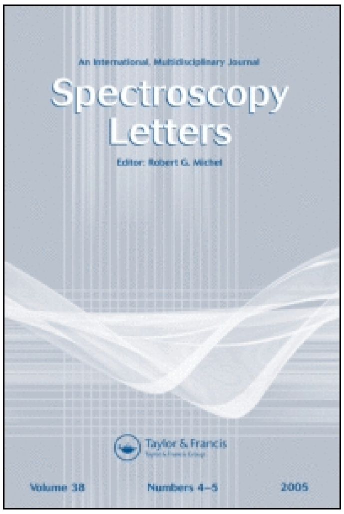

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Temperature-Dependent Amplitude of a Torsional Libration Observed by High Resolution N.M.R. Spectroscopy

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TEMPERATURE-DEPENDENT AMPLITUDE OF A TORSIONAL LIBRATION OBSERVED BY HIGH RESOLUTION N.M.R. SPECTROSCOPY.[1]

Keywords: 1-(2'-Hydroxythiobenzoyl)piperidine, thioamide, n.m.r., librational coalescence temperature, amplitude of torsional libration.

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ABSTRACT

Low temperature 220 and 300 MHz ^1H n.m.r. spectra of 1-(2'-hydroxythiobenzoyl)piperidine in $CDCl_3$ and acetone-d_6 show evidence for the temperature dependence of the amplitude of torsional librations about the thioamide C-N bond. The coalescence of the signals from the piperidine α-CH_2 protons *cis* to the thiocarbonyl group before those of the *trans* α-CH_2 protons (where the librational coalescence temperature is near 0°C) as the temperature is raised is ascribed to more effective equalization of the two *cis* protons in the magnetic field of the C=S bond.

INTRODUCTION

In a previous paper[2] we have shown that the piperidine ring in 1-(2'-hydroxythiobenzoyl)piperidine (1) exists in two interchanging chair conformations with unequal populations, the N-thiobenzoyl substituent nearly eclipsing the equatorial α-CH_2 protons of the piperidine ring in both

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conformations, with the fractional population of the most favoured conformation being 0.54 and K_e = 1.17 in $CDCl_3$ at -30°C. The fact that the piperidine C_2 protons (*cis*) coalesce before the C_6 protons (*trans*) as the temperature is raised (Fig. 1 in ref. 2) deserves careful examination, as it is the first experimental observation of the temperature-dependent amplitude of a torsional libration.

RESULTS AND DISCUSSION

^{1}H 220 and 300 MHz n.m.r. spectra of **1** at low temperatures are shown in Figs. 1 to 4.

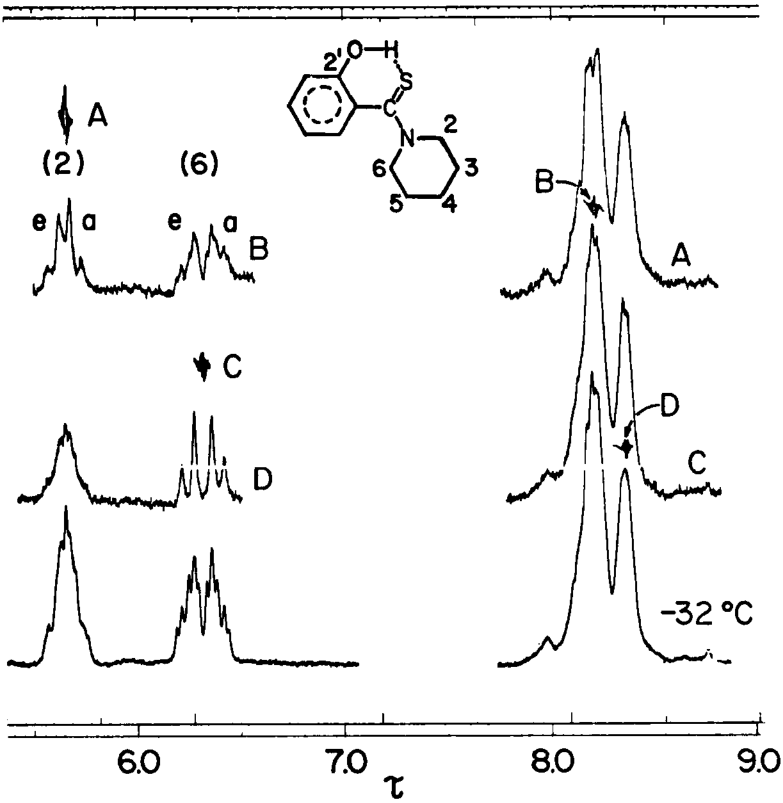

FIG. 1
Decoupled ^{1}H 220 MHz nmr spectra of piperidine protons in **1** at -32°C, in $CDCl_3$ solution. Assignments to piperidine ring protons given. Assignments in other figures also according to structural formula given here.

