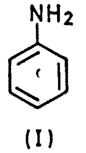
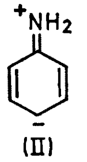
Substituent Effects in Benzene: the Microwave Spectrum of *p*-Fluoroaniline

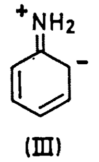
By A. HASTIE, D. G. LISTER, R. L. MCNEIL, and J. K. TYLER*
(*Chemistry Department, The University, Glasgow, W.2*)

Summary Microwave spectra have been observed for two isotopic species of *p*-fluoroaniline: the molecule is found to be more non-planar than aniline itself and this result is interpreted in terms of there being π-mesomeric involvement of fluorine electrons with the ring system.

IT is now established that in its ground electronic state aniline has a non-planar structure, at least in the gas phase.[1–3] A detailed microwave study[2] has shown that the angle (ϕ) between the HNH plane and the plane formed by the remaining atoms is close to 38°. This angle would be 54°44′ for a tetrahedral configuration of bonds at nitrogen and thus in aniline the $-NH_2$ pyramid is somewhat flattened towards the planar situation. One interpretation of this is to consider that the nitrogen "lone-pair" electrons are involved in the π-system of the whole molecule, or, in a simple view, to consider structures such as (II) and (III), which imply planarity at nitrogen, to be important.


(I)


(II)


(III)

Other ring substituents may facilitate or hinder this electron shift and this might well be reflected in the $-NH_2$ geometry. To obtain an idea of the magnitude of such effects we have studied the microwave spectrum of *p*-fluoroaniline.

The general appearance of the microwave spectrum, observed at room temperature, of *p*-fluoroaniline closely resembles that due to aniline itself. Each μa, *R*-branch ground-state line is accompanied by a single vibrational satellite of comparable intensity and this strongly suggests a non-planar configuration undergoing inversion. Spectra were also obtained for FC_6H_4NHD with a view to locating the $-NH_2$ protons. The ground-state rotational constants were obtained from the observed line frequencies by a rigid-rotor least-squares fitting procedure and are listed for both isotopic species in the Table. The moments of inertia derived from these constants and the inertial defects are also given. As in aniline, the large negative value of Δ^0 for $FC_6H_4NH_2$ and its behaviour on deuteriation confirms the non-planar nature of the molecule.

TABLE

$FC_6H_4NH_2$				
A_0	5594·28		I_a^0	90·3657
B_0	1449·12		I_b^0	348·8528
C_0	1152·16		I_c^0	438·7676
			Δ^0	−0·4509
FC_6H_4NHD				
A_0	5545·70		I_a^0	91·1572
B_0	1404·99		I_b^0	359·8099
C_0	1122·78		I_c^0	450·2492
			Δ^0	−0·7179

$\Delta^0 = I_c^0 - I_a^0 - I_b^0$.
Rotational constants are given in MHz and moments of inertia in a.m.u. Å².

The data enable the moments of inertia of the FC_6H_4N fragment to be derived as (in a.m.u. Å²): $I_a' = 88·6772$, $I_b' = 326·3512$, $I_c' = 415·1873$, and $\Delta' = I_c' - I_a' - I_b' = +0·1589$. The value of Δ' is good evidence for the planarity of this fragment.

If the N–H distance is set at the reasonable figure of 1·00 Å, and the general dimensions of the FC_6H_4N fragment estimated from the known structures of aniline and fluorobenzene in a way consistent with the moments of inertia, the $-NH_2$ geometry can readily be calculated. The H–N–H angle (θ) is determined as 111°52′, and the out-of-plane angle (ϕ) as 46°22′. The corresponding angles in aniline calculated in the same way with N–H = 1·00 Å are: θ = 113°16′,

$\phi = 37°39'$. Variation of the N–H bond distances by $\pm 0{\cdot}01$ Å results in changes in the region of $\pm 2°$ in θ and ϕ in both cases. Therefore, unless the respective N–H distances differ to an unexpectedly large degree, *p*-fluoroaniline is considerably more non-planar than aniline itself.

The presence of the *p*-fluorine may have two effects. First, this atom could withdraw electrons from the ring *via* the σ-system by an inductive mechanism. Such an effect has been invoked to explain the opening of the C-6–C-1–C-2 angle in fluorobenzene,[4] but this is a very localised effect. The extent to which this could facilitate electron transfer from nitrogen to the ring, favouring a more nearly planar configuration at nitrogen in $FC_6H_4NH_2$, is probably very slight. Second, two of the fluorine "lone-pair" electrons may become involved in the π-system of the ring by a mesomeric process. This would inhibit the π-mesomerism of the nitrogen electrons and thus favour a more nearly tetrahedral nitrogen situation. The observed results suggest this latter effect to be important.

One of us (D. G. L.) thanks the S.R.C. for a maintenance grant.

(*Received, December* 1*st*, 1969; *Com.* 1820.)

[1] D. G. Lister and J. K. Tyler, *Chem. Comm.*, 1966, 152.
[2] D. G. Lister, Ph.D. Thesis, University of Glasgow, 1968.
[3] J. C. D. Brand, D. R. Williams, and T. J. Cook, *J. Mol. Spectroscopy*, 1966, **20**, 359.
[4] L. Nygaard, I. Bojesen, T. Pedersen, and J. Rastrup-Andersen, *J. Mol. Structure*, 1968, **2**, 209.