Conformational Studies by Dynamic Nuclear Magnetic Resonance. Part 24.[1] Gear Effect in Di-isopropyl-nitrosoamine and -phenyltriazene studied by Carbon-13 Nuclear Magnetic Resonance and Molecular Mechanics

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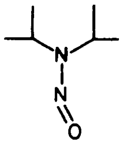
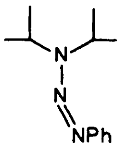
Evidence of the existence of correlated intramolecular orientation (gear effect) has been observed in $\mathrm{Pr^i{}_2NNO}$ (1) and $\mathrm{Pr^i{}_2NNNPh}$ (2) by ^{13}C n.m.r. In the first case two conformers have been detected in a 92 : 8 ratio at −120 °C. The corresponding activation parameters have been measured ($\Delta G^{\ddagger}$ 9.7 kcal mol^{-1}) and the structures of the two conformers assigned. Molecular mechanics calculations reproduce all the experimental observations and indicate, in addition, that this dynamic process is not synchronous but follows a two-step pathway. In the case of (2) the existence of the phenomenon could be detected through the interpretation of the selective broadening of one spectral line, and the free energy of activation could be measured ($\Delta G^{\ddagger}$ 10.2 kcal mol^{-1}) even though the spectrum of the less populated conformer was not directly detected.

THE existence of a correlated orientation due to polyhedral substituents has been observed for a number of di-isopropyl derivatives using n.m.r. techniques. The phenomenon has been named the ' gear effect ' since the two isopropyl groups appear to behave as a pair of interlocking rotors. This gives rise to a number of interchangeable conformational isomers (usually four), some of which can be detected by n.m.r. spectroscopy. The examples collected so far involve derivatives where one (or both) of the two isopropyls are bonded to a nitrogen atom which conjugates with another group. Accordingly, the gear effect has been reported in amides,[2,3] thioamides,[3,4] carbamates,[5] and thio- and seleno-carbamates,[5] as well as in a number of heterocyclic derivatives where the nitrogen bearing one of the isopropyls is bonded to a carbonyl[3] or a thiocarbonyl group.[3,4,6-9] We have recently shown that the gear effect also occurs in the *N*-sulphinylhydrazine $\mathrm{Pr^i{}_2NNSO}$[10] where the *sp*^{3} nitrogen bearing the isopropyl group conjugates with the NSO moiety.

The conjugation gives some *sp*^{2} character to the *sp*^{3} nitrogen, thus making its structure more planar; it seems therefore that this geometrical situation places the isopropyl groups in a suitable position for the existence of the gear effect. Thus, it seems legitimate to wonder whether any molecule, where two isopropyls are bonded to a nitrogen, with some *sp*^{2} character due to conjugation, should always display such an effect. There are, however, two well known counter-examples where such conjugation is certainly present but no gear effect has been reported. We refer to *N*-nitroso-amines[11-18] ($R_2N{-}NO$) and triazenes[19-22] ($R_2N{-}NNAr$). In these molecules the *sp*^{3} nitrogen conjugates, respectively, with N=O and N=NAr. Indeed restricted rotation about the N–N bond has been observed and attributed to forms such as $R_2\overset{+}{N}{=}N{-}O^-$ and $R_2\overset{+}{N}{=}N{-}\overset{-}{N}Ar$. According to our prediction, the gear effect should be present when R = isopropyl and therefore we reinvestigated $\mathrm{Pr^i{}_2NNO}$ (1) and $\mathrm{Pr^i{}_2NNNPh}$ (2) to obtain evidence for the ' missing ' gear effect.


(1)


(2)

RESULTS AND DISCUSSION

The ^1H n.m.r. spectrum (100 MHz) of $\mathrm{Pr^i{}_2NNO}$ (1) does show, in the range −45 to −100 °C, selective broadening of the two CH multiplets (*syn* and *anti* to NO) which are typical of a gear effect. The phenomenon is even more evident in the ^{13}C n.m.r. spectrum, where not only the two CH signals, but also those of the two methyls (*syn* and *anti* to NO) broaden and eventually split into two. As Figure 1 shows, the ^{13}C spectrum of (1) exhibits, at −40 °C, the two pairs of methyne and methyl signals, with a 1 : 1 relative intensity, generated by the NN restricted rotation. At −120 °C each line is further split in two, in a 92 : 8 intensity. The observation of these two signals with such different intensities is consistent with a dynamic process involving at least two conformations adopted by the isopropyl groups. Molecular mechanics calculations carried out on (1) show that there are, in principle, four such conformations, corresponding to four energy minima along the $Me_2CH{-}N$ rotation pathway. These conformers are represented in Figure 2 as projections of the two isopropyl groups on planes perpendicular to the respective $N{-}Pr^i$ bonds. The *sp*^{3} nitrogen atom (underneath the plane of the paper) is not indicated, and the NO moiety (also underneath the plane of the paper) is in parentheses.

