6	23.1 ± 0.6	0.3 ± 1.5	$C_6H_5NO_2$
Me_2N-NO	(17)	23.0 ± 0.1				$C_6H_5NO_2$

[a] kcal mol^{-1}. [b] cal (mol^{-1} deg^{-1}). [c] Data at 100 MHz from ref 6.

Scheme I



lations of structures I to IV the averaged distance $\overline{ab}$ will always be different from the averaged distance $\overline{ac}$. It is therefore reasonable to expect that the averaged chemical shifts of b and c will also be different. Therefore, we conclude that even in the perpendicular conformation the TMP ring has two pairs of nonequivalent methyls, provided rotation about the N-N bond is slow.[16] However, if rotation is fast, then there will be an interchange between b and c and they will become magnetically equivalent.

It is now necessary to choose between the coplanar and the perpendicular conformations. For hydrazone **1** this choice could, in principle, be made on the basis of Me-Me coupling in its ^1H NMR spectrum. That is, in the planar conformation the equivalence of the chemical shifts of b and c would prevent the detection of such coupling, whereas in the perpendicular conformation the different shifts of b and c might allow Me-Me coupling to be observed. In the event, although this coupling could not be detected in **1**, the line width of the piperidyl methyls in the absence of exchange (−5 °C in C_2Cl_4) was greater (0.6 Hz) than that of *N*-nitrosoTMP, **12**, under the same conditions (0.4 Hz). Since the NO group in **12** is coplanar with the piperidyl ring,[4,5,8] the hydrazone will prefer the perpendicular conformation if we can assume that the greater line width in **1** is due to an unresolved Me-Me coupling.

In order to have a more reliable method for distinguishing between the perpendicular and coplanar conformations, the rotational barriers were measured in a homologous series of TMP hydrazones having iminyl groups of different size (see Table I).

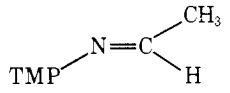
On the one hand, if the coplanar conformation is preferred, the barrier should decrease as the iminyl group gets larger because the ground state will be destabilized by steric interactions, but the (perpendicular) transition state will be only slightly perturbed.[17] A somewhat similar[18] steric destabilization of the ground state can be observed in the hindered rotation of the coplanar nitrosoamines **12**, . . . , **17** (see Table II). That is, the barrier for the less hindered nitrosoamines **14**, . . . , **17** is larger than for the more hindered compounds, **12** and **13**.

On the other hand, if the perpendicular conformation is preferred, the barrier should increase as the iminyl group gets larger, because of greater steric hindrance in the (coplanar) transition state.

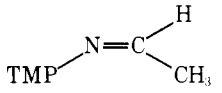
Examination of the data listed in Table I leaves no doubt that the barrier increases with increasing size of the iminyl group. For example, in the least hindered hydrazone, **2**, the piperidyl methyls become nonequivalent only below −122 °C ($\Delta G^{\ddagger} = 7.5_5 \pm 0.05$ kcal/mol^{-1}),[19] whereas in the cyclobutyl- (**5**, see Figure 2), cyclopentyl- (**6**), and cyclohexyl ketimines

(7) $\Delta G^{\ddagger}$ increases[20] to 11.6, 14.3$_5$, and 18.0 kcal/mol, respectively. Although further increases in ring size do not increase $\Delta G^{\ddagger}$ (presumably because of the flexibility of the larger rings) there can be no doubt that these and other hydrazones derived from TMP all adopt the perpendicular conformation.

Additional support for a perpendicular conformation comes from a comparison of TMPN=CH_2 (**2**, $\Delta G^{\ddagger}$ = 7.5$_5$), TMPN=$CHCH_3$ (**3**, $\Delta G^{\ddagger}$ = 8.9), and TMPN=$C(CH3)_2$ (**1**, $\Delta G^{\ddagger}$ = 16.6 kcal/mol). Since the $\Delta G^{\ddagger}$ value for **3** is closer to that for **2** than to that for **1** we conclude that the single isomer of **3** that could be detected is (as would be expected on steric grounds) the trans isomer, rather than the cis isomer.

