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An Electron-Diffraction Investigation of Nitrogen Trifluoride[1]

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Introduction and Discussion.—Since its first preparation[3] in 1928 by Otto Ruff, nitrogen trifluoride has been of obvious interest to chemists because it is one of the very few known substances containing the nitrogen–fluorine bond. Although Ruff and his associates continued the study of the preparation and reactions of nitrogen trifluoride and measured its heat of formation, density, melting point, boiling point and vapor pressures, little other work has been reported. Watson, Kane and Ramaswamy found the electric moment to be very small,[4] only about 0.2×10^{-18} e. s. u., and concluded from this value and from a comparison with the value for ammonia ($\mu_{NH_3} = 1.46 \times 10^{-18}$ e. s. u.), that the molecule is nearly, but not quite, planar. Bailey, Hale and Thompson[5] reported values and assignments for three of the vibrational frequencies of the molecule from observations of the infrared spectrum, derived the value 4.10×10^5 dynes/cm. for the stretching force-constant of the N–F bond (and from this 1.45 Å. for the bond length according to Badger's rule[6]) and concluded, perhaps with the help of a normal-coördinate treatment for a special potential function or a study of band contours, that the molecule is a very flat pyramid with bond angle greater than 110°. Neither of these structural conclusions is accurate, as we shall see, but the electric moments mentioned above are interesting and will be discussed briefly, in connection with the results of our work.

According to our electron-diffraction investigation, the nitrogen trifluoride molecule, assumed to be a symmetrical pyramid, has a bond angle ($\angle$FNF) of $102.5 \pm 1.5°$, a bond distance (r_{N-F}) of 1.37 ± 0.02 Å., and a non-bond distance ($r_{F\ldots F}$) of 2.14 ± 0.02 Å. We have made a normal coördinate treatment for a molecular model with these parameters. On neglecting the interaction force constants involving adjacent N–F stretchings, adjacent F–N–F bendings, and non-adjacent stretching and bending, the following force constants are found to correspond to the observed frequencies:[3] N–F stretching, 3.724×10^5 dynes/cm.; F–N–F bending, 1.434×10^{-11} dyne-cm./radian^2; stretching-bending interaction, 0.015×10^{-3} dyne/radian. The unobserved fundamental frequency is calculated to be 400 cm.$^{-1}$; Bailey, *et al.*,[5] gave an estimate of 420 cm.$^{-1}$. Since our values for the force constants are reasonable (the magnitude of the interaction constant may, to be sure, not have any significance) the conclusion regarding the molecular configuration of nitrogen fluoride arrived at by Bailey, *et al.*,[5] on the basis of the infrared spectra is at least not demanded by the frequencies of the observed bands.

As stated above, the molecule is by no means a nearly flat pyramid, but instead has a less than tetrahedral bond angle comparable to those observed[7] for other fifth group halides and for oxygen fluoride and appreciably less than the approximately tetrahedral value found in the amines, ammonia, the ethers and water. We believe that the surprisingly small value of the electric moment of nitrogen trifluoride may nevertheless be accounted for, as the result of an almost perfect cancellation of the expected moment due to the ionic character of the bonds by a moment of opposite sign, arising from such further electrical asymmetries of the molecule as would be present even with purely covalent bonds, which is mainly due in this case to an imperfect balancing of the electric moment contribution of the unshared electrons of the nitrogen and fluorine atoms. This lack of balance could result from a difference[8] in the hybrid character of the nitrogen and fluorine bond orbitals.

In the ammonia molecule, on the other hand, the resultant ionic moment is reversed (with presumably little change in magnitude), so that the two contributions are of the same sign, and a large total moment is observed.

The suggested interpretation of the electric moments of ammonia and nitrogen trifluoride may be of significance also in connection with the bond angle values. It is notable that when a nitrogen or oxygen atom is singly bonded to less electronegative atoms such as carbon or hydrogen, the bond angle tends to be larger than when the nitrogen or oxygen atom is bonded to the more electronegative fluorine atom. We suggest that part or all of this effect may arise, in the way de-

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[3] O. Ruff, J. Fischer and F. Luft, *Z. anorg. allgem. Chem.*, **172**, 417 (1928).

[4] H. E. Watson, G. P. Kane and K. L. Ramaswamy, *Proc. Roy. Soc. (London)*, **A156**, 137 (1936).

