Nuclear Magnetic Resonance Study of Furan-2-carbaldehyde *N*-Alkylimines

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A cmr and pmr study of furan-2-carbaldehyde *N*-alkylimines is reported.

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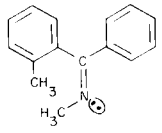
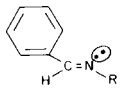
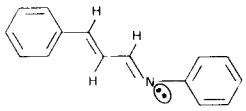
Ketimines are known to exist in isomeric forms and the stability of isomers is not exclusively dictated by steric factors. Thus in *N*-methylbenzophenonimine the most stable isomer is the *cis* isomer I (1).



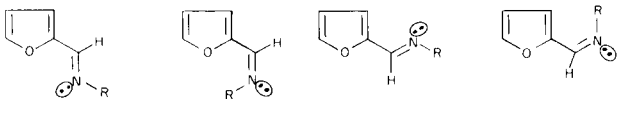
I



II



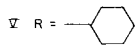
Aldimines derived from benzaldehyde and cinnamaldehyde have been established to exist in *anti*forms only II (2). However, cases are reported where aldimines are found to exist in *syn* and *anti* isomers (3). For rationalising this isomerism, views expressed lay emphasis on the effective size of the lone pair on the nitrogen atom and also "*N*-repulsive interaction" between the lone pair of electrons on the Sp^2-nitrogen atom and the electrons of the aryl ring. Furan-2-carbaldehyde has been shown to exist in two rotational isomers *O-O cis* and *O-O trans*. Here we report a nmr study of furan-2-carbaldehyde *N*-alkylimines which could have four rotational isomers III.



a b c d

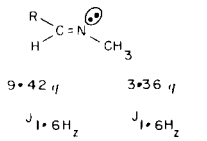
III R = CH_3

IV R = C_2H_5

V R = 

The imines were prepared from freshly distilled furan-2-carbaldehyde and freshly distilled amines. In the case of methyl amine, the aqueous solution (containing an equimolar amount of methyl amine) was mixed slowly with furan-2-carbaldehyde (equimolar). The reaction was exothermic and the temperature was maintained below 20° either by slow addition of the amine solution or by external cooling. This clear aqueous solution when brought to *p*H 10.5 separated into two layers. The organic layer containing the imine was dried and distilled under vacuum. The required sample could be obtained after several distillations. Similarly, the *N*-ethylimine was prepared. In the case of cyclohexylimine no layer separation was required and the imine was distilled directly. All the distillations were carried out under a nitrogen atmosphere. The cmr and pmr data of these imines is given in Table I-III, chemicals shifts are in ppm relative to TMS.

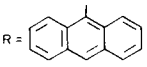
The cmr data show clear C-H couplings as well as other long range coupling. Since the pmr required further examination, the *N*-methylimine sample was run in deuteriochloroform at 300 MHz which showed the azomethine proton as a clear quartet and the methyl as a doublet (CH_3d $J_1 \in_{6\ Hz}$ 3.498 C = Nq $J_1 \doteqdot_{6\ Hz}$ 8.13) and the furan ring protons as usual; however, none of them showed long range coupling with the azomethine proton. The doublet because of methyl could collapse to a singlet when the azomethine proton was decoupled and *vice-versa*. Pmr spectra was also recorded as low as -90° and no further splitting of the signals was observed indicating the presence of a single rotamer or the fast equilibrating mixture of a-d. In case of aldimine VI (3) and VII the nmr data is as shown below:

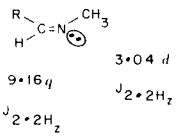


9·42 q 3·36 q

$J_{1\cdot6H_z}$ $J_{1\cdot6H_z}$

VI

R = 



3·04 d

9·16 q

$J_{2\cdot2H_z}$

$J_{2\cdot2H_z}$

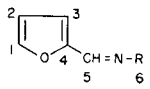
VII

Regarding the cmr, C = CC-CH and C-N = CH coupling constants reported in the case of C_6H_5CH = N-CH_3 are 9 and 13.5, respectively (4) which are comparable with our experimental data. Also the magnitude of the C-H (imine carbon) coupling constant is in agreement with *E trans* structure only. The dipole moment was also in agreement with this assignment (5).

0022-152X/79/051073-02$02.25

Table I

Carbon-13 Chemical Shifts of Furan-2-carbaldehyde *N*-methylimine (III)



Assignments	Multiplicity	Coupling Constant	Chemical Shift	H¹ Chemical Shift
1	dt	J_{CH} = 206	144.6	7.49 broad
		J_{CCH} and J_{CCCH} = 9.5		
2	m	J_{CH} = 176	111.9	6.40 dd
3	m	J_{CH} = 176	112.6	6.74 d
4	m		152.9	
5	dq	J_{CH} = 160 J_{CNCH} = 9.5	151.3	8.03 d
6	dq	J_{CH} = 135 J_{CNCH} = 13	48.0	3.38 d

Table II

Carbon-13 Chemical Shifts of Furan-2-carbaldehyde *N*-ethylimine (IV)

Assignments	Multiplicity	Coupling Constant	Chemical Shift	H¹ Chemical Shift
1	dt	J_{CH} = 203	144.5	7.45 d
		J_{CCH} and J_{CCCH} = 8.5		
2	dd	J_{CH} = 176 J_{CCH} = 3.6	111.8	6.40 dd
3	dd	J_{CH} = 176 J_{CCH} & J_{CCCH} = 3.6	112.3	6.74 d
4	m		152.9	
5	dt	J_{CH} = 158 & J_{CNCH} = 9.5	149.1	8.03 d
6	tm	J_{CH} = 134	56.0	3.54 dq
7	q	J_{CH} = 127	16.4	1.23 t

Table III

Carbon-13 Chemical Shifts of Furan-2-carbaldehyde *N*-Cyclohexylimine (V)

Assignments	Multiplicity	Coupling Constant	Chemical Shift	H¹ Chemical Shift
1	dt	J_{CH} = 203,	144.2	7.42 d
		J_{CCH} and J_{CCCH} = 8.5		
2	d	J_{CH} = 176	111.6	6.38 dd
3	d	J_{CH} = 176	111.8	6.72 d
4	m		152.9	
5	dd	J_{CH} = 158 and J_{CNCH} = 9.5	147.22	8.07 broad
6	dm	J_{CH} = 127	69.9	3.07 m
Others	m		34.7 ◊	
			24.9 ◊	1-2 m.m.
			26.0 ◊	

Acknowledgment.

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(4) G. Binch, J. B. Lambert, B. W. Roberts and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 5564 (1974).

(5) The diple moment of furan-2-carbaldehyde *N*-Methylimine is 1.55 in carbon tetrachloride at 25°.