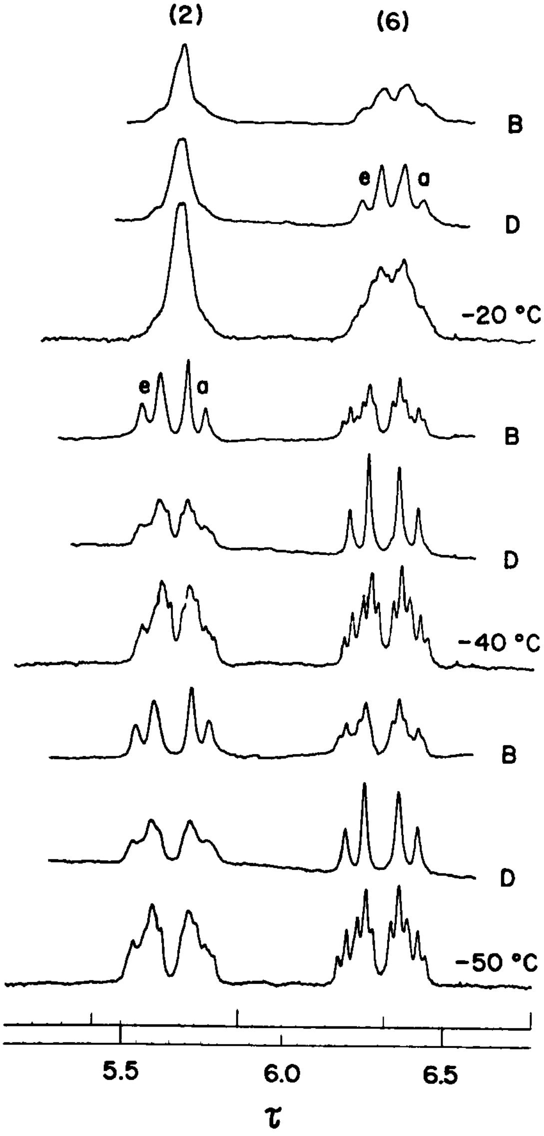

FIG. 2
Decoupled ^1H 220 MHz nmr spectra of C_2 and C_6 protons in 1 at -20, -40, and -50°C, in $CDCl_3$ solution. B and D are identified in Fig. 1.