Molecular mechanics calculations also show that conformers (II) and (IV) have much higher energy than conformers (I) and (III) (Table 1). This suggests that the species detected in the low temperature n.m.r.

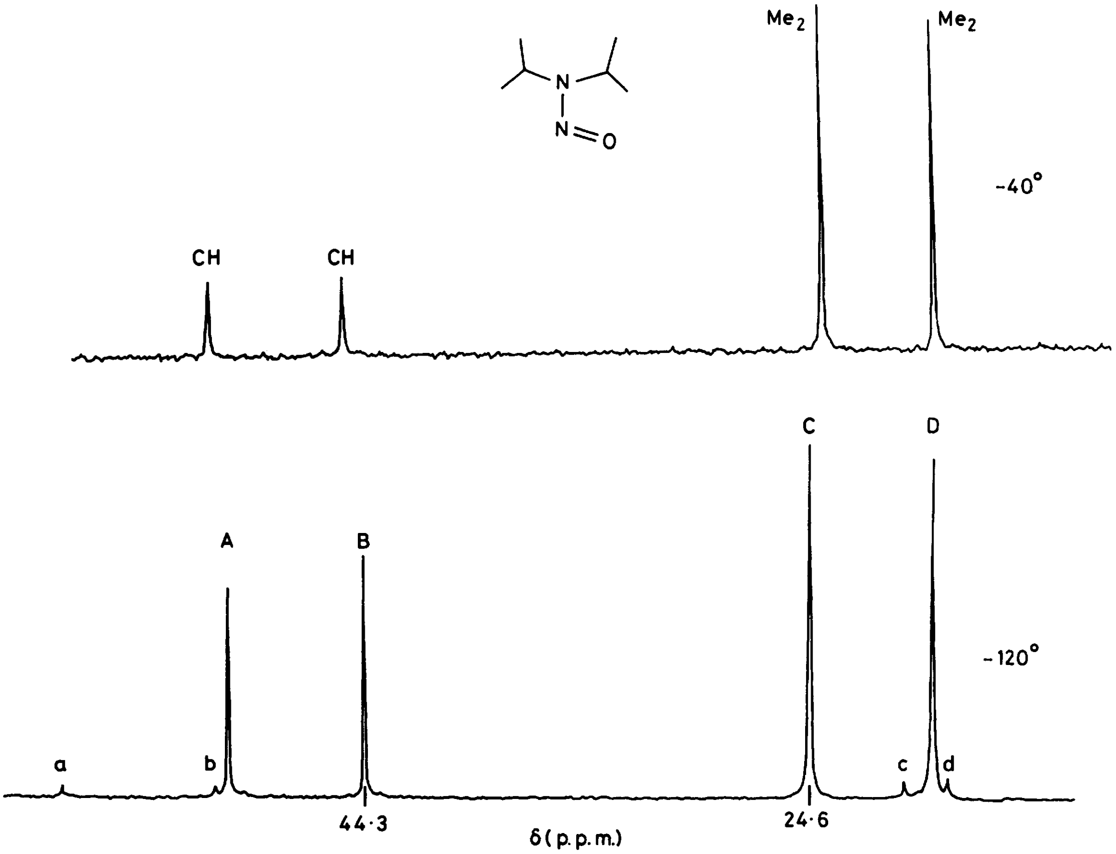


FIGURE 1 ^{13}C 25.16 MHz spectrum of Pr$^i_2$NNO (1) in CHF$_2$Cl at −40 °C (upper), showing non-equivalence of the two isopropyl groups, and at −120 °C, where four additional signals due to the gear effect are observed. The signals labelled with capital letters exchange with those labelled with the corresponding lower case letters

experiment should be assigned structures (I) and (III). Within the framework of these calculations, conformer (I) appears to be more stable than (III) by 0.75 kcal mol^{-1}. This corresponds (assuming a negligible $\Delta S°$) to a conformer ratio of 92 : 8 at −120 °C; a value that matches remarkably well the observed ratio. In order to examine on an experimental basis which, between (I) and (III), is the preferred conformer and to check the theoretical predictions, the ^{13}C n.m.r. spectrum of t-butyl(isopropyl)-*N*-nitrosoamine (3) was investigated.

