

## MOLECULAR STRUCTURE OF NITROGEN TRICHLORIDE AS DETERMINED BY ELECTRON DIFFRACTION

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## ABSTRACT

Nitrogen trichloride was found to have a bond length of  $r_g = 1.759 \pm 0.002 \text{ \AA}$  and a Cl-N-Cl angle of  $107.1 \pm 0.5^\circ$ . The bond angle is larger than that found in  $\text{NF}_3$ , consistent with the (recently revised) trends displayed by the trihalides of phosphorus and arsenic, but much lower than the  $120^\circ$  angle reported for the isoelectronic molecule  $\text{N}(\text{SiH}_3)_3$ . Moreover, a comparison between selected compounds reveals that the N-Cl bond length is appreciably greater, relatively, than the N-Si bond length. Accordingly, the bond angles and bond lengths suggest a greater reluctance of the nitrogen lone pairs to delocalize onto Cl than onto  $\text{SiH}_3$  groups. Mean amplitudes of vibration of  $\text{NCl}_3$  were derived both from the diffraction data and from recently published infrared and Raman frequencies. The values agree within the estimated uncertainties.

## INTRODUCTION

Nitrogen trichloride, a simple molecule, has long invited speculation about its unknown structure. On the one hand it is isoelectronic with  $\text{N}(\text{SiH}_3)_3$ <sup>1</sup>, a planar molecule. On the other hand, it is expected to be pyramidal according to the Valence-Shell-Electron-Pair-Repulsion (VSEPR) model of Sidgwick and Powell, and Gillespie and Nyholm<sup>2</sup>. Indeed, the VSEPR postulates call for bond angles smaller than tetrahedral and smaller, even, than those in  $\text{NH}_3$  because of the high electronegativity of chlorine. Until recently, the propensity of the compound to explode discouraged direct structural studies. Improved techniques for handling the material led to infrared and Raman work in the liquid and vapor phases<sup>3-5</sup>, in which the compound was diluted by inert substances. These investigations revealed that  $\text{NCl}_3$  is pyramidal rather than planar. They have also suggested that the bond angle is in the vicinity of  $108^\circ$ . It looked possible to extend the dilu-

tion technique to gas-phase electron diffraction studies of the compound and thereby to establish the structure with some precision.

#### EXPERIMENTAL

It should be emphasized at the outset that this compound is fickle and dangerously explosive and should be handled with all proper precautions. Because the liquid will detonate if allowed to warm up from 195° K under vacuum, the handling and purification always involved the addition of some inert gas prior to warmup.

The preparation was based on a procedure described by Clark<sup>6</sup>, but was modified in accordance with our requirement of a vapor sample mixed with the minimum possible amount of inert gas of low atomic number (He), rather than a dilute liquid sample. A 4:1 mixture of chlorine and nitrogen was passed into a wash bottle containing a solution of slightly acidified ammonium sulphate. The resulting  $\text{NCl}_3/\text{Cl}_2/\text{N}_2$  mixture was dried with concentrated  $\text{H}_2\text{SO}_4$  and collected at 195 °K in a well-shielded Pyrex trap filled with glass rings. The contents of the trap were pumped at 195 °K until vapor pressure measurement, by means of a quartz spiral gauge, indicated that all the chlorine had been removed. The trap was then evacuated, filled to 200 torr with pure dry helium and allowed to warm up to 0 °C. This shielded trap, which was isolated by teflon needle valves, was now removed from the rest of the preparation apparatus and attached to the metal inlet system of the electron diffraction unit<sup>7</sup>.

In order to reduce decomposition on the metal surface, the unit's inlet valve was fully opened and the teflon needle valve was used as the limiting aperture for the admission of  $\text{NCl}_3$ .

The unpredictable nature of this compound and its liability to decompose are illustrated by the first five plates, exposed consecutively under identical conditions from the same sample. All gave patterns of the decomposition product, chlorine, except the third, which was nearly pure, undecomposed  $\text{NCl}_3$ . Similar unpredictable behavior continued throughout the series of experiments.

Since the compound is subject to decomposition on opening a stopcock to an evacuated region, the teflon needle was only opened very gently. Once it was open, a sequence of five photographic diffraction patterns was recorded. This technique gave more reproducible samples, and also served to enrich the incoming vapors in  $\text{NCl}_3$  by depletion of the helium diluent. The patterns were recorded on Kodak Electron Image plates.