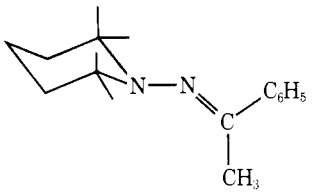


3, trans



3, cis (not observed)

Finally, the structure of *N*-acetophenoneimineTMP, **4**, was determined by x-ray diffraction.[21] It was found to have the perpendicular conformation with the phenyl (which is bulkier than methyl) trans to the TMP ring. Furthermore, of the four possible structures shown in Scheme I, this hydrazone adopts conformation **IV** in the crystalline state, i.e.,



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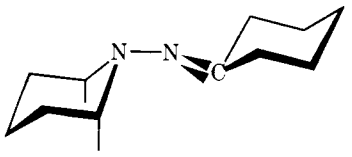
The substantial barriers to N-N bond rotation in the *N*-ketimineTMP compounds led us to look for an analogous barrier in *N*-cyclohexanoneimine-*cis*-2,6-dimethylpiperidine, **18**. However, the doublet ($J_{H,Me}$ = 6.4 Hz) corresponding to the two methyls did not split into two doublets even at −160 °C. If we accept the general belief[4,5,7,8] that the two methyl groups are in the axial, axial conformation, this negative result could be explained in several possible ways. However, the most attractive explanation is that the absence of the two equatorial methyls allows the molecule to adopt a planar conformation in its ground state, i.e.,



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Rotation about the N-N bond would therefore proceed through a perpendicular transition state and the barrier for this process might easily be too small for us to detect. Unfortunately, structural studies of *N*-ketiminyl-*cis*-2,6-dimethylpiperidines by x-ray diffraction have not yet been successful.

Experimental Section

Materials. The hydrazones **1**, . . . , **10** were prepared by condensation[11] of 2,2,6,6-tetramethylpiperidylhydrazine[22] (**11**) with the appropriate carbonyl compound. The following preparation of 2,2,6,6-tetramethylpiperidylacetophenoneimine (**4**) is fairly typical.

A mixture consisting of 1 g (0.0063 mol) of $TMPNH_2$ (**11**) and 0.7 g (0.0058 mol) of acetophenone, together with a few crystals of *p*-toluenesulfonic acid as a catalyst, was refluxed for 8 h. On cooling to room temperature, a precipitate of **4** was obtained. The solid was filtered and crystallized from aqueous ethanol: mp 89–90 °C; yield 0.8 g. Anal. Calcd for $C_{17}H_{26}N_2$: C, 79.02; H, 10.14; N, 10.84; mol wt, 258.41. Found: C, 78.9; H, 10.1; N, 10.9; mol wt, 258 (mass spectrum).

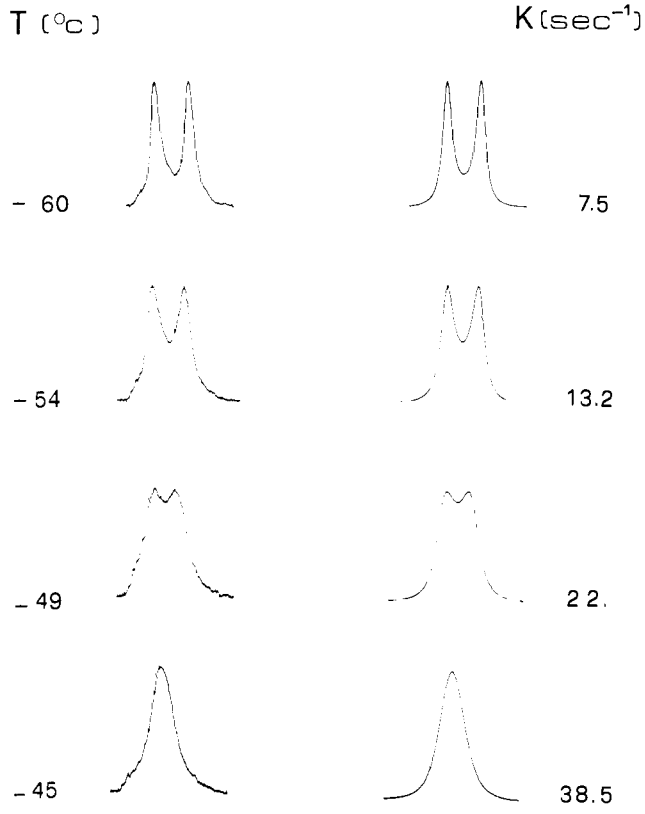

Figure 2. Example of nonequivalence in hydrazones at low temperature. Experimental (left) and computed (right) NMR signals of piperidyl methyls of TMP—N=$C(CH_2)_3$ (**5**) as a function of temperature. The separations of the peaks is 13.5 Hz (at 60 MHz), the solvent is CS_2.