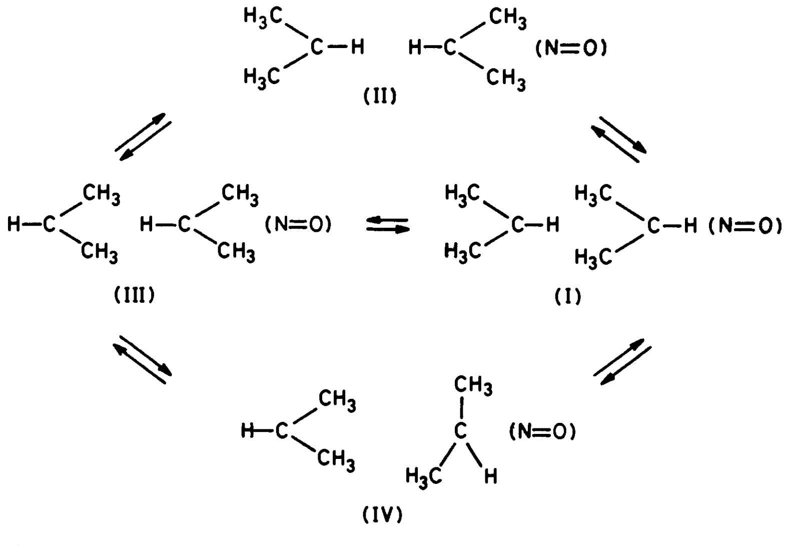


FIGURE 2 Representation of the gear conformers (I)—(IV), corresponding to four energy minima, as computed by molecular mechanics for Pr$^i_2$NNO (1). The isopropyl groups are represented as projections on planes perpendicular to the CH–N bonds. The *sp*^{3} nitrogen lies underneath the plane of the paper and is not indicated for simplicity. The NO group is also underneath the plane of the paper and is indicated in parentheses

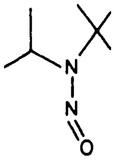
At room, as well as at lower temperature, this derivative yields two different spectra due to the presence of two species having the NO respectively ***anti*** (5%) (3a) or *syn* (95%) (3b) to the isopropyl group.

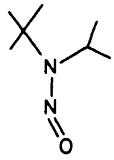
TABLE 1

Relative energies (kcal mol^{-1}) of conformers (I)–(IV) corresponding to minimum values in the C–N rotation pathway of the isopropyl groups of $Pr^i{}_2NNO$ (1) as computed by molecular mechanics

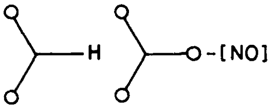
Conformer	Energy
(I)	0
(II)	2.0
(III)	0.75
(IV)	9.5

Owing to the steric hindrance brought about by the introduction of the bulky t-butyl group, it is conceivable that only one of the two possible gear conformers of types (I) and (III) is present in (3). That with the CH bond geared inside the t-butyl is thus expected to be the only gear conformer, either in (3a) [conformer (V)] or in (3b) [conformer (VI)].

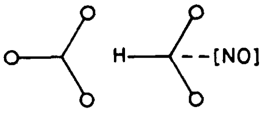

(3a)


(3b)

The observed CH shift is 48.0 for (V) (3a) and 52.1 p.p.m. for (VI) (3b). Accordingly, no line broadening was detected in (3) at low temperature because there are not, as opposed to (1), two exchanging gear conformers. We have now the possibility of comparing the ^{13}C methine shift of isopropyl in the known structures (V) and (VI) with the corresponding values of (I) and (III) (Table 2); in this way we can assign the latter structures by comparison. To do so, however, we need to know which is the ^{13}C shift of the CH *syn* (*Z*) and which that of the ***anti*** (*E*) isomer in derivative (1). This information was obtained performing experiments with a lanthanide complex, $Yb(fod)_3$. Since $Yb(fod)_3$ associates itself with the oxygen of the NO moiety, the carbons more shifted by addition of the lanthanide are those *syn* to NO. It turned out that the ^{13}C signal of CH *syn* (*Z*) to NO lies upfield with respect to the ***anti*** (*E*), as observed in other alkyl-*N*-nitroso-derivatives [23] (Table 2).



