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Abstract

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ELECTRON-DIFFRACTION STUDY OF THE STRUCTURE OF MOLECULES OF COMPOUNDS OF TRIVALENT NITROGEN

N-DIMETHYLANILINE

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It has been established that a trivalent nitrogen atom changes the coordination of its bonds from substantially pyramidal in molecules of ammonia and its saturated derivatives (the average valence angle at the N atom is $\sim 109^\circ$) to nearly planar in molecules of amides of organic acids ($^{1-4}$), pyrrole and its derivatives (^{5,2}), and cyanamide (^{6}) ($\sim$ 116—117°). It is of interest to determine which other functional groups exert such an influence on the trivalent nitrogen atom.

Analysis of the literature data shows that the greatest amount of information and the most contradictory opinions concern the configuration of the nitrogen atom in aniline and its derivatives. Thus, purely qualitative conclusions have been drawn about the pyramidal configuration of the bonds of the nitrogen atom in aniline, with an average valence angle at the N atom close to the tetrahedral one, on the basis of measurements of dipole moments (^{7}), measurements of the Kerr constant (^{8}), dipole relaxation (^{9}), and UV absorption spectra (^{10}).

Fig. 1. Experimental scattering-intensity curve for short and long camera distances, salt plate. The drawing of the background line is shown.

From data obtained by Evans in the analysis of the vibrational spectra of aniline, a conclusion was drawn about a nonplanar configuration of the aniline molecule, and, assuming model II (Fig. 4), $\angle$CNH = 116° and $\angle$HNH = 112° were calculated (^{11}). These data cannot be regarded as direct structural studies. The available X-ray structural results for 2,6-dichloro-4-nitrodimethylaniline (^{12}) and 2-bromo-4′-dimethylaniline-α-cyanostilbene (^{13}) indicate a planar arrangement of the bonds of the nitrogen atom in the molecules of these compounds, with $\angle$CNC $\sim 120^\circ$.

In connection with the foregoing, we undertook an electron-diffraction study of the structure of the dimethylaniline molecule in the vapor phase. It should be noted that in the crystal a change in $\angle$CNC is possible owing to the effect of the crystal lattice.

Fig. 2

Figure 1: Fig. 2

Experimental Part

Electron diffraction patterns of dimethylaniline vapor were obtained by the method described earlier (14), with an r^3 sector at small (~ 140 mm) and large (~ 260 mm) distances between the nozzle and the plate.

Fig. 2. Experimental and theoretical curves $sM(s)$

The best 10 electron diffraction patterns were selected; the microphotometric records were recalculated to blackenings, taken, for $D < 1$, as equal to the electron scattering intensity. Two intensity curves are presented in Fig. 1, which shows the smoothed tracing of the background line with orientation to the zero points of the theoretical $sM(s)$ curves.

The experimentally averaged curve

$$sM(s) = s\frac{I(s) - I^{(s)}_{\text{background}}}{I^{(s)}_{\text{background}}}$$

is shown in Fig. 2 (from 5 to 30 Å^{-1} in s). On the basis of the experimental curve $sM(s)$, curves $f(r)$ were calculated with different extrapolations of the experimental curve $sM(s)$ from 5 Å^{-1} in s to zero according to theoretical $sM(s)$ curves for models 2, 5, and 6 (Table 1). No noticeable differences were found. Fig. 3 gives the experimental curve with extrapolation of $sM(s)$ according to model 5.

The first principal peak at $r = 1.42$ Å was resolved into components by the method of successive refinement of variables. It was assumed that the complex peak is the sum of Gaussian peaks corresponding to the internuclear distances C–C in the phenyl ring, C_{ar}—N, and N–CH_3. For the mean amplitudes of vibration of the atoms $l(\text{C—C}) = l(\text{C—N}) = 0.05$ Å, $l(\text{C—H}) = 0.08$ Å, and $r(\text{C—H}) = 1.10$ Å in CH_3 and 1.08 Å in C_6H_5, the following were calculated: $r(\text{C—C}) = 1.405 \pm 0.005$ Å, $r(\text{C}_{ar}\text{—N}) = 1.43 \pm 0.02$ Å, and $r(\text{N—CH}_3) = 1.46 \pm 0.01$ Å. The errors were calculated by equation (12a) of work (15).

