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VARIABLE-TEMPERATURE INFRA RED AND PROTON, FLUORINE-19, AND CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTROMETRIC EVIDENCE FOR ROTATIONAL ISOMERISM IN FURAN-2-CARBONYL FLUORIDE

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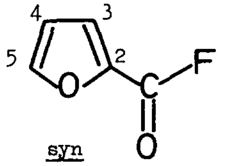
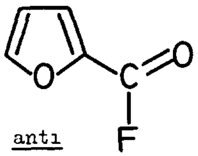
IT has been convincingly demonstrated by low temperature proton[1] and carbon-13[2] n.m.r. spectrometry that furan-2-carbaldehyde exists in solution as a mixture of rotational isomers, but the i.r. carbonyl band doublet observed for this compound arises from Fermi resonance and not rotational isomerism[3]: the 5-deuterio analogue has a single carbonyl band. The data presented here for furan-2-carbonyl fluoride and its 5-deuterio analogue reveal a very different situation.

Whereas in CCl_4 the protio compound has three i.r. C=O bands, the 5-deuterio compound has two bands: the relative intensities of these closely parallel those of the overtone C=O bands, and vary with change of temperature in a manner consistent with the occurrence of an equilibrium between rotamers having only a small enthalpy difference.



syn



anti

No coalescence phenomenon is observed in the proton (in CH_3CHCl_2) or carbon-13 (in CD_2Cl_2) n.m.r. spectra for furan-2-carbonyl fluoride at temperatures down to *ca.* -80°C; the critical changes as temperature is decreased are the gradual decrease of the 4,H-F coupling and the gradual increase of the 5,H-F coupling, and the gradual appearance of a long-range 2,C-F coupling which is *absent* in the room temperature spectra. The carbon-13 result is best explained by assuming that *syn* and *anti* forms have $J_{2,C\text{-}F}$'s of opposite sign which are fortuitously balanced to about zero at room temperature in CD_2Cl_2. Further details concerning this unusual result will be given in a full paper.

Fluorine-19 n.m.r. provides the clearest evidence for the occurrence of rotational isomerism. With decrease in temperature, the fluorine resonances coalesce, and when temperature is decreased further they sharpen to pairs of signals. Solutions of the fluoride in three solvents (Table) contain appreciable amounts of both rotamers both at low and room temperatures, but the ratios are very different from the figure of unity assumed for a 10% solution in diethyl ether at 32°C[4]. That the isomer predominant at low temperatures is already predominant at room temperature follows directly from the fluorine resonances' chemical shifts: this predominant isomer has the higher field fluorine signals (at temperatures below coalescence), is proton-coupled mainly to 5,H, and (on 5-deuteriation) produces the higher wavenumber (larger) component of the i.r. C=O doublet. If the W-rule established for H-H coupling in heterocyclic systems[5] applies also to H-F couplings, then this predominant isomer must be *syn*. The F-H coupling at room temperature (observed as a weighted average in the fluorine n.m.r. spectra) is significantly lower than either of the individual rotamers' F-H couplings determined at low temperature in CD_2Cl_2. This may arise from the intrinsic temperature dependence of coupling constants; alternatively, the individual $\underline{J}_{F,H}$ values may be opposite in sign. The small effect of change of solvent on the position of equilibrium contrasts markedly with the behaviour of furan-2-carbaldehyde[8] and indicates that the difference in dipole moment between *syn* and *anti* forms of the fluoride is less than with the aldehyde.

TABLE

Rotamer percentages at 183°K. *H* and *L* refer to higher and lower wavenumber (i.r.) or field (n.m.r.) absorptions. The i.r. results refer to data from the 5-deuterio analogue and are calculated assuming that pairs of rotamers have equal integrated absorption coefficients[6]. Of the three solvents, only CCl_3F allowed accurate curve resolution[7] of the fluoride's C=O doublet.

	$\nu_{\underline{H}}$	$\nu_{\underline{L}}$	$\Phi_{\underline{H}}$	$\Phi_{\underline{L}}$
in CCl_3F	78	22	72	28
in CD_2Cl_2	-	-	84	16
in CH_3CHCl_2	-	-	80	20

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