(V)



(VI)

Accordingly, the chemical shift of CH (*E*) of isomer (V) in (3) (δ 48.0 p.p.m.) has to be compared with the two values observed for CH (*E*) in (1) (*i.e.* δ 50.4 or 57.9 p.p.m., Table 2). On the other hand the shift of CH (*Z*) of isomer (VI) in (3) (δ 52.1 p.p.m.) has to be compared with the values observed in (1) for CH (*Z*) (*i.e.* δ 44.3 and 51.1 p.p.m., Table 2). There is little doubt that in (1) the CH (*E*) shift matching the CH (*E*) of (3) is δ 50.4 p.p.m.; since this corresponds to the more intense gear conformer the latter must have structure (I). Also, the CH (*Z*) shift of (1) matching CH (*Z*) of (3) is δ 51.1 p.p.m.; this corresponds to the less intense gear conformer so that its assignment to structure (III) is confirmed. These conclusions not only agree with the theoretical predictions, but also with the conformational behaviour of a similar molecule ($Pr^i{}_2NNSO$) whose structure was determined by *X*-ray diffraction.[10]

TABLE 2

^{13}C Chemical shifts (p.p.m. at 25.16 MHz with respect to Me_4Si) of the methyl and methine carbons of the two gear conformers of $Pr^i{}_2NNO$ (1) at −120 °C in CHF_2Cl. See text for the conformational assignments

Gear conformer	(I) (92%)	(III) (8%)
CH_3	19.2 (*Z*) 24.6 (*E*)	18.5 (*Z*) 20.4 (*E*)
CH	44.3 (*Z*) 50.4 (*E*)	51.1 (*Z*) 57.9 (*E*)

An analysis of the molecular mechanics calculations also suggests that conformer (III) is less stable than (I), owing to a distortion of the isopropyl group (III) (*Z*) with respect to the isopropyl (I) (*E*). In fact the energy difference of the bending of the former, with respect to the latter, accounts for 95% of the whole energy difference between the two gear conformers.

Computer analysis of the line shape of the ^{13}C spectra (Figure 3) allowed us to determine the rate of exchange of conformers (I) and (III) at six different temperatures. The simulation was performed on both lines (CH and CH_3) and the activation parameters are as follows: $\Delta H^{\ddagger}$ 8.7 ± 0.5 kcal mol^{-1}, $\Delta S^{\ddagger}$ -5 ± 3 cal mol^{-1} K^{-1}, and $\Delta G^{\ddagger}$ $9.7_0 \pm 0.06$ kcal mol^{-1} (between −89 and −65 °C).

These parameters refer to the process interconverting the more into the less stable gear conformer. The entropy was found slightly negative and usually such a small value should not be considered significant, owing to the large experimental errors in measuring the temperatures of the n.m.r. experiments.[9,24] However, in every case where activation parameters connected with the gear effect have been measured, $\Delta S^{\ddagger}$ was always found [5,9] to lie in the range −3 to −5 cal mol^{-1} K^{-1}. It seems therefore reasonable to assume that the slightly negative value is due to a decrease of the rotational freedom of the methyl groups in the transition with respect to the ground state.[9]

As shown in Figure 1 there are three possible pathways through which conformer I can interchange with III, *i.e.* (i) direct interconversion (I) ⟶ (III), (ii) interconversion (I) ⟶ (II), followed by interconversion (II) ⟶ (III), and (iii) interconversion (I) ⟶ (IV), followed by interconversion (IV) ⟶ (III).