Hydrazone **10** was also a solid, mp 74–75 °C. The other hydrazones were liquids having the following boiling points: **1**, 85 °C (12 mm); **2**, 65 °C (12 mm); **3**, 70 °C (12 mm); **6**, 127 °C (12 mm); **8**, 145 °C (12 mm); **9**, 155 °C (6 mm). **5** and **7** were distilled on a molecular still at about 25 and 50 °C, respectively, and at a pressure of 10^{-2} to 10^{-3} mm. All hydrazones prepared in this work had the expected molecular weight (mass spectrometry) and appropriate NMR spectra (see Table **III**).

2,6-*cis*-Dimethylpiperidylhydrazine ($DMPNH_2$) was prepared by the dropwise addition of a solution of 9 g of 2,6-*cis*-dimethylpiperidyl-*N*-nitrosoamine[23] (**13**) in 35 cm^3 of anhydrous ethyl ether to a well-stirred slurry of 4 g of $LiAlH_4$ in 150 cm^3 of anhydrous ether. The reaction, which is strongly exothermic, was carried out under nitrogen, and the temperature was kept at about 25 °C by means of an ice bath. The reaction was complete after 2 h. The excess $LiAlH_4$ was destroyed with ethanol/ether (1:1 v/v). The resulting solution was poured onto a mixture of ice and dilute NaOH and this slurry was filtered. The organic layer was separated, combined with ether extracts of the aqueous layer, and dried over $MgSO_4$. The ether was removed on a rotary evaporator and the remaining liquid was distilled at 60 °C (17 mm), yield 4.0 g. The hydrazone **18** was obtained by condensation of $DMPNH_2$ with cyclohexanone, bp 138 °C (18 mm).

Diisopropyl-*N*-nitrosoamine (**15**) was prepared by addition of 50.6 g (0.5 mol) of diisopropylamine to 100 ml of 5 N HCl, followed by addition of this solution to a solution of 39 g of $NaNO_2$ in 45 ml of water at 90–95 °C with vigorous stirring. The pH was maintained at 5–6 by addition of HCl or $NaNO_2$. The solution separated into two phases. It was cooled and acidified to a pH of 3 and then warmed to 60 °C and the organic layer was separated. The organic layer solidified on cooling (mp 48 °C). It was purified by distillation (bp 78 °C at 12 mm): yield, 75%; mol wt, 130 (mass spectrum). NMR spectrum in CCl_4 had two doublets (methyls) at 1.12 and 1.46 ppm and two septets (methine H) at 4.1 and 4.7 ppm (J = 6.8 Hz).

Nitrosamines **16** and **17** were commercial products (Merck-Schuchardt), while the preparations of **12**,[22] **13**,[23] and **14**[6] have been described previously.

Table III. NMR Data for Hydrazones in CCl_4[a]

1[11]	TMP: $(CH_3)_2$ 0.7 (s); $(CH_3)_2$ 1.07 (s); $(CH_2)_3$ 1.54 (m, broad) $=CMe_2$: CH_3 1.87 (s); CH_3 1.88 (s)
2[11]	TMP: $(CH_3)_4$ 1.02 (s); $(CH_2)_3$ 1.5 (m, broad) $=CH_2$: 7.07 (d) and 6.70 (d) (J = 14)
3	TMP: $(CH_3)_4$ 0.95 (s); $(CH_2)_3$ 1.5 (m, broad) $=CHCH_3$, 2.0 (d, J = 5.6); $=CHCH_3$, (q, J = 5.6)
4	TMP: $(CH_3)_2$ 0.80 (s, broad); $(CH_3)_2$ 1.18 (s, broad); $(CH_2)_3$ 1.58 (m, broad) $=C(CH_3)C_6H_5$, 2.38 (s); $=C(CH_3)C_6H_5$ 7.3 (m, 3 H), and 7.8 (m, 2 H)
5	TMP: $(CH_3)_4$ 0.95 (s); $(CH_2)_3$ 1.52 (m, broad) $=C(CH_2)_3$: 2.9 (m, 4 H) and 2.06 (m, 2 H)
6	TMP: $(CH_3)_4$ 1.0 (s) $(CH_2)_5$ 1.5 (m, broad); $(CH_2)_2$ 2.5 (m)
7	TMP: $(CH_3)_2$ 0.65 (s); $(CH_3)_2$ 1.04 (s) $(CH_2)_6$ 1.5 (m, broad); $(CH_2)_2$ 2.5 (m)
8	TMP: $(CH_3)_2$ 0.75 (s); $(CH_3)_2$ 1.07 (s) $(CH_2)_7$ 1.5 (m); $(CH_2)_2$ 2.56 (m)
9	TMP: $(CH_3)_2$ 0.75 (s); $(CH_3)_2$ 1.07 (s) $(CH_2)_8$ 1.5 (m); $(CH_2)_2$ 2.5 (m)
10	TMP: $(CH_3)_2$ 0.7 (s); $(CH_3)_2$ 1.07 (s) $(CH_2)_{12}$ 1.5 (m); $(CH_2)_2$ 2.5 m

