Gas-phase High-resolution N.M.R. Spectroscopy: a Potential Tool for Structural Chemistry

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A method of gas-phase ^1H n.m.r. measurement is outlined and its applications to conformational analysis and intramolecular hydrogen-bond studies are described.

The importance of gas-phase data is obvious. They are free of solvent effects and intermolecular interactions. Yet, very little attention has been paid to gas-phase n.m.r. spectroscopy. All previous studies, except the most recent one,[1] have been limited to small molecules under high pressure, because of the low sensitivity of earlier instruments.

We have been studying the *gauche*-oxygen effect in polyethers experimentally[2–4] and theoretically.[3,4] To check the molecular orbital predictions, we needed the conformer population in the gas phase of 1,2-dimethoxypropane, the simplest model compound for poly(oxypropylene).

After several attempts on a 200 MHz Fourier-transform n.m.r. instrument using a superconducting magnet, we were able to obtain ^1H n.m.r. spectra adequately resolved for analysis of the complex spin-system. Aware of the potential utility of gas-phase n.m.r., we report here our method of measurement and some applications to structural chemistry.

The sample (1—10 µl; to give a partial pressure of 0.05—1 atm at its boiling point) containing Me_4Si (*ca.* 0.02 equiv.) was placed in an 8 mm o.d. × 10 cm tube by a micro-syringe under a nitrogen atmosphere. The tube was degassed at −78 °C, filled with 1 atm (at room temperature) of nitrogen, and then sealed. This tube was fixed by a Teflon inner stopper in a 10 mm o.d. standard tube containing the appropriate lock solvent, *e.g.* C_6D_6, with Me_4Si (if necessary). For 400 MHz measurements, the combination of 3 and 5 mm o.d. tubes gave similar, successful results. For some measurements at higher temperatures, part of the sample condensed at the colder top part of the inner sample tube and vapourized on dripping down the tube wall. A longer inner sample tube was necessary for better spectrum resolution since the magnetic flux of the superconducting solenoid is parallel with the sample tube axis. Measurements were made on a JEOL FX-200 (200 MHz) instrument with a 10 mm o.d. probe and on a JEOL GX-400 (400 MHz) instrument with a 5 mm o.d. probe, with 45° flip angle pulse, and 100—1000 accumulations at *ca.* 10 s pulse intervals. Some of the excited molecules escape from the effective detector area during the free induction decay (f.i.d.) acquisition, giving results corresponding to the heavy exponential window trimming of normal f.i.d. signals. Because of this dissipation and collision with coexisting nitrogen molecules, the apparent T_1 determined by the inversion-recovery method was of the order of 1 s. All the chemical shifts are given in p.p.m. downfield from the internal gas-phase Me_4Si signal.

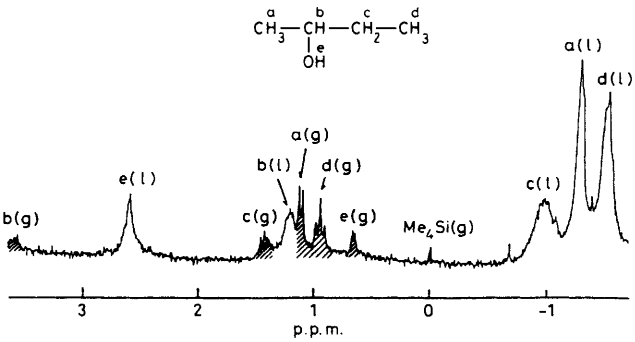

Figure 1. 200 MHz ^1H N.m.r. spectrum of butan-2-ol at 22 °C; an example of simultaneous observation of gas-phase (g: hatched) and liquid-phase (l) signals.

Figure 1 shows the spectrum of butan-2-ol at 22 °C, where the signals from the gas phase (bulk) and the liquid phase (scattered as a thin film on the inner wall by spinning) can be observed simultaneously. The gas-phase signals, except for that of the OH proton, are all shifted downfield relative to the corresponding liquid-phase signals by *ca.* 2.4 p.p.m. These

Table 1. The hydroxy proton ^1H n.m.r. chemical shifts for various alcohols in the gas phase (200 MHz).

	OH proton (δ, p.p.m.)[a]	
Alcohol	27 °C	70 °C
Methanol	0.09	0.12
Ethanol	0.46	0.49
Propan-2-ol	0.59	0.63
Butan-2-ol	0.67	0.68
2-Methoxyethanol	1.54[b]	1.47
1-Methoxypropan-2-ol	2.03	1.93

[a] Relative to the internal gas-phase Me_4Si. [b] 40 °C.