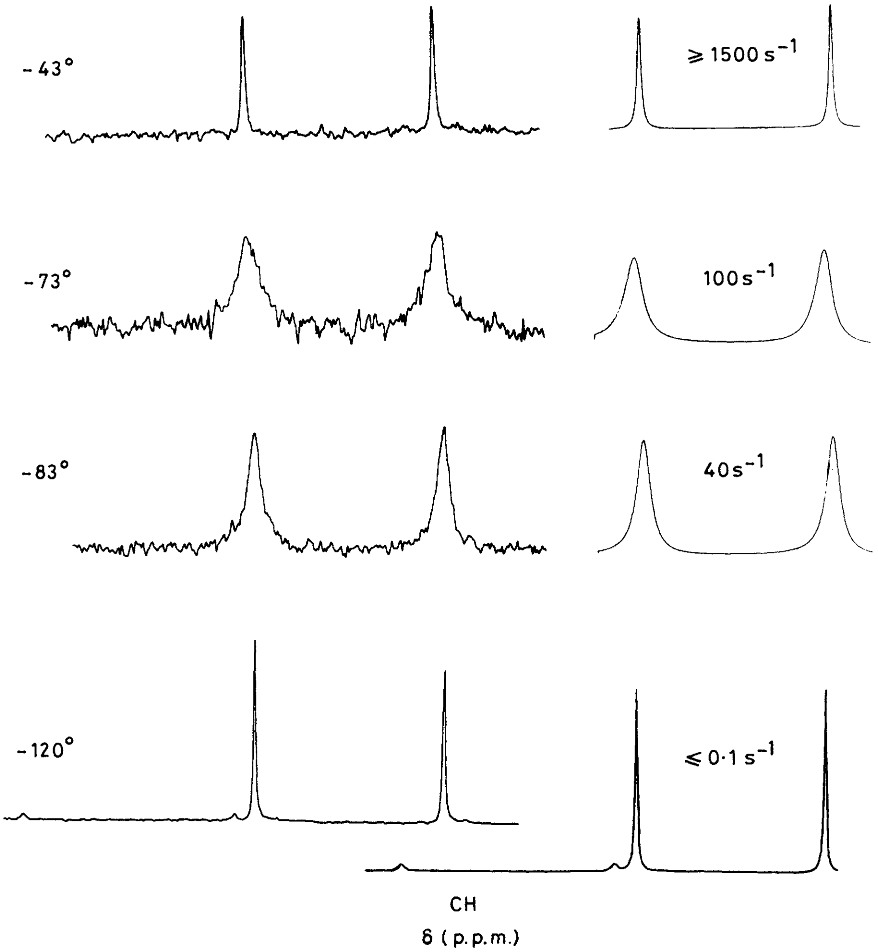


FIGURE 3 Temperature dependence of the ^{13}C CH signal of (1) (left). On the right hand side is given the computer-simulated line shape

The first mechanism requires a ' concerted ' rotation of the two isopropyl groups whereas the ' two step ' mechanisms (ii) and (iii) require a stepwise rotation of one isopropyl after the other. In this case the experimental evidence cannot decide among the three possibilities and we resorted to molecular mechanics calculations for elucidating the process. The results are summarized in Table 1 where the minimal energies, corresponding to the four conformers are reported, and in Table 3 where the $\Delta H^{\ddagger}$ for each single step, as well as for the overall process, are given. The concerted mechanism (i) may occur with a simultaneous rotation of the isopropyl groups either in a conrotatory or disrotatory mode. The two activation energies are, however, rather close and much higher (Table 3) than the experimental value. Accordingly, this pathway must be discarded: such a conclusion agrees with those reached for other molecules displaying the gear effect.[3-5] The second pathway (ii) has the energy of the transition state relative to the first step higher than for the second step (9.6 *versus* 6.0 kcal mol⁻¹): accordingly 9.6 kcal mol⁻¹ represents the $\Delta H^{\ddagger}$ value for the whole process. The value agrees satisfactorily with the experimental determination (8.7 ± 0.5 kcal mol⁻¹). On the other hand in the third possible pathway (iii) the energy of the transition state relative to the first step is lower than for

TABLE 3

Computed enthalpies of activation (kcal mol⁻¹) for three possible interconversion pathways between the two conformers (I) and (III) (see text). The synchronous mechanism (i) might, in principle, occur either in a conrotatory or a disrotatory manner with slightly different $\Delta H^{\ddagger}$ values. The value found experimentally is also given

Interconversion pathway	Single step barrier	Overall barrier	Experimental barrier
(i) conrotatory	$(I) \xrightarrow{21.3} (III)$	21.3	
(i) disrotatory	$(I) \xrightarrow{18.0} (III)$	18.0	
(ii)	$(I) \xrightarrow{9.6} (II) \xrightarrow{4.0} (III)$	9.6	8.7 ± 0.5
(iii)	$(I) \xrightarrow{13.4} (IV) \xrightarrow{6.1} (III)$	15.6	

the second step (13.4 *versus* 15.6 kcal mol^{-1}). The latter value thus represents the enthalpy of activation for the whole process and not only is it higher than for pathway (ii), but it is quite different from the experimental value. On the basis of these calculations the exchange between conformers (I) and (III) thus requires a two-step pathway involving, as intermediate, conformer (II). The computations also predict that, at the temperature of our measurements, the amount of intermediate (II) is too low (<0.2%) to be detected.

