Non-planarity of the Aniline Molecule

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ANILINE may be considered to be a member of a class of molecules of general type NH_2X in which X is an unsaturated system which may act as an electron sink. In a valence-bond picture, the structure $\overset{+}{N}H_2 = \overset{-}{X}$ may well be an important contributor to the overall state of such a molecule. Formamide (X = CHO), cyanamide (X = CN), and nitramide ($X = NO_2$) are further molecules of this type and recent microwave studies[1-7] have shown that, while the NH_2–X bonds are short in these molecules, the amino-nitrogen atoms retain, to a greater or lesser extent, pyramidal configurations. We have now made a study of the microwave spectrum of aniline and conclude that this molecule is also non-planar.

A striking feature of the spectrum, observed at room temperature, is that each ground-state transition is accompanied by a vibrational satellite of comparable intensity. This observation strongly suggests that the molecule is non-planar and that we are observing rotational transitions due to molecules in O^+ and O^- inversion states. Both the O^+ and O^- lines closely follow the behaviour expected for a rigid asymmetric rotor and their relative intensities depend on the particular transition in a way consistent with a molecule having three equivalent pairs of protons.

Some fifty μa, *R*-branch lines were measured for normal aniline in the 20—30 KMc./sec. region and rotational constants obtained from a rigid-rotor least-squares fit to the observed frequencies. Ground-state lines have also been measured for C_6H_5NHD. The rotational constants (in Mc./sec.) and moments of inertia (in a.m.u. Å^2) are summarized in the Table.

The large negative value of Δ^0 and its behaviour

on deuteration confirms the pyramidal nature of the nitrogen atom. The inertial constants of the C_6H_5N fragment are readily calculable from the data as: $Ia' = 88{\cdot}3667$, $Ib' = 178{\cdot}7791$, $Ic' = 267{\cdot}1659$ (all in a.m.u. Å^2), resulting in a value of $+0{\cdot}0201$ a.m.u. Å^2 or Δ'. This figure is good evidence for the planarity of this fragment. If we now make the rather crude assumption that C_6H_5 fragment has a regular geometry and take C–H = 1·084 Å as in benzene[8] we calculate: C–C = 1·392 Å, C–N = 1·431 Å, N–H = 0·998 Å, $\angle$HNH = 113° 54′, ϕ = 39° 21′ = angle between the C–N bond extended and $\angle$HNH bisector.

The C–N bond length of 1·431 Å may be compared with that of 1·474 Å in methylamine[9] and the short bonds found in formamide[2] (1·376 Å) and cyanamide[4] (1·346 Å). The degree of non-planarity is very similar to that of cyanamide for which ϕ is about 38° and in this respect aniline is intermediate between formamide ($\phi \sim 17°$) and nitramide[7] ($\phi \sim 51°$). No precise estimate of the NH_2 inversion barrier in aniline can be made at this time, although the relative intensities of the O^+ and O^- transitions suggest that the $O^- - O^+$ separation is probably less than 100 cm.$^{-1}$ The corresponding barriers in formamide,[2] cyanamide,[4] and nitramide[4,7] have been determined as 370, 710, and 950 cm.$^{-1}$ respectively.

TABLE

$C_6H_5NH_2$	O^+	O^-		
A	5617·40	5615·57	I^0a	89·9938
B	2593·84	2592·24	I^0b	194·8968
C	1777·04	1776·73	I^0c	284·4792
			Δ^0	−0·4114
C_6H_5NHD				
A	5571·51	—	I^0a	90·7350
B	2493·59	—	I^0b	202·7322
C	1726·11	—	I^0c	292·8730
$\Delta^0 = I^0c - I^0a - I^0b$			Δ^0	−0·5942

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[1] R. J. Kurland and E. B. Wilson, Jr., *J. Chem. Phys.*, 1957, **27**, 585.
[2] C. C. Costain and J. M. Dowling, *J. Chem. Phys.*, 1960, **32**, 158.
[3] J. K. Tyler, L. F. Thomas, and J. Sheridan, *Proc. Chem. Soc.*, 1959, 155.
[4] J. K. Tyler, J. Sheridan, and C. C. Costain, to be published.
[5] G. P. Shipulo, *Optics and Spectroscopy*, 1961, **10**, 288; 1962, **13**, 335.
[6] D. J. Millen, G. Topping, and D. R. Lide, Jr., *J. Mol. Spectroscopy*, 1962, **8**, 153.
[7] J. K. Tyler, *J. Mol. Spectroscopy*, 1963, **11**, 39.
[8] A. Langseth and B. P. Stoicheff, *Canad. J. Phys.*, 1956, **34**. 350.
[9] D. R. Lide, Jr., *J. Chem. Phys.*, 1957, **27**, 343.