Table 1

Principal parameters of the theoretical curves $sM(s)$ and $f(r)$, and the positions of the principal peaks of the experimental and theoretical curves $f(r)$ (Figs. 1, 2, 3)

Nos.	Isomer (Fig. 4)	$\angle CH_3NCH_3$	$\angle C_{ar}NCH_3$	φ^{**}	Positions of peaks of the curve $f(r)$ for $r > 2$ Å
Experimental	–	–	–	–	2.44; 2.82; 3.42; 3.75; 4.25; 4.87
1	II	108°	108°	–	2.41; – 3.61; ——
2	II	112	112	–	2.42; 2.74; – 3.70; 4.15; 4.80
3	I	112	112	–	2.42; 2.78; 3.41; 3.76; 4.27; 4.82; 4.97
4	II	116	116	–	2.44; 2.78; 3.38; 3.74; 4.18; 4.89
5	–	120	120	0	2.45; 2.80; – 3.74; 4.24; 4.97
6	–	120	120	45°	2.44; 2.79; – 3.68; 4.29; 4.80

Fig. 3. Experimental and theoretical curves $f(r)$

Figure 2: Fig. 3. Experimental and theoretical curves $f(r)$

Nos.	Isomer (Fig. 4)	$\angle CH_3NCH_3$	$\angle C_{ar}NCH_3$	φ**	Positions of peaks of the curve $f(r)$ for $r > 2$ Å
7	II	109	120	–	2.46; 2.82; 3.34; 3.75; 4.25; 4.98

* In the $sM(s)$ curves the following were not varied: $r(C—H) = 1.10$ Å in CH_3, $r(C—H) = 1.08$ Å in the C_6H_5 group, $r(C—C) = 1.40$ Å, $r(C_{ar}—N) = 1.42$ Å, $r(N—CH_3) = 1.46$ Å, $\angle CCC = 120°$, $\angle HCH = 109.5°$.

** φ is the angle of rotation of the planar groups C_6H_5 and $N(CH_3)_2$ about the C–N bond.

Determination of the bond configuration of the nitrogen atom and of the form of the rotational isomer was carried out by comparing the experimental and theoretical curves $sM(s)$ and $f(r)$ for models of the dimethylaniline molecule (Figs. 2, 3, 4, Table 1). In isomer I of C_s symmetry, the methyl groups are arranged symmetrically on both sides of the benzene ring. In isomer II, also of C_s symmetry, the methyl groups are on one side of the plane of the benzene ring.

Comparison of the $sM(s)$ and $f(r)$ curves shows that the best agreement is achieved for isomer II and CNC angles on average not less than $116 \pm 2°$ (model 4). Establishing the inequality of the valence angles of the nitrogen atom is difficult. However, it can be said with certainty that the mean value of the angle in the dimethylaniline molecule is considerably higher than that in the trimethylamine molecule. It should be noted, however, that the accuracy of determining $\angle C_{ar}NCH_3$ is noticeably higher than the accuracy of determining $\angle CH_3NCH_3$ in the dimethylaniline molecule.

Fig. 3. Experimental and theoretical curves $f(r)$

Fig. 4. Models of the skeletons of rotational isomers of the N-dimethylaniline molecule

Figure 3: Fig. 4. Models of the skeletons of rotational isomers of the N-dimethylaniline molecule