The interconversion pathway is summarized in Figure 4, where the surface corresponding to the dependence of the computed energy upon the torsional angles ω_1 and ω_2 is reported. The broken line represents the reaction co-ordinate of the forbidden concerted mechanism and the full line the co-ordinate of the allowed two-step mechanism.

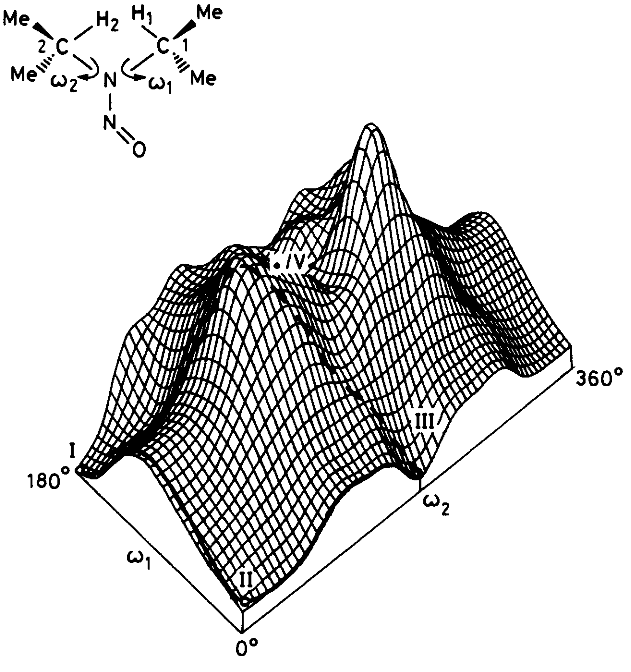


FIGURE 4 Potential energy surface of $\mathrm{Pr^i_2NNO}$ obtained by means of molecular mechanics calculations. The surface is presented as function of the dihedral angles, $\omega_1 = 180 - \omega_{\mathrm{NNC(1)H(1)}}$ and $\omega_2 = 180 - \omega_{\mathrm{NNC(2)H(2)}}$, thus showing the dependence of the potential energy on rotation of the isopropyl groups. The full line indicates the allowed two-step pathway between the conformers (I), and (III) whereas the dotted line indicates the forbidden synchronous pathway (conrotatory) between the same conformers

An analogous, albeit less detailed, investigation was also carried out on (2) ($\mathrm{Pr^i_2NNNPh}$). The ^{13}C n.m.r. spectrum at room temperature shows, as expected, a single line for the two CH_3 and the two CH groups of isopropyl. These lines split in two of equal intensity at −40 °C, because of restricted N–N rotation.[22] When the temperature is lowered further (−75 °C) one of the two CH lines (that at lower field) broadens and eventually sharpens again at −100 °C. Although we could not detect the signal due to the second gear conformer, this effect shows that a second conformer with a very low intensity and a non-negligible chemical shift difference is actually present. The fact that only the downfield CH line is broadened, whereas that upfield is not, means that the shift difference of the invisible companion is too small for the upfield line.[10,25] In the case of very biased equilibria the maximum line width due to exchange depends on the chemical shift difference ($\delta\nu$/Hz) and on the percentage of the less intense isomer (c).[10] The simulation of the maximum linewidth experimentally observed (5.5 ± 0.5 Hz) could only be attained with a '$c\cdot\delta\nu$' product equal to 3, and with a rate constant $k = 20 \pm 5$ s^{-1}. This means, for instance, that the presence of 2% of the less intense conformer (amount not detectable in our conditions) with a shift difference of 150 Hz [a reasonable figure compared with the shift of (1)] can account for the observed line broadening. On this basis the free energy of activation for converting the more into the less stable gear conformer is 10.2 ± 0.2 kcal mol^{-1}. This value is only slightly larger than that determined for (1) ($\Delta G^{\ddagger}$ 9.7 kcal mol^{-1} at the same temperature, −75 °C) but much lower than the barrier determined for N–N rotation ($\Delta G^{\ddagger}$ 14.4 kcal mol^{-1}).[22]

The finding that both (1) and (2) do show the gear effect confirms the assumption that all molecules of the type $\mathrm{Pr^i_2N{-}X{=}Y}$ (where X=Y is an asymmetric moiety which conjugates with nitrogen) are expected to display such dynamic behaviour. Furthermore, theoretical calculations indicate that the rotation of the two isopropyl groups is a two step rather than a synchronous process.