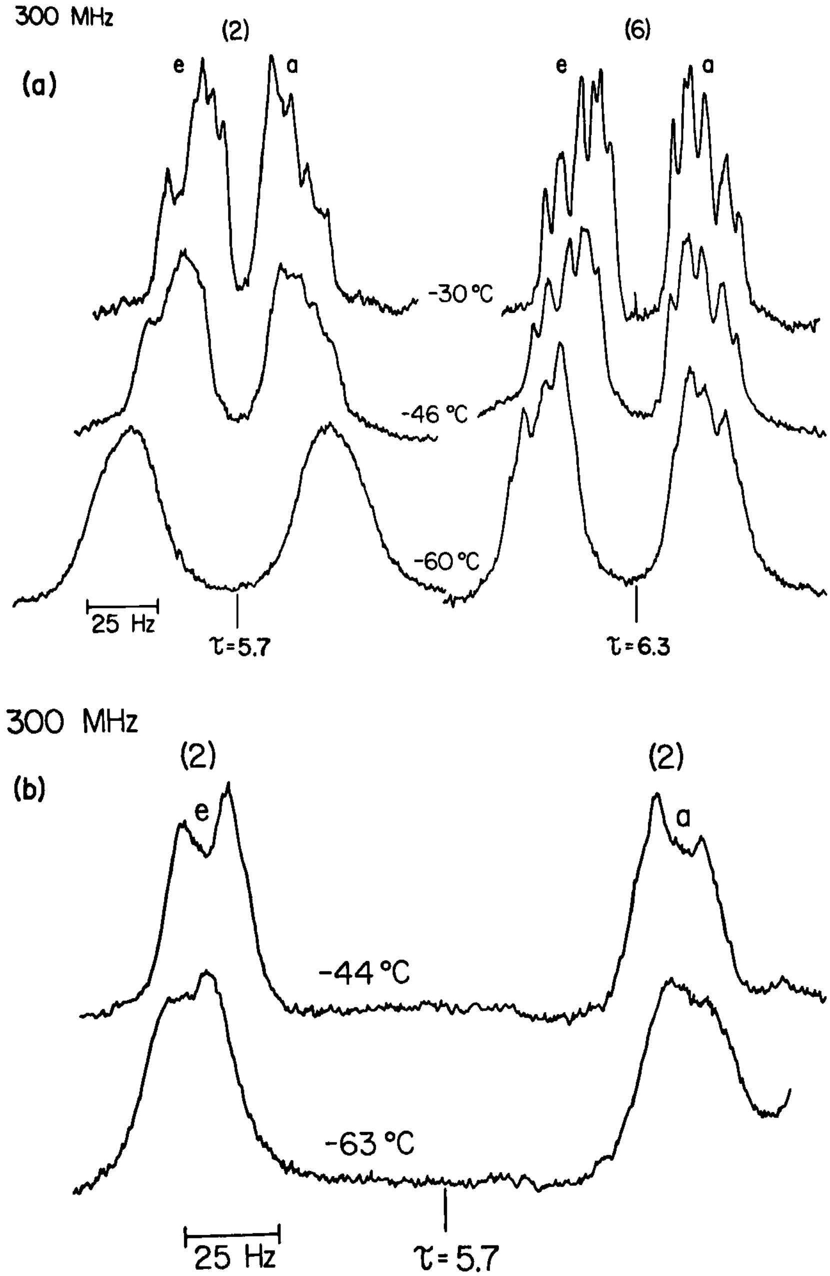

FIG. 3
^{1}H 300 MHz nmr spectra of (a) C_2 and C_6 protons in **1** at -30, -46, and -60°C, in $CDCl_3$ solution, (b) C_2 protons in **1** at -44 and -63°C in acetone-d_6 solution.

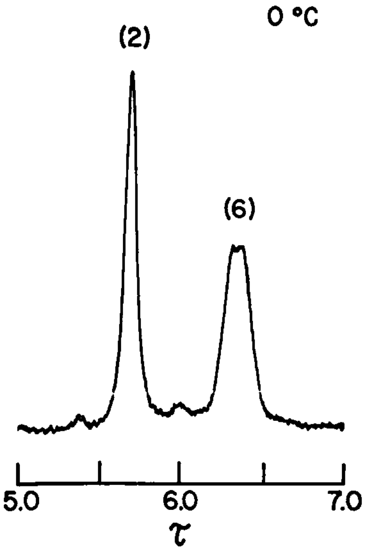

FIG. 4
^{1}H 220 MHz nmr spectrum of C_2 and C_6 protons in **1** at 0°C in $CDCl_3$ solution, showing librational coalescence of C_6 protons.

The first hypothesis to be considered is that the proportions of the two conformers approach 0.50/0.50 as the temperature is raised. This can be rejected because of the following reasons: (1) The calculated difference in free enthalpy between the conformers is $\Delta G° \approx 70$ cal/mole (from K_e at -30°C). Because the difference in the entropy of the two chair conformations can be presumed to be zero, $\Delta G° = \Delta H°$, and from $\Delta G°$ a value of K_e = 1.15 at -20°C is obtained, which should result in a spectrum nearly identical with that at -50°C. Fig. 1 in ref. 2 shows this is not so. (2) In this case the following relation should hold for the C_2 (*cis*) and C_6 (*trans*) methylene protons at all temperatures;

$$\Delta\tau^{cis} - \Delta\tau^{trans} = \{(2p-1)[(\tau_a^{cis} - \tau_e^{cis}) - (\tau_a^{trans} - \tau_e^{trans})]\} \geqslant 0 \qquad [1]$$

if the fractional population of the most favoured conformer is $p \geqslant 0.5$, because it is known that[2]