Discussion of the results

The data obtained in the present work on the geometrical structure of the dimethylaniline molecule permit the following comparisons and conclusions. The internuclear distance $r(C—C) = 1.40$ Å agrees well with the result of determining $r(C—C) = 1.397$ Å in benzene (^{16}). The value $r(N—CH_3) = 1.46$ Å coincides, within the experimental error, with $r(N—C) = 1.47$ Å in $N(CH_3)_3$ (^{17}). Of interest is the determination of $r(C_{\text{ar}}—N) = 1.43 \pm 0.02$ Å, which agrees well with the corresponding distance in triphenylamine, 1.42 Å (^{18}), in dichlorodimethylaniline, 1.407 Å (^{19}), and in 2,6-dichloro-4-nitrodimethylaniline, 1.41 Å (^{12}). From these data it follows that the distance

$$r(\rangle C - N\langle)_{\text{cp}} = 1.42 \text{ Å}$$

between the nitrogen atom and the carbon atom of the phenyl ring is appreciably greater than

$$r\left(\overset{O}{\overset{\|}{C}} - N\right)_{\text{cp}} = 1.35 \text{ Å}$$

–the distance between the nitrogen atom and the carbon atom of the carbonyl group.

In dimethylaniline vapors, isomer of configuration II is predominantly present (Fig. 4), with an average $\angle CNC = 116°$. The same angle, $\angle CNC = 116°$, was found in triphenylamine (^{18}). Apparently, it may be concluded that, under the influence of the phenyl ring, the nitrogen atom changes its valence state somewhat from the essentially pyramidal one in ammonia and its derivatives to one close to planar in aniline, pyrrole, formamide, and their derivatives.

Fig. 4. Models of the skeletons of rotational isomers of the N-dimethylaniline molecule

Such a conclusion cannot be replaced by the assumption of a significant increase in $\angle CNC$ in dimethylaniline under the influence of steric hindrances–

properties, since in various substituted ammonias the mean angle and the inequality of the angles about the N atom are, respectively, 109 and 3-5° (20).

The authors of a study of the structure of the triphenylamine molecule (18) proposed that the equilibrium configuration of the nitrogen atom is planar, while the small pyramidality observed experimentally is explained by nonplanar vibrations of the "inversion" type. A similar situation has been analyzed for boron derivatives BX_3 (21). In that work it was shown that the experimentally observed configuration of BX_3 molecules will differ from the planar one because of perpendicular vibrations. The effect of shortening of the internuclear distance $X \dots X$ was calculated: $\delta = r_0(XX) - \bar{r}(XX)$, where δ is the shortening effect, $r_0(XX)$ is the value of the internuclear distance for the planar model, and $\bar{r}(XX)$ is the value of the internuclear distance obtained with allowance for perpendicular vibrations. From the values of $\bar{r}(XX)$ we calculated the effective XBX angles for the molecules: BF_3 119°48′, BCl_3 119°28′, BBr_3 119°18′, and BI_3 119°22′. It seems to us that if the nitrogen atom had an equilibrium planar configuration of bonds, then the effective valence angles of the nitrogen atom would also lie in the range 119–120°. The most probable configuration of the bonds of the nitrogen atom in the molecules listed above appears to be pyramidal, although close to planar. Further investigations will make it possible to clarify the true situation.

Further, the nearly planar arrangement of the skeletal atoms of the dimethylaniline molecule is of interest. The configuration that is considerably more favorable from the standpoint of reducing steric strain—configuration I (Fig. 4) —is not realized.

The accepted explanation of this situation is considered to be conjugation of the lone pair of the nitrogen atom with the Λ-electrons of the phenyl ring.

Generally speaking, a somewhat different description of the configuration of the rotational isomer is possible, as the position of the minimum of the rotational potential about the C—N bond of two rotors, C_6H_5 and $N(CH_3)_2$. The group $N(CH_3)_2$ may be regarded as a fragment of a tetrahedron. Unfortunately, at present there are not enough data on rotational isomerism about a bond of the type $:> A - B <$ or $:> A - D <$.

Thus, in CF_3NO_2 and CBr_3NO_2 an isomer is realized with a parallel arrangement of the NO_2 group and the $F \dots F$ and $Br \dots Br$ lines, respectively, i.e., a form similar to configuration II (Fig. 4) (22).

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