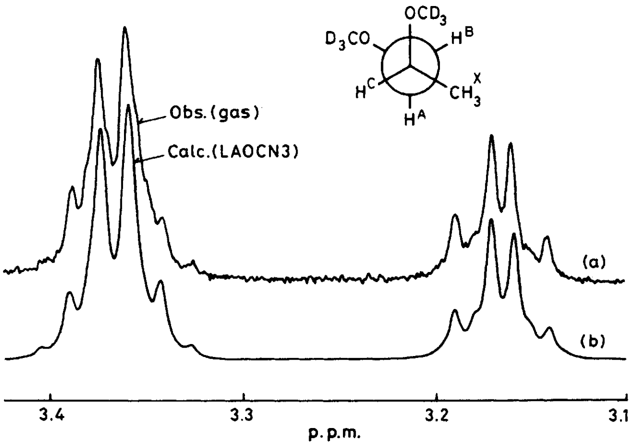

Figure 2. The methylene and methine part of the 400 MHz ^1H n.m.r. spectrum of gas-phase 1,2-di[$^2H_3$]methoxypropane at 72 °C. (a) Observed spectrum; (b) simulated spectrum as $ABCX_3$ spin system [δ_A 3.16(8), δ_B 3.36(8), δ_C 3.36(7) p.p.m.; $^2J_{AB}$ −9.46, $^3J_{AC}$ 4.89, $^3J_{BC}$ 6.38 Hz]. Spin assignment was carried out by following the logic developed previously[5] for the $OCHCH_3$–CH_2O moiety. Inset is the Newman projection of the most populated G^- conformer for the (*R*)-antipode.

parallel downfield shifts can be explained primarily by the difference in the volume magnetic susceptibility, χ_v, of each phase.[†] Owing to the negligibly small χ_v value for the gaseous sample, the gas-phase Me_4Si signal can be used as an absolute chemical shift standard,[†] barely affected by χ_v and hence by temperature.

Figure 2 shows the methylene and methine part of the spectrum of gas-phase 1,2-di[$^2H_3$]methoxypropane. The spin-system analysis as $ABCX_3$ by the LAOCN3[6] program gives vicinal coupling constants $^3J_{AC}$ 4.89 Hz and $^3J_{BC}$ 6.38 Hz at 72 °C (see Figure 2 for A, B, and C). Assuming ^3J values for antiperiplanar and synclinal couplings of 9.1 and 2.6 Hz, respectively,[‡] the conformational energies for the G^- and G^+ conformers of the (*R*)-antipode are determined to be -0.5 and 0.8 kcal mol^{-1},[§] respectively, relative to that for the *T* conformer. These values are in reasonable agreement with those predicted by geometrically optimized MNDO[7] molecular orbital calculations (-0.8 and 0.4 kcal mol^{-1},[§] respectively). Thus, *gauche* stabilization is intrinsic to the O–C–C–O bond sequence even without solvent perturbation.

Table 1 shows the gas-phase ^{1}H chemical shifts of several alcohol OH protons. The free OH signals of the unsubstituted primary and secondary alcohols appear at 0.1—0.7 p.p.m. The shift for the ethanol OH proton is in good agreement with the previous one by Schneider.[8] In contrast, 1-methoxypropan-2-ol and 2-methoxyethanol show their OH signals at *ca.* 2.0 and 1.5 p.p.m., respectively. For 1-methoxypropan-2-ol, we reported[9] that the predominant species in dilute, nonpolar solution is an intramolecularly hydrogen-bonded species. The present gas-phase shift (2.0 p.p.m.) of the OH proton coincides with the value (1.9 p.p.m.)[9] extrapolated to infinite dilution in carbon tetrachloride, indicating that, in the gas-phase as well, the molecule preferentially takes the intramolecularly hydrogen-bonded form.

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[†] When the magnetic field is parallel with the sample tube axis, the difference of the chemical shifts $\Delta\delta$ ($= \delta_2 - \delta_1$) of a nucleus in media 1 and 2 is given by $\Delta\delta = \delta_2 - \delta_1 = (4\pi/3)(\chi_{v_2} - \chi_{v_1})$, using a long, thin rod approximation (see ref. 10).

[‡] ^3J values observed for the intramolecularly hydrogen-bonded 1-methoxypropan-2-ol in $CHCl_3$ at -43 °C, K. Tsuji, T. Hirano, and T. Tsuruta, *Makromol. Chem.*, 1975, Suppl. **1,** 55.

[§] 1 kcal = 4.184 kJ.