[5] C. R. Bailey, J. B. Hale and J. W. Thompson, *J. Chem. Phys.*, **5**, 274 (1937).

[6] R. M. Badger, *ibid.*, **3**, 710 (1935).

[7] See L. Pauling, "The Nature of the Chemical Bond," 2nd edition, Cornell University Press, Ithaca, New York, 1940, p. 79.

[8] If, for example, the nitrogen bond orbital were of the pure tetrahedral, sp^3, type, while the fluorine bond orbital was an unhybridized p orbital with zero moment, its contribution would be very large and unbalanced. The resultant of the moment of all the orbitals would be equal to the moment relative to a corresponding positive charge at the nitrogen nucleus of one of the electrons of the unshared pair occupying the fourth tetrahedral nitrogen orbital. See C. A. Coulson, *Trans. Faraday Soc.*, **38**, 433 (1942), for a discussion showing that effects of this kind can be significant.

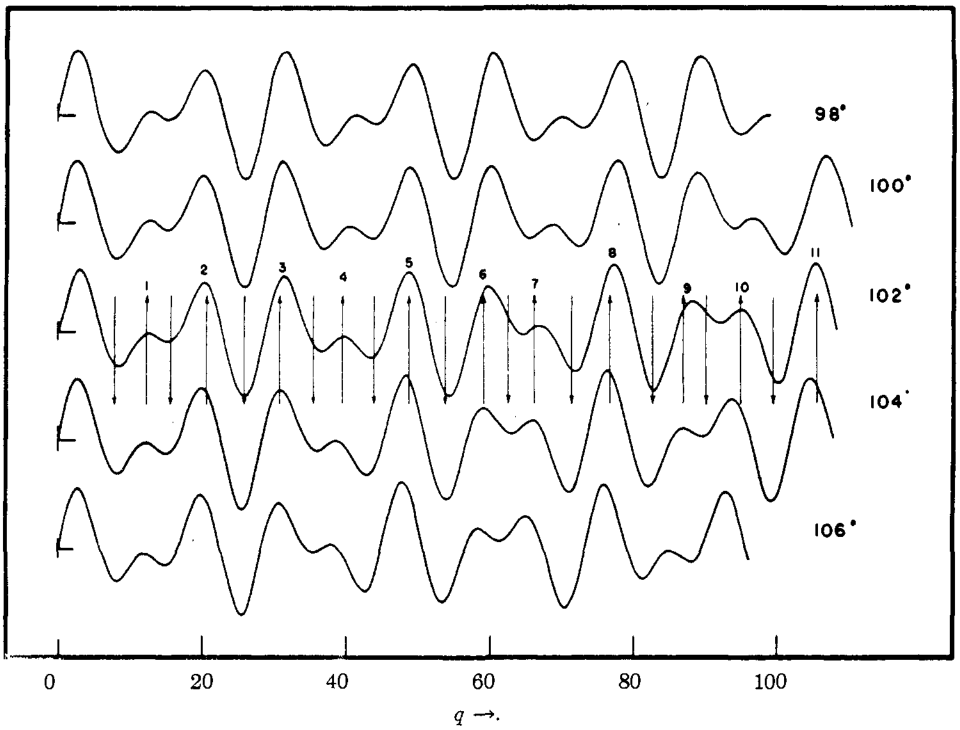

Fig. 1.—Simplified theoretical intensity curves for symmetrical pyramidal models of nitrogen trifluoride with the N–F distance 1.37 Å. and the indicated bond angles. The arrows indicate the measured positions of features of the diffraction pattern.