$$\tau_a^{cis} > \tau_a^{trans} > \tau_e^{trans} > \tau_e^{cis} \qquad [2]$$

While this expression is based on an undistorted chair conformation, the pseudo-axial and pseudo-equatorial chemical shifts ($\tau_{a'}^{trans}$ and $\tau_{e'}^{trans}$, respectively) are known to follow the inequality

$$(\tau_{a'}^{trans} - \tau_{e'}^{trans}) < (\tau_a^{trans} - \tau_e^{trans}) \qquad [3]$$

so that eq. [1] should still hold for a piperidine ring distorted at C_6. Again, the n.m.r. spectrum of 1 at -20°C (Fig. 2) contradicts eq. [1], since the *cis* protons coalesce *before* the *trans* protons as the temperature is raised. At 0°C the *cis* protons still give rise to a sharp singlet (Fig. 4), proving that the rotation around the C-N bond is still frozen out on the 220 MHz scale. At higher temperatures both the *cis* and *trans* proton signals begin to broaden due to rotation around the C-N bond.

The separation of the two peaks for the *cis* and *trans* protons as a function of temperature is best seen in the decoupled 220 MHz n.m.r. spectra in Figs. 1 and 2. Above -40°C, $\Delta\tau^{cis} < \Delta\tau^{trans}$; at -40°C, $\Delta\tau^{trans} = \Delta\tau^{cis} = 0.13$ ppm; at -50°C, $\Delta\tau^{cis} = 0.16$ ppm and $\Delta\tau^{trans} = 0.14$ ppm. The spectra at 300 MHz show the same trend with temperature, and better peak separations (Fig. 3).

The broadening of the *cis* proton signal pattern at -60°C in the 300 MHz spectra indicates a kinetic phenomenon in a very asymmetric local environment, in contrast to the sharp pattern still observed for the *trans* protons which are in a local environment where the asymmetry of the deshielding is smaller. This is a very nice example of how the *same* kinetic phenomenon, i.e. libration around the C-N bond and hence equal movement of the *cis* and *trans* α-CH_2 atoms, can be observed by line broadening on the *cis* side where the magnetic anisotropy is high, but not on the *trans* side where the anisotropy is lower. At -60°C in the 300 MHz spectrum, $\Delta\tau^{cis} \simeq 0.25$ ppm and $\Delta\tau^{trans} \simeq 0.20$ ppm.

We interpret these results as a progressive freezing of higher energy C-N torsional librations and therefore a reduction in their amplitude as the temperature is lowered[3]. The temperature dependence of the amplitude of vibrations has been discussed in detail by Cyvin[4]. The reduction in the C-N vibrational amplitude as the temperature is lowered has a greater effect on the *cis* proton signals, where the gradient of deshielding from the C=S bond is higher; furthermore, it is higher in the equatorial position than in the axial position. This explains why the *cis* equatorial proton signals are broader than the *cis* axial proton signals in the decoupled spectra. This effect is also seen in the 300 MHz n.m.r. spectra in $CDCl_3$ (Fig. 3a) and in acetone-d_6 (Fig. 3b). In $CDCl_3$, as the temperature is lowered from -30 to -60°C the following estimated peak displacements are observed: *cis* "e" - 25 cps, *cis* "a" - 15 cps, *trans* "e" - 10 cps, *trans* "a" - 0 cps. In acetone-d_6, as the temperature is lowered from -44 to -63°C the *cis* "e" protons are displaced by 7.5 cps and the *cis* "a" protons by 5 cps.

The coalescence of the *cis* NCH_2 proton signals before those of the *trans* NCH_2 signals as the temperature is raised is therefore due to the more effective equalization of the two *cis* protons in the magnetic field of the C=S bond, relative to that for the two *trans* protons, for a given amplitude of the C-N torsional libration at a given temperature. This phenomenon is the first example, to our knowledge, where "exchange of Larmor frequencies" is clearly distinguished from "exchange of sites" and not subject to criticisms[5]. In **1** H_a and H_e at C_2 (and also at C_6) become magnetically equivalent by small motions which bring them into positions where the magnetic field is the same for both of them and not by interchanging their positions, i.e. H_a remains predominantly axial and H_e predominantly equatorial.

