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^{13}C N.M.R. STUDY OF ROTATIONAL ISOMERISM IN FURAN-, THIOPHEN-, AND *N*-METHYLPYRROLE-2-CARBALDEHYDES, 2-ACETYLFURAN, FURAN-2-CARBONYL CHLORIDE, AND *t*-BUTYL FURAN-2-CARBOXYLATE

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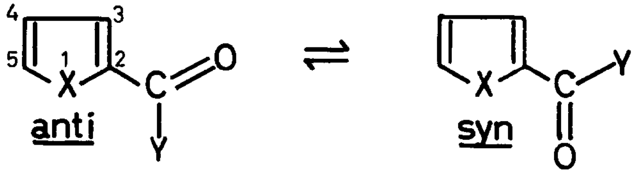
Variable-temperature ^{13}C n.m.r. is a sensitive method for detecting rotational isomerism in the Title compounds, and in some cases this technique reveals features not detectable by other spectrometric methods.

THERE have been many investigations, by proton magnetic resonance techniques, into the rotational isomerism of the Title aldehydes and ketones (generally as solutions in non-polar solvents). The most recent work suggests (see formulae) that while furan-2-carbaldehyde (I) has *K* *ca.* 6 at -90°C and *K* *ca.* 1 at 30°C,[1,2,3,4] and *N*-methylpyrrole-2-carbaldehyde (II) has *K* = 22 at -60°C and *K* = 9 at 30°C,[5,6] 2-acetylfuran (IV) has *K* *ca.* 1 over the whole temperature range.[4,7] Only the *syn* conformation of thiophen-2-aldehyde (III) has been detected,[3] and with t-butyl furan-2-carboxylate (VI) we cannot find p.m.r. evidence for rotational isomerism even though appreciable amounts of the two rotamers are probably present at 30°C.[8]

The failure of p.m.r. to detect rotational isomerism may arise from the presence of a very low proportion of one rotamer, a very small barrier to rotation, or an insufficient difference between the rotamers' spectral characteristics. We have found that the sensitivity of ^{13}C chemical shifts to environmental change provides a powerful method for studying rotameric equilibria; in some cases the ^{13}C resonances reveal features not observable using the p.m.r. method.

K = [*syn*]/[*anti*]



(I) X=O, Y=H; (II) X=NMe, Y=H; (III) X=S, Y=H; (IV) X=O, Y=Me; (V) X=O, Y=Bu^{t}O; (VI) X=O, Y=Cl

The ^{13}C resonances of compounds (I)-(VI) in suitable non-polar solvents were examined, using proton noise decoupling, from 30°C to -90°C: resonance assignments were made from off-resonance decoupling and deuteriation experiments which will be described later. In all of the compounds, the C-3 resonances broaden with decrease in temperature; in some cases more striking effects also occur. Thus, below -60°C furan-2-carbaldehyde (I) in CH_2Cl_2/CD_2Cl_2 shows two C-3 resonances [intensity ratio (higher to lower field signals) 1:10 at -70°C, separation ca. 9 p.p.m.] and two C=O resonances (10:1, ca. 3 p.p.m.). The intensity ratio may not reflect exactly the ratio of the rotamers because of the possible differences in relative Overhauser enhancements: the use of a solution in $CDCl_3$ containing $Cr(acac)_3$, which minimises this difference but which may alter the equilibrium position by a dielectric effect,[2] leads to a ratio of 5:1. Shielding considerations[9,1] suggest, in agreement with but independently of the p.m.r. work, that the *syn* form predominates.

Solutions of aldehydes (II) and (III) do not show similar splitting of the signals as the temperature is lowered. The C-3 resonances broaden to maximal values at a certain temperature and then sharpen to resume their original heights at a lower temperature. For *N*-methylpyrrole-2-carbaldehyde (II) the temperatures are -20°C and -50°C, and for thiophen-2-carbaldehyde (III) -75°C and ca. -90°C. Thus, although both compounds exist very largely in preferred forms (from the p.m.r. results, the *syn* conformations) over the whole temperature range, the ^{13}C results still demonstrate the occurrence of rotational isomerism. With t-butyl furan-2-carboxylate (V) the broadening has not passed its maximum even at -90°C, presumably because of a lower rotational energy barrier.

Splitting of signals is most dramatic with the furan ketone (IV) and acid chloride (VI). At -80°C the former shows pairs of signals with intensity ratios 3.5:1 (higher to lower field absorptions) for the *C*=O and *C*-2 resonances, and pairs with ratios 1:3.5 for the *C*-3 and *C*-5 resonances; the latter has pairs with ratios 10:1 for *C*=O and *C*-4, and 1:10 for *C*-3 and *C*-5. The *syn* form of the ketone is considered to be the major rotamer at low temperature, and this will also apply to the acid chloride if the compounds' substituents are similar in their shielding characteristics.

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