scribed below, from the nature of the charge distributions used to explain the observed dipole moments. It may be noted that there is no obvious regularity which suggests a correlation between the observed bond angles and either the steric forces or the coulombic repulsions[9] arising from the ionic character of the bonds which might be expected in these examples. Thus, the ionic character of the N–H bond is expected to be about equal to that of the N–F bond, with changed sign, while it seems probable that the steric interactions, if repulsive, are greater for F...F than for H...H. Neither is there an obvious general correlation with the strengths of the bonds, such as would be significant because the strengths of the bonds in some degree determine the hybridization of the nitrogen or oxygen bond-forming orbitals and, hence, the bond angle. If the distribution of charges invoked in the electric moment discussion is considered, however, it is seen that in nitrogen trifluoride, for example, the repulsions among the negatively charged fluorine atoms are almost balanced by the repulsions between the fluorine atoms and a center of negative charge (representing the uncompensated member of the unshared pair of electrons) on the backside of the nitrogen atom, whereas in ammonia the repulsions among the positively charged hydrogen atoms are augmented by the attractions between the hydrogen atoms and the negative backside of the nitrogen atom. Consequently, the bond angle value adopted by the nitrogen trifluoride molecule is only slightly increased by these coulombic interactions over that which it would have in their absence, while in ammonia there may be a considerable increase due to these forces. Quantitative calculations of this effect, carried out with reasonable assumptions regarding the magnitude and disposition of the charges involved and the force constant for symmetrical bending of the bond angles, gave results of the right magnitude; according to these calculations it is not improbable that the increase in the bond angle due to these coulombic forces is several degrees in ammonia, but only a fraction of a degree in nitrogen trifluoride.

This interpretation of the bond angles and dipole moments of nitrogen trifluoride and ammonia must be applicable also to other series of pyramidal or bent molecules involving a given apical atom and a series of peripheral atoms of varying electronegativity. As has been mentioned, the usual bond-angle variations do agree with the interpretation; it is not so easy to see whether the dipole moment evidence will in general fit in as satisfactorily.

The N–F bond distance in nitrogen trifluoride is 0.07 Å. shorter than the distance 1.44 Å. reported[10] for difluorodiazine, F–N=N–F, by Bauer. However, it is just equal to the value

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(9) Reference 5, p. 78.

(10) S. H. Bauer, THIS JOURNAL, 69, 3104 (1947).

given by the empirical equation

$$r_{\mathrm{A-B}} = r_{\mathrm{A}} + r_{\mathrm{B}} - 0.09\,|X_{\mathrm{A}} - X_{\mathrm{B}}|$$

$$(r_{\mathrm{N}} = 0.74\text{ Å., } r_{\mathrm{F}} = 0.72\text{ Å., } |X_{\mathrm{F}} - X_{\mathrm{N}}| = 1.0,\ (r_{\mathrm{N-F}})_{\mathrm{calcd.}} = 1.37\text{ Å.})$$

which was found[11] by Schomaker and Stevenson to relate the length of a partially ionic single covalent bond to the normal covalent single bond radii of the component atoms and the difference of their electronegativities; it is appreciably greater than the sum, 1.34 Å., of the Pauling-Huggins radii for nitrogen and fluorine.

Experimental Method and Results.—The sample of nitrogen trifluoride used was provided by Professor Anton B. Burg. According to Professor Burg it contained no significant amount of any impurity. The sample was condensed to a liquid, an appreciable fraction was pumped off through the apparatus before making the pictures, and the pictures were made with gas in equilibrium with the remaining liquid at temperatures determined by the required pressure. Fifteen diffraction pictures of various densities were made with the apparatus described by Brockway.[12] The electron wave length, 0.0610 Å. on the Siegbahn scale, was corrected for the (measured) expansion of the photographic film used in making the zinc oxide and gold calibration pictures.

The pictures show as many as eleven rings with an apparent intensity distribution which is very well represented, except at large scattering angles, by the theoretical intensity curves "102°" and "104°" of the Fig. 1. At large angles the appearance of the sixth and seventh maxima and the observed equality of the ninth and tenth maxima would correspond perfectly to an interpolated curve for a bond angle of about 102.5°. The simplified theoretical intensity curves shown in the Fig. 1 are plots of the function[13]

$$I(q) = \frac{3Z_{\mathrm{F}}Z_{\mathrm{N}}}{r_{\mathrm{N-F}}} \sin\left(\frac{\pi}{10} r_{\mathrm{N-F}}\, q\right) + \frac{3Z_{\mathrm{F}}{}^2}{r_{\mathrm{F-F}}} \sin\left(\frac{\pi}{10} r_{\mathrm{F--F}}\, q\right)$$

$\left(q = \frac{40}{\lambda} \sin \varphi = \frac{10}{\pi} s\right.$, φ is the scattering angle and the Z's are the atomic members) corresponding to rigid, symmetrical, pyramidal models of the nitrogen trifluoride molecule with various bond angles. We conclude that to the precision afforded by our diffraction data (extending to $q = 106$) the nitrogen trifluoride molecule is such a symmetrical triangular pyramid. A model with the unreasonable parameters $r_{\mathrm{N-F}} = 2.14$ Å., $r_{\mathrm{F-F}} = 1.37$ Å., and $\angle$FNF = 37.3° would agree well with the data because of the similarity in scattering power of the nitrogen and fluorine atoms, but it is not possible that any other symmetrical model with a bond angle widely different from those represented in the Fig. 1 should lead to a curve closely resembling the observed diffraction pattern.

