Tetrahedron Letters No.53, pp. 5495-5496, 1968. Pergamon Press. Printed in Great Britain.

A Conformational Study of 1-tert. Butyl-2-formylpyrrole

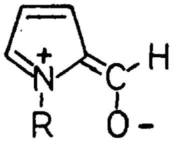
R. Alan Jones and P. H. Wright

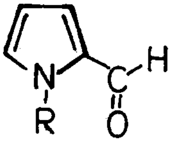
School of Chemical Sciences, University of East Anglia.

(Received in UK 6 September 1968; accepted for publication 1 October 1968)

The importance of the zwitterionic canonical form I for 2-formylpyrroles imparts restricted rotation upon the formyl group such that two conformers II and III may exist. An investigation[1] of the dipole moment of 2-formyl pyrrole (II or III, R=H) suggests that it is conformer II which is the more stable. This is further supported by infrared[2] and nuclear magnetic resonance[3] studies. The formyl proton has been shown conclusively[4] to couple with the hydrogen in the 5-position of the ring and, by an application of "zigzag" rule[5], this implies the predominance of conformer II. Such results may be rationalized for 2-formylpyrrole in that, although steric effects for the two conformers are almost identical, the dipole moments of the pyrrole ring and the carbonyl group for conformer II are not repulsive, whereas for conformer III they will tend to repel each other (cf. m-substituted benzaldehydes[3]). This treatment ignores the contribution to the dipole of a conjugative interaction moment. Also when R=H, weak intramolecular hydrogen bonding will tend to stabilize conformer II compared with III[2,6].

It was of interest, therefore, to consider the position where hydrogen bonding was absent and where steric effects were considerable (e.g. II ⇋ III, R = $(CH_3)_3C$-). One might expect that the steric effect would force the formyl group to assume conformation III (cf. o-substituted benzaldehydes[3]) which would have an unfavourable disposition of dipoles. In Table 1 we present spectroscopic data for a series of 1-alkyl-2-formylpyrroles. The infrared and ultraviolet spectroscopic data clearly indicate a decrease in conjugation of the formyl group with the ring as the alkyl group is increased in size and, although the J_{5H-CHO} coupling constants are less conclusive, the results tend to suggest that the conformation remains approximately the same throughout the series. Thus by extrapolation from 2-formylpyrrole it appears that the conformation of 1-tert butyl-2-formyl pyrrole approximates to II and that the steric interaction is accommodated by the formyl group twisting slightly out of the plane of the ring. A variable temperature n.m.r. study on all aldehydes mentioned, together with 1-benzyl- and 1-phenyl-2-formylpyrrole, is in progress.


[I]


[II]

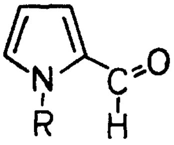

[III]

Table 1

II or III	$CO^{(a)}$ (cm^{-1})		λ max$^{(b)}$ nm (ϵ)		$J_{5H\text{-}CHO}^{(c)}$ (Hz)
R = H	1667	246 (7,000)	279 (15,200)		1.1_5
Methyl	1671.5	253 (7,500)	280 (16,100)	288* (12,700)	0.9
Ethyl	1670.5	254 (7,800)	280.5 (16,400)	289* (12,900)	1.0_5
iso-Propyl	1672	254 (7,100)	281.5 (14,800)	289.5*(11,500)	1.1_5
tert-Butyl	1677	249 (7,000)	282 (12,000)		1.2

(a) Measured as 0.005 M solutions in CCl_4 on a Perkin-Elmer Model 125 spectrometer. (b) Measured as 10^{-5} M solutions in hexane. * inflexion. (c) Measured as ca. 30% solutions in CCl_4 on a HA 100 spectrometer.

1. A. Marinangelli, Ann.Chim. (Rome), 44, 219 (1954).
2. R. Alan Jones and A.G. Moritz, Spectrochim. Acta, 21, 295 (1965).
3. G.J.Karabatsos and F.M.Vane, J.Amer.Chem.Soc., 85, 3886 (1963).
4. S.Gronowitz, A-B. Hörnfeldt, B.Gestblom, and R.A.Hoffman, Arkiv. Kemi, 18, 133 (1961).
5. C. N. Banwell and N.Sheppard, Discuss. Faraday Soc., 34, 115 (1962).
6. R. W. Guy and R. Alan Jones, Austral. J. Chem., 19, 107 (1966).