#### ANALYSIS OF DATA

Of the plates taken at the 21-cm camera distance, four plates were selected

which seemed to have minimum contamination by chlorine. Five plates were chosen for the 11-cm camera distance. Microphotometer readings and the processing of the data are described elsewhere<sup>7</sup>. The emulsion calibration applied was of the form<sup>8</sup>  $2cA = (1 - e^{-2cE})$ , with the constant  $c$  taken as 0.1. Exposure values were not corrected for extraneous scattering. The variation of the chlorine contamination of different plates was not investigated quantitatively, but visual comparison of levelled intensity curves and theoretical intensity data suggested that for a given camera distance the composition of the gas sample was fairly constant in the plates selected. Levelled experimental intensities  $I_0$  were related to reduced molecular intensities  $M(s)_{\text{exp}} = [(I_0/I_B) - 1]$  via a background function  $I_B$  chosen to have the form

$$I_B = \sum_{n=1}^6 a_n \cdot s^{n-1} + a_7 \cdot \exp(-3.355s).$$

Experimental levelled intensity curves\* were compared to calculated curves  $(I_0)_{\text{calc}} = I_B(1 + RM(s)_{\text{calc}})$  by a least-squares process. Analytical approximations to the elastic<sup>9</sup> and inelastic<sup>10</sup> scattering factors, as well as to the phase shifts<sup>11</sup> were used. Asymmetry constants  $a$  were taken as  $2.0 \text{ \AA}^{-1}$  for all internuclear distances. The nonbonded shrinkage correction was calculated to be  $0.0009 \text{ \AA}$ . The data were treated assuming that nitrogen trichloride was contaminated by a 3:1 mol ratio of chlorine to nitrogen.

Various fixed percentages of contamination were fed into refinement cycles. For the 21-cm camera data the derived internuclear distances and thermal parameters of nitrogen trichloride did not change significantly in the range of composition considered (65 to 85 mole % of nitrogen trichloride). In the radial distribution functions the presence of chlorine was conspicuous but the presence of nitrogen could neither be proven nor excluded. The data were refined by allowing simultaneous variation of the two distances, the two thermal parameters, seven intensity background coefficients  $a_n$  and the index of resolution. Parameters for chlorine and nitrogen were held constant at their known values<sup>12</sup> during refinement.

For the 11-cm camera distance data, a composition corresponding to only about 15 % nitrogen trichloride was found. The composition was correlated rather strongly with the distance  $r(\text{N-Cl})$  and both thermal parameters; it did not affect the distance  $r(\text{Cl} \cdots \text{Cl})$ . Varying only the bonded N-Cl distance, the N-Cl amplitude of vibration and the background coefficients, the results of least-squares refinement on the 11-cm data were ambiguous and dependent on the starting value of the N-Cl bond length. This, in itself is of small consequence in deriving the present structure since the 11-cm data are relatively unimportant compared with the 21-cm data. Nevertheless, the existence of a double minimum in a least-squares

\* For a listing of experimental intensity data order document NAPS 01439 from ASIS-National Auxiliary Publications Service, c/o CCM Information Corporation, 909 Third Avenue, New York, N.Y. 10022; remitting \$2.00 for each microfiche or \$5.00 for each photocopy.

TABLE I

RESULTS OF LEAST-SQUARES REFINEMENT FOR NITROGEN TRICHLORIDE

	21-cm camera data	11-cm camera data
Mol % $\text{NCl}_3$	$77\% \pm 4\%$	$15\% \pm 5\%$
$r_z(\text{NCl})$	$1.759 \pm 0.001_3^a(0.002)^b$	$1.761 \pm 0.011^b$
$r_z(\text{Cl} \cdots \text{Cl})$	$2.830 \pm 0.000_7(0.002)$	$2.821 \pm 0.006$
$l_z(\text{NCl})$	$0.061 \pm 0.001_9(0.003)$	$[0.061]^c$
$l_z(\text{Cl} \cdots \text{Cl})$	$0.074 \pm 0.000_9(0.002)$	$0.076 \pm 0.005$
$\angle \text{ClNCl}$	$107.1 \pm 0.3^\circ (0.5)$	$106.5 \pm 2.5^\circ$
$R$	$0.967 \pm 0.01 (0.03)^d$	$0.855 \pm 0.09^d$
$[\sigma(I)/I_0]_{\text{av}}$	0.0012	0.0014

<sup>a</sup> Standard deviations calculated on the basis of the error matrix, at fixed composition.

<sup>b</sup> Estimated standard deviations taking into account systematic errors, uncertainty in composition, as well as random errors.

<sup>c</sup> Assumed.

