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THE NEMATIC PHASE NMR SPECTRA OF FURAN- AND THIOPHENE-2,5-DIALDEHYDE A NEW APPROACH TO CONFORMATIONAL ANALYSIS

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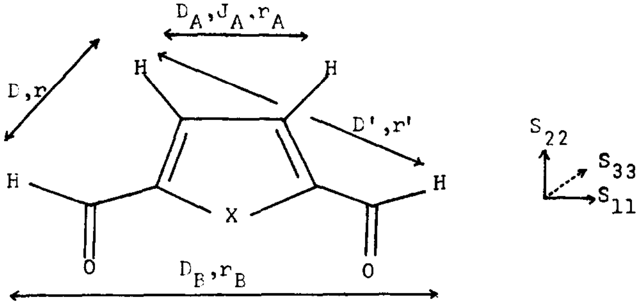
If molecules such as furan- and thiophene-2,5-dialdehyde (Ia,b), in undergoing rotational isomerisation yield on the NMR timescale averaged structures which obey C_{2v} symmetry, their NMR spectra when oriented in the nematic phase of a liquid crystal should be potentially interpretable in terms of time-averaged internuclear distance ratios.

Since there has been much recent interest and some controversy concerning the solution conformational preferences of heterocyclic aldehydes and ketones, the liquid-crystal technique has been applied to Ia,b (chosen because of their symmetry) in an attempt to derive independent evidence concerning their favoured molecular orientations.



Ia X = O

Ib X = S

The Table shows the spectral parameters derived by an iterative analysis of their 220 MHz spectra in the nematic phase of 4,4-di-n-hexyloxyazoxybenzene. The dipolar couplings given have been reduced by a factor of two from those produced by a modified LAOCOON program (1), in order to make them compatible with the C_{2v} equations given by Diehl et al. (2), which were used in a Newtonian numerical search for the values (tabulated) of r/r_A, and in the calculation of r_B/r_A and r'/r_A.

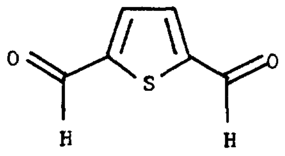
TABLE

	Ia(X = O)†	Ib(X = S)†
$\lvert\nu_A-\nu_B\rvert$	550.0	406.4
J_A(assumed)	+3.5	+3.9
D_A	-1096.25±0.65	-1570.77±0.57
D_B	- 128.15±1.2	- 96.19±0.57
D	- 246.9 ±0.65	- 765.69±0.47
D'	- 90.9 ±1.2	- 186.88±0.66
r/r_A	-1.122	1.195
r'/r_A	1.818	1.991
r_B/r_A	2.045	2.537

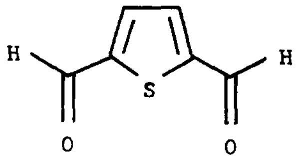
† all shifts and couplings are given in Hz

It can be seen that although a reasonable solution is found for the thienyl derivative, no such solution would appear to exist for the furan, where the observed value for r/r_A (-1.122) can have no physical meaning although its magnitude is readily acceptable in terms of an assumed geometry.

From published microwave data for thiophene (3) a value of r_A = 2.61 A° was assumed, and from this and x-ray data for 2-thienyl carboxylic acid (4) a reasonable model for the molecular geometry of thiophene-2,5-dialdehyde in its di-s-cis (II) and di-s-trans (III) forms was constructed. This value of r_A affords values of r = 3.10, r' = 5.20 and r_B = 6.62 A° respectively using the internuclear distance ratios derived from the liquid crystal data. Superimposition of these dimensions on the geometrical model indicates that the equilibrium position of the aldehyde protons lies approximately 65% towards the transoid structure (III). I.e., the aldehyde groups are twice as likely to be found in the s-trans configuration than in the s-cis position.



II



III

Further refinement of these parameters is in progress, together with a more detailed assessment of the geometrical situation in furan-2,5-dialdehyde, and will be described in a full paper. It is tentatively suggested at this time that the energy minima for the s-cis and s-trans rotamers in Ia do not lie in the plane of the heterocyclic ring, and impose a C_2 rather than a C_{2v} symmetry on the hydrogen nuclei in the NMR timescale. This may be caused by carbonyl oxygen-ring oxygen repulsions, which are replaced in Ib by a small attractive interaction between oxygen and sulphur which would maintain coplanarity of the rotational energy minima with the thiophene ring.

It is of interest to note that since the completion of this work a paper has appeared (5) in which the effective C_{2v} symmetry in 1,2,2,3-tetrachloropropane is used to determine the most probable conformation.

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