[a] Probe temperature. Chemical shifts in ppm downfield from Me_4Si. J is in Hz.

Spectral Studies. NMR spectra were recorded at 60 or 100 MHz on JEOL C-60-HL and JEOL PS 100 spectrometers, respectively. After each spectrum was recorded, the temperature was measured by placing a thermocouple in a dummy tube. When CHF_2Cl was used as the solvent, ordinary NMR tubes were sealed under vacuum at liquid nitrogen temperatures. Only occasionally did these tubes burst on warming to room temperature. The DNMR computer program[24] was used for line shape analysis.

The x-ray diffraction data were collected on a Siemens AED apparatus and the structure was resolved using a MULTAN computer program.[21]

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References and Notes

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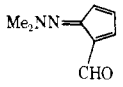
(9) The following hydrazones showed no sign of restricted rotation in their 100 MHz ^1H NMR spectra even at temperatures as low as −150 °C: Me_2N-N=CH_2; Me_2NN=CMe_2; Me_2NN=CPh_2; $(Me_2CH)_2NN$=$C(CH_2)_5$; Me(Ph)NN=$C(CH_2)_5$. This implies that $\Delta G^{\ddagger}$ for rotation is less than 6 kcal/mol.
(10) There is a rather odd exception to this statement. A. Mannschreck and U. Koelle (*Tetrahedron Lett.*, 863 (1967)) reported restricted rotation in



and attributed it to slow rotation around the N–N bond. However, since the corresponding compound lacking the CHO group did not show similar effects, one cannot rule out the possibility the motion was due to restricted rotation of the –CHO group.
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(16) As a general rule, the piperidyl methyls in the perpendicular conformation will be nonequivalent if the group attached to the piperidyl nitrogen lacks a symmetry axis on the NMR time scale. When such an axis is dynamically created (e.g., by fast N–N rotation in the hydrazones or by fast inversion at the NH_2 nitrogen in **11**) then the nonequivalence vanishes.
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(18) This comparison may not be completely appropriate since the decreased $\Delta G^{\ddagger}$ value for **13**, relative to the less hindered nitrosoamines **14**, . . . , **17**, is due mainly to repulsion between the two axial methyl groups.[5,8]
(19) The calculated line shapes exactly fit the experimental spectra for all the compounds listed in Tables I and II, *except* for **2**. In the case of **2**, there were small discrepancies which may be due to the fact that motions 2 and 3 are not sufficiently fast at −140 to −120 °C to be completely ignored. For this reason, only $\Delta G^{\ddagger}$ (measured from the coalescence temperature) is given for this compound.
(20) In all the cases in which $\Delta S^{\ddagger}$ was measured it was found to be negligible. For this reason $\Delta G^{\ddagger}$ (which can be determined more accurately than $\Delta H^{\ddagger}$) will be used as a measure of the rotational barrier.
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Electronic Properties of Aliphatic Xanthate Ions

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Abstract: The CNDO/2 method has been used to examine the electronic structure of aliphatic xanthate ions, especially by the participation of the 3d orbitals of sulfur. With the ASMO SCF method it is also applied to confirm three ultraviolet absorption peaks to be due to n → π*, π → π*, and n → σ* transitions, respectively. The inductive effect of the polar groups in homologues of xanthic acids, carboxylic acids, and amines is transmitted to five, six, and three successive carbon atoms in their ionic forms, while the effect of fluorine in the fluorinated compounds is transmitted to five or more. The induced charges seem to alternate in a decaying manner. The total energy of a homologous series of a few compounds has an approximately additive property per CH_2 or CF_2 group.

Various organic compounds including the second row elements of the periodic table have recently attracted many experimental and theoretical chemists, who have in a systematic manner studied them. Organic sulfur compounds in this category are of great importance and interest not only from the point of their utilitarian aspects as rubber vulcanizers, pesti-