<sup>d</sup> The influence of the (estimated) emulsion calibration constant on this result is uncertain.

analysis with only a 0.04 Å separation between minima was unexpected. It is a sobering example of pitfalls which can be encountered in electron diffraction and is worthy of note for this reason. A trial value of 1.78 Å for  $r(\text{N-Cl})$  led to a refined

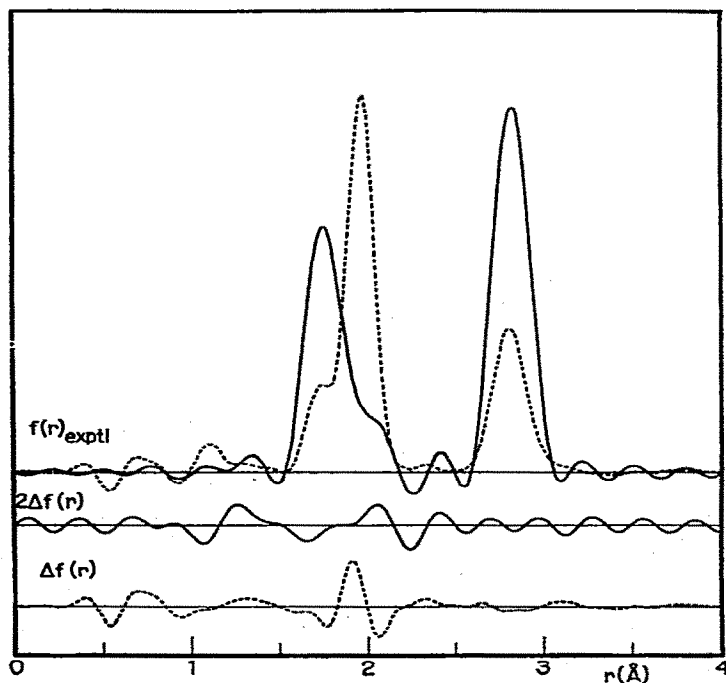


Fig. 1. Radial distribution function for  $\text{NCl}_3$ .  $\Delta f(r) = f(r)_{\text{exptl}} - f(r)_{\text{calc}}$ ; (—) 21-cm camera distance data; (---) 11-cm camera distance data.

value of 1.796 Å. A trial value of 1.76 Å resulted in a refined value of 1.759 Å and a different background curve, the first ten background points differing by about 0.1 to 0.2 %. Various approaches to the minima confirmed that in the space of the background coefficients, bond length, and amplitude of vibration, the minima were distinct. The standard deviation in intensity  $[\sigma(I)/I_0]_{av}$  was 0.0013 in the first case and 0.0014 in the second, and  $l_g(\text{N-Cl})$  refined to a value about 50 % too high. Constraining only the mean amplitude  $l_g(\text{N-Cl})$  to the value found for the 21-cm camera distance removed the ambiguity and led to the results listed in Table 1.

Estimates of standard deviation are based on a diagonal weight matrix proportional to  $s^2$  and on an additional procedure which accounts for correlation<sup>13</sup>. Standard deviations in structure parameters are about five times higher for 11-cm camera data than for the 21-cm data as a consequence of the low concentration of  $\text{NCl}_3$  in the former. Detailed results for both camera distances are given in Table 1.

Experimental radial distribution functions  $f(r)_{exp}$  and difference curves  $\Delta f(r) = f(r)_{exp} - f(r)_{th}$  are shown in Fig. 1. Experimental long distance data ranged from  $3.282 \leq s \leq 21.401 \text{ \AA}^{-1}$  and were blended with theoretical data from  $0 \leq s \leq 4.712 \text{ \AA}^{-1}$ .

#### SPECTROSCOPIC AMPLITUDES OF VIBRATION

Partial overlap of the  $r_g(\text{N-Cl})$  peak with the  $r_g(\text{Cl-Cl})$  peak interfered with the determinations of the mean square amplitude  $l_g(\text{N-Cl})$ . Therefore, it seemed worthwhile to calculate spectroscopic values of  $l(\text{N-Cl})$  and  $l(\text{Cl} \cdots \text{Cl})$  with the help of recently published infrared and Raman data<sup>5</sup> for  $^{14}\text{NCl}$  and  $^{15}\text{NCl}_3$ . The force field was redetermined by a least-squares procedure<sup>14</sup>. Root mean square amplitudes  $\Sigma$  for symmetry coordinates were calculated from the equation<sup>15</sup>

$$\Sigma = LAL' \quad (1)$$

in which  $A$  is a diagonal matrix with elements

$$\delta_k = \frac{h}{8\pi^2 c \omega_k} \coth \frac{hc\omega_k}{kT}, \quad (2)$$

and  $L$ , the matrix transforming normal coordinates to pure stretch and bend symmetry coordinates.