The values of q_{obs} shown in the Table I are averages, with an average deviation of 0.6% (excluding the first ring), obtained from two sets of measurements of the ring diameters by each of the authors. Except for the first, second, ninth, tenth and eleventh rings, for which fewer readings were taken, each of these four sets included from five to twenty individual measurements made in the usual way.[10] The q_{obs} values have been corrected for film expansion.

TABLE I

Max.	Min.	$q_{\mathrm{obs.}}$	$q_{\mathrm{calcd.}}/q_{\mathrm{obs.}}$ 100°	102°	104°	Weight[a]
	1	7.97	1.054	1.054	1.035	0
1		12.39	1.037	1.017	0.977	0
	2	15.77	0.977	0.951	.945	0
2		20.76	0.978	0.973	.963	0
	3	25.95	1.004	0.996	.983	3
3		30.89	1.021	1.010	1.002	3
	4	35.61	1.038	1.026	1.011	2
4		39.57	1.027	0.998	0.975	2
	5	43.94	0.999	0.987	.976	2
5		48.75	1.007	1.003	.989	3
	6	53.84	1.020	1.009	.999	3
6		59.15	1.019	1.009	.999	2
	7	62.62	1.049	1.033	1.006	0
7		66.27	1.038	1.008	0.994	0
	8	71.45	1.015	1.005	.996	2
8		76.72	1.015	1.006	.997	3
	9	82.6	1.011	1.004	.993	2
9		87.0	1.024	1.014	1.000	1
	10	90.2	1.044	1.018	0.991	1
10		94.9	1.021	0.999	.989	1
	11	99.6	1.016	1.006	.997	2
11		105.7	1.011	1.001	.991	2
All features with equal wts.		Av.	1.019	1.006	0.991	
		Av. dev.	0.0142	0.0129	.0122	
Quoted wts.		Av.	1.017	1.005	.993	
		Av. dev.	0.0076	0.0060	.0073	
Quoted wts. 3rd min. to 8th max. only		Av.	1.016	1.005	.993	
		Av. dev.	0.0079	0.0065	.0089	
Five features with triple wt., only		Av.	1.013	1.005	.994	
		Av. dev.	0.0064	0.0041	.0064	
Best value			1.016	1.005	0.993	
$r_{\mathrm{N-F}}$			1.392	1.377	1.360	
$r_{\mathrm{N-F}}$			2.134	2.141	2.145	

[a] These weights are based on the probable reliability of the measurements, rings close in or very far out and unsymmetrical or doubled rings being considered relatively unreliable.

The quantitative comparison of these values with the positions of the maxima and minima of the theoretical curves is given in the table for bond angles of 100, 102 and 104° and is summarized by means of averages and average deviations calculated with various weightings of the q/q_{obs} values. **The best consistency is found for**

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[11] V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

[12] L. O. Brockway, *Rev. Modern Phys.*, **8**, 234 (1936).

[13] R. Spurr and V. Schomaker, THIS JOURNAL, **64**, 2695 (1942), second paragraph, footnote 6.

102° with perhaps a slight tendency toward 104°. No significant uncertainty in the values of $\overline{q/q_{\text{obs}}}$ is introduced by the question of the best weights to be used in taking the average.

From the qualitative comparisons and these consistency measures we believe it is very unlikely that the correct bond angle value lies outside limits given by our final result $\angle$FNF = 102.5 ± 1.5°. Our final values for the nitrogen-fluorine distance $r_{\text{N-F}} = 1.37 \pm 0.02$ Å. and the fluorine–fluorine distance $r_{\text{F}\ldots\text{F}} = 2.14 \pm 0.02$ Å. are taken from plots of the values of $r_{\text{N-F}}$ and $r_{\text{F}\ldots\text{F}}$ (from Table I) as functions of the assumed bond angle. The quoted uncertainties for these quantities we also regard as limits of error within which the correct values almost certainly lie. They include the variation corresponding to the quoted uncertainty of the bond angle and the estimated uncertainty of $\overline{q/q_{\text{obs}}}$ (± 0.007, corresponding to ±0.01 Å. in $r_{\text{N-F}}$) for the given bond angle.