EXPERIMENTAL

Derivatives (1) and (2) were prepared as in the literature.[14,23] t-Butyl(isopropyl)-*N*-nitrosoamine (3) was obtained by reaction of t-butyl(isopropyl)amine (5.75 g) with $NaNO_2$ (4.1 g) in 10% HCl (15 ml). The mixture was boiled with stirring for 2 h, maintaining the pH at 4 with acetic acid. The upper yellow organic layer was extracted, dried and distilled, giving (3) (4 g), b.p. 98 °C at 20 mmHg, m.p. 88—89 °C. The low-temperature spectra were obtained by dissolving the compounds in CHF_2Cl and sealing the 10 mm n.m.r. tubes *in vacuo*. The spectra were recorded at 25.16 MHz (Varian XL-100) using ^{19}F as an external lock. The temperature was monitored with a thermocouple inserted in a dummy tube before or after each spectral determination.

Calculations.—Molecular mechanics calculations were carried out on (1) in order to determine the energy minima and the interconversion mechanism. A potential energy surface (Figure 4) was built up as a function of the dihedral angles $\omega_1 = 180 - \omega_{\mathrm{NNC(1)H(1)}}$ and $\omega_2 = 180 - \omega_{\mathrm{NNC(2)H(2)}}$: the numbering is that of Figure 4. This surface describes the rotation of the two isopropyl groups with respect to the NNO moiety. The dihedral angle ω_2 was allowed to vary between 0 and 360° whereas ω_1 only covered the interval 0—180° since the NNO moiety turned out to be nearly planar. The grid in Figure 4 was obtained by varying these angles, independently, in steps of 15°. The angles were constrained at pre-set values of ω_i^0 (i = 1,2) by adding to the potential, in the minimization process, two extra quadratic torsional terms [26] that force deviations to be smaller than 0.2°: $E_{\text{extra}} = K\,(\omega_i - \omega_i^0)^2$ where $K = 3$ kcal mol^{-1} degree^{-2}.

The following procedure was chosen for the framework of our general forcefield computer program. As starting geometry for each point of the grid the most stable geometry was taken among those generated by rotating each methyl group independently by 15°. The optimized geometry was obtained by means of the steepest descents,[27] followed by modified Newton–Raphson iterations.[28]

The parameters developed by Allinger *et al.*[29] for alkenes were employed for the two isopropyl groups. On the other hand the parameters for N–NO were determined by fitting the geometry,[30] the vibrational frequencies,[31] the dipole moments,[32] and the rotational barrier about the N–N bond [33] of the *NN*-dimethyl-*N*-nitrosoamine as well as the torsional barriers of the ethyl and methyl groups computed by *ab initio* calculations (STO-3G level)[34] on *NN*-dimethyl- and *N*-ethyl-*N*-methyl-*N*-nitrosoamine. The force-field parameters are summarized in Table 4.

TABLE 4

Force-field parameters [a] employed in the molecular mechanics calculations of Pr^i_2NNO (1)

Dipole moment	μ/D	
N–O	0.95	
C–N	1.95 [b]	
Stretching constants	l/Å	K_s/mdyn Å^{-1}
N–N	1.348	3.8
N–O	1.236	8.1
C–N	1.45	3.7
Bending constants	θ (°)	K_b/mdyn Å rad^{-2}
N–N–O	112.6	2.3
C–N–N	118.4	0.78
C–N–C	120.	0.78
H–C–N	110.74 [b]	0.48 [b]
C–C–N	108.5 [b]	0.38 [b]
Torsional constants	V_2/kcal mol^{-1}	V_3/kcal mol^{-1}
CNNO	13.05	
CCNN		−0.4
HCNN		−1.0
HCCN		0.53
HCNC		0
CCNC		−0.2

[a] Force field equations, hydrocarbon parameters, van der Waal, and bend stretching parameters are those tabulated in N. L. Allinger, Quantum Chemistry Program Exchange, 1976, vol. 11, no. 318. [b] From D. C. Crans and J. P. Snyder, *Chem. Ber.*, 1980, **113**, 1201.

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