It should be noted that the small difference in the time which a given α-proton spends in the equatorial and in the axial position, respectively, makes the torsional amplitude dependence of the chemical shift detectable. As this time difference increases, as in 4-(2'-hydroxythiobenzoyl)morpholine (**2**), the morpholine analog of **1**, the torsional oscillation is no longer able to equalize the chemical shifts and therefore the n.m.r. spectrum is temperature independent.[2] In acetone-d_6 solutions of **1** the chemical shifts at 300 MHz for the two *cis* NCH_2 protons differ more than they do in $CDCl_3$ solution, and here no significant temperature dependence is observed from +18°C to -44°C, and only a small change below that temperature (Fig. 3b).

The coalescence temperature observed for the *trans* NCH_2 protons in **1** near 0°C (Fig. 4) is a *librational* T_c, i.e. the "axial" and "equatorial" protons whose signals collapse do not interchange places but are equalized by librations in the local magnetic field. A similar coalescence point for the *cis* NCH_2 protons lies at a lower temperature. Just as for the kinetic phenomenon where the protons are interchanging, this coalescence temperature is a function of the magnetic environment. Contrary to all other kinetic phenomena studied by n.m.r., this librational T_c is lower for the protons having the greater chemical shift difference, i.e. at -60°C, $\Delta\tau^{cis} = 0.25$ ppm while $\Delta\tau^{trans} = 0.2$ ppm. If the difference in chemical shift is too high equalization by torsional libration cannot be achieved.

The equilibrium constant (K) for the conformational equilibrium in **1** at high temperature, obtained by Eliel's method of chemical shifts,[6] is lower than the true K value; a K constant determined from coupling constants as was done for **2**[2] will be less affected by the torsional amplitude.

Experimental studies of torsional amplitudes, particularly as the resolving power of n.m.r. instruments increases, may be very useful in connection with polymers, since configurational changes in macromolecules are related by torsional movements.[7,8] The field strength of the spectrometer is an important factor; thus at 300 MHz broadening of the *cis* NCH_2 protons is already present due to the freezing of the higher amplitude oscillations, whereas at 100 MHz at the same temperature the *cis* peaks are sharp.

The study of temperature dependent torsional amplitudes by n.m.r. spectroscopy may be particularly relevant to the following problems: (1) weak molecular association between solute and solvent molecules, where n.m.r. relaxation measurements have shown that the component molecules rotate separately by large angle jumps,[9] and (2) accurate calculation of the barriers to rotation around the C-N bond, especially where there are considerable variations in the chemical shifts with temperature.[10,11]

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1. This work was supported by the National Research Council of Canada. 220 MHz n.m.r. spectra were obtained at the Canadian 220 MHz N.m.r. Centre, Sheridan Park, Ontario, under the direction of Dr. A. E. Gray. We are indebted to Prof. M. Anteunis, State University of Gent, Belgium, for the 300 MHz spectra. Compounds **1** and **2** were synthesized by Mrs. C. Fulea, University of Bucharest, Romania.

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3. (a) The fact that the peaks are *sharp* before and after the onset of splitting supports this interpretation.
   (b) The idea of different rate processes for C_2 and C_6 protons is not consistent with rotational motion around the C-N bond, or with ring inversion or N inversion; no other phenomenon could be envisaged which would lead to different rate processes.
   (c) The effect of internal molecular motion on chemical shifts has been considered previously and found to be very small for the particular chemical systems investigated. (L. Petrakis and C. H. Sederholm, J. Chem. Phys., 35, 1174 (1961), and references cited therein).

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8. Since this method characterizes the torsional motion about selected bonds it is complementary to the e.p.r. and n.m.r. methods, which only give information about the mobility of statistical segments, and could in some respects be a more powerful technique in structural investigations of macromolecules. The application of e.p.r. and n.m.r. techniques to polymers have been reviewed recently by M. Leca and A. O. Fulea, Materiale plastice, 10, 200 (1973) and V. J. McBrierty, Polymer, 15, 503 (1974), respectively.

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11. Extrapolation of measurements around 150-200°C (J. A. Lepoivre, H. O. Desseyn and F. C. Alderweireldt, Org. Mag. Res., 6, 284 (1974), J. Dabrovski and L. Kozerski, J. Chem. Soc. (B), 345 (1971)) gives only the energy from a Boltzmann distribution in excited torsional levels to the top of the barrier. In N,N-disubstituted thioamides the 0 → 1 torsional transition is probably lower than 100 cm^{-1} and at high temperature the excited torsional states will be extensively populated.

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