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A CONFORMATIONAL STUDY OF SOME TRANS-2-(2-FURYL)- AND TRANS-2-(2-THIENYL)ETHYLENES USING NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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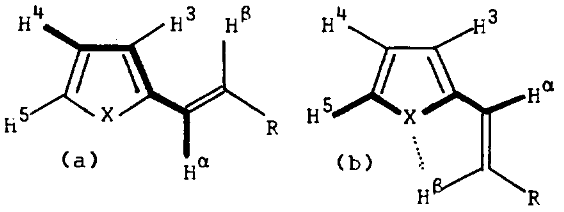
Recent interest in the conformational preferences of thiophene-, (1,2,3) furan-, (1,2) and pyrrole-2-aldehyde (1,4) and other related compounds prompts me to report preliminary NMR spectroscopic data for some simple condensation products (I) of furan- and thiophene-2-aldehyde.



(I)

The NMR spectra have been determined at 60 MHz and fully analysed as ABCDE or $ABCDEX_3$ systems by iterative procedures using the computer programs LAME (5) and UEANMR ITERATIVE (6). Partial parameters are summarised in the Table.

By analogy with the heterocyclic aldehydes, two contributing conformations must be considered, viz I a, b. Both forms contain one 5-bond W arrangement of atoms, through which enhanced coupling might be expected. Examination of the Table shows that in all cases $^5J_{4\alpha}$ is either very small or not observable, whereas in 2-formylpyridine, which exists (7) as ca. 70% (II), the ^5J coupling

Table

X	R	$^4J_{3\alpha}$	$^5J_{4\alpha}$	$^5J_{5\alpha}$	$^5J_{3\beta}$	$^6J_{5\beta}$
O	NO_2[a]	0.231 ±0.031	0.216 ±0.030	0.547 ±0.031	0.537 ±0.027	0.479 ±0.027
O	COOH[b]	0.434 ±0.075	<0.1	0.463 ±0.069	0.476 ±0.079	0.502 ±0.072
O	$COCH_3$[a,c]	0.460 ±0.006	0.190 ±0.005	0.474 ±0.005	0.291 ±0.006	0.473 ±0.005
S	NO_2[a]	0.631 ±0.025	0.168 ±0.022	0.783 ±0.031	0.419 ±0.023	0.328 ±0.032
S	COOH[b]	0.587 ±0.014	<0.1	0.771 ±0.010	0.418 ±0.014	0.326 ±0.010
S	$COCH_3$[a,d]	0.581 ±0.060	0.069 ±0.055	0.880 ±0.057	0.388 ±0.061	0.276 ±0.059

All couplings are in Hz

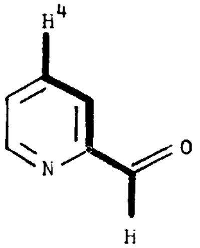
a. in carbon disulphide

b. in acetone

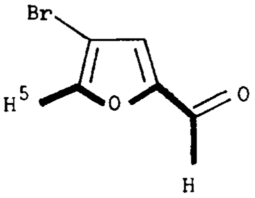
c. from an 8-spin calculation

d. from an ABCDE approximation

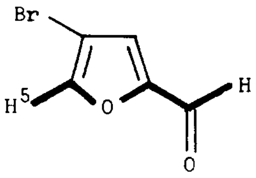
between the formyl proton and H^4 is 0.60 Hz (in DMSO solution). It has very recently been demonstrated (2) that the $^5J_{5,CHO}$ couplings in 2-formyl-4-bromo furan frozen into its cisoid (III) and transoid (IV) conformers are 0 and 1 Hz respectively. The values found for $^5J_{5\alpha}$ in I (X=O) would therefore suggest that Ib is the major contributor, and is possibly not present to as great an extent as in the aldehydes. (The effects of replacing the aldehyde oxygen by doubly bound carbon, and of the R substituents on the magnitudes of these couplings are not considered here).



II



III



IV

Perhaps the most striking piece of evidence for a transoid configuration is to be found in the magnitude of the $^6J_{5\beta}$ coupling. It is most unlikely that the configuration Ia would make a significant contribution, and this remarkable long range coupling reaching 0.5 Hz in I (X=O, $R=NO_2$) may well arise partly from a weak associative bond between H^β and the heteroatom, as shown in Ib. The relatively large values for $^5J_{3\beta}$ are also probably the results of dominant transoid configuration of the 2,3- and exocyclic double bonds. (Compare $^5J_{cc}$ in some halogenated butadienes which ranges from 0.59 to 0.83 Hz (8)).

This work is continuing, and a full discussion of the NMR spectra for these and related molecules will appear in a full publication. It is a pleasure to thank Professor K.J. Morgan and Dr. R.W.H. Small for valuable discussions.

1. D.J. Chadwick and G.D. Meakins, Chem.Comm., 637 (1970)
2. B. Roques, S. Combrisson, C. Riche and C. Pascard-Billy, Tetrahedron, 26, 3555 (1970)
3. H. Lumbroso and P. Pastour, Compt.rend., 261, 1279 (1965); H. Lumbroso, D.M. Bertin, M. Robba and B. Roques, Compt.rend., 262C, 36 (1966)
4. R.A. Jones and P.H. Wright, Tetrahedron Letters, 5495 (1968)
5. A revised and improved version of LAOCN3 with magnetic equivalence factorisation; C.W. Haigh, University of Swansea, personal communication.
6. Made available on the S.R.C. Atlas Computer, Chilton, by the University of East Anglia.
7. G.J. Karabatsos and F.M. Vane, J.Amer.Chem.Soc., 85, 3886 (1963)
8. A.A. Bothner-By and R.K. Harris, J.Amer.Chem.Soc., 87, 3445 (1965)