Acknowledgment.—We are indebted to Professor Burg for the sample of nitrogen trifluoride and to Professor Pauling, especially for discussion of the dipole moment problem. The late Dr. Horace Russell, Jr., helped us in making the photographs.

Summary

An electron-diffraction investigation of nitrogen trifluoride has been made. The molecule may be represented by a symmetrical, pyramidal model with bond distance $r_{\text{N-F}} = 1.37$ Å. and bond angle $\angle$FNF = 102.5° ($r_{\text{F}\ldots\text{F}} = 2.14$ Å.), values which are almost certainly in error by less than ±0.02 Å. for the distances and +1.5° for the bond angle.

A simple interpretation, which should be applicable to other, analogous situations, is given for the very small dipole moment and relatively small bond angle of the nitrogen trifluoride molecule, in contrast to the relatively large dipole moment and bond angle of the ammonia molecule.

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Some Heats of Wetting of Unit Surfaces[1]

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Introduction

Previous studies in this Laboratory and elsewhere have shown interesting correlations between heats of wetting of various solid–liquid systems and such other properties as the apparent density of the pulverized solid,[3] polarity,[4] adsorptive capacity,[5] coking quality of coal,[6] and hygroscopicity of soils.[7] Most of the available data have been reported in terms of the weight of solid wetted. However, in the study of surface phenomena it is desirable that the pertinent thermodynamic data be based on the surface area involved.[8]

Harkins and co-workers[8,9,10] have reported heats of emersion (the reverse of heats of wetting, as used here) on this basis for a number of systems, and have discussed in detail the theory and the experimental difficulties of such measurements.

This investigation was designed to measure the heats (enthalpies) of wetting of solid surfaces in terms of the wetted surface area.

Experimental

The solids chosen were the sulfides galena and sphalerite, the halides sylvite and fluorite, and quartz. With one exception, the solids employed were selected mineral crystals; these were reduced by dry milling to powders with specific surface area ranging, approximately, from 0.1 to 2 square meters per gram. (The sylvite was C. P. KCl.) Water, *n*-heptane and carbon tetrachloride as wetting liquids represented polar, non-polar and polarizable types, respectively.

The pulverized solid sample, of from 5 to 20 g., was weighed into the powder chamber of the wetting apparatus (Fig. 1), evacuated at 300° for an hour, then sealed under vacuum. The liquid reservoir chamber was filled with the wetting liquid, plus enough powder to ensure saturation with the solid phase. This precaution was deemed desirable to avoid any possible error from heat of solution of the solid phase in the liquid. Carbon tetrachloride and *n*-heptane, when used, had activated alumina or sodium amalgam added to maintain their anhydrous condition. A loop of fine constantan wire was engaged with the hook-shaped septum between the reaction and reservoir chambers. The wetting apparatus was then inserted in the calorimeter and permitted to come to thermal equilibrium at 25°.

The adiabatic calorimeter comprised two concentric metal vessels, the inner one containing the wetting apparatus, while the outer one carried a compensating heating coil which served to maintain the temperature equality

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(3) Culbertson and Winter, THIS JOURNAL, **59**, 308 (1937).

(4) Boyd and Harkins, *ibid.*, **64**, 1190 (1942).

(5) Harman and Parmelee, *J. Am. Ceram. Soc.*, **28**, 110 (1945).

(6) Cannon, Griffith and Hirst, Proc. Conf. Ultra-fine Structure of Coals and Cokes, Brit. Coal Utilization Research Assoc., **1944**, 131; *Chem. Abstracts*, **39**, 1274.[2]

(7) Behrens, *Z. Pflanzenernährh., Düngung u. Bodenk.*, **40**, 257 (1935).

(8) Harkins and Boyd, THIS JOURNAL, **64**, 1195 (1942).

(9) Basford, Jura and Harkins, *ibid.*, **70**, 1444 (1948),

(10) Jura and Harkins, *ibid.*, **66**, 1356 (1944).