Numerical results are given in Table 2 for  $^{14}\text{NCl}_3$ . Standard deviations of the force constants are high, a result of the marginal independence of the isotopic data in the least-squares normal equations. Nevertheless, amplitudes of vibration determined from electron diffraction agree with the amplitudes calculated from infrared spectroscopy within their standard deviations.

TABLE 2

FORCE FIELD ANALYSIS AND SPECTROSCOPIC AMPLITUDES OF VIBRATION OF  $^{14}\text{NCl}_3^a$ 

$F(A_1) = \begin{pmatrix} 3.15 & 0.88 \\ 0.88 & 1.76 \end{pmatrix}$	$\sigma(F)^b = \begin{pmatrix} 0.23 & 0.07 \\ 0.07 & 0.09 \end{pmatrix}$		
$\Sigma(A_1) = \begin{pmatrix} 0.00223 & -0.00131 \\ -0.00131 & 0.00373 \end{pmatrix}$			
$F(E) = \begin{pmatrix} 2.50 & -0.73 \\ -0.73 & 1.12 \end{pmatrix}$	$\sigma(F)^b = \begin{pmatrix} 0.43 & 0.39 \\ 0.39 & 0.04 \end{pmatrix}$		
$\Sigma(E) = \begin{pmatrix} 0.00346 & -0.00217 \\ -0.00217 & 0.00549 \end{pmatrix}$			
	<i>Spectroscopic</i> <i>21-cm diffraction data</i> <i>11-cm diffraction data</i>		
$l(\text{N-Cl})$	0.055	$0.061 \pm 0.003$	$0.094 \pm 0.02$
$l(\text{Cl} \cdots \text{Cl})$	0.075	$0.074 \pm 0.002$	$0.076 \pm 0.005$

<sup>a</sup> Experimental values for the fundamental frequencies were taken from ref. 5. The force constants are given in units of m dyn/Å, m dyn/rad, and m dyn Å/rad<sup>2</sup>; the  $\Sigma$ -matrices are in units of Å<sup>2</sup>; the amplitudes of vibration are in Å. The amplitudes of vibration were calculated at 298.15 °K, using the molecular geometry determined in this study. Symmetry displacement coordinates,  $G$ -matrices and formulas for amplitudes of vibration are given in ref. 15b.

<sup>b</sup> Standard deviations were calculated from the inverted matrix of normal equations as described in ref. 14.

## DISCUSSION

The pyramidal structure of  $\text{NCl}_3$  found by IR- and Raman spectroscopy is confirmed. The bond angle of 107.1° lays to rest conjectures of a planar structure akin to that of  $(\text{SiH}_3)_3\text{N}$ , but is in accord with a description of the structure in terms of Gillespie's VSEPR-model. As expected on this basis, the bond angle of  $\text{NCl}_3$  is greater than the bond angle of  $\text{NF}_3$ <sup>16</sup>. Exactly analogous findings are reported for  $\text{PF}_3$  and  $\text{PCl}_3$ <sup>17</sup>, and for  $\text{AsF}_3$  and  $\text{AsCl}_3$ <sup>18</sup> where recent results contradict Gillespie's subrule to account for the anomalous bond angles once thought to exist in Group V trifluorides. On the other hand, the bond angle is approximately the same as that in  $\text{NH}_3$  (107.3°)<sup>19</sup> even though the ligand electronegativity is much greater. This failure to comply with Gillespie's electronegativity rule is shown even more markedly in the phosphorus, arsenic, and oxygen analogues. In comparisons of this type it seems more reasonable to consider H, rather than Cl or F, the anomalous ligand.

Bond lengths available for different nitrogen chloride species are:  $\text{NCl}_2\text{CH}_3$ : 1.74(2)<sup>20</sup> or 1.75(4) Å<sup>21</sup>;  $\text{NCl}(\text{CH}_3)_2$ : 1.77(2)<sup>20</sup> or 1.75(5) Å<sup>21</sup>;  $\text{NHCl}_2$ : 1.76 Å<sup>22</sup>;  $\text{NH}_2\text{Cl}$ : 1.77(2) Å<sup>22</sup>, or 1.750 Å<sup>23</sup>, in reasonable conformity with the present results. In the only determination of sufficient precision to warrant a close comparison with the present results, the microwave result by Millen<sup>23</sup> for  $\text{NH}_2\text{Cl}$  shows another anomalous comparison between H and Cl. Rather than increasing the N-Cl bond length as called for by Gillespie's rules, substitution of H for Cl seems to have little influence on the distance  $r(\text{N-Cl})$ <sup>23</sup>.

TABLE 3

A COMPARISON BETWEEN R-SiH<sub>3</sub> AND R-Cl BOND LENGTHS WHERE R = C, N, OR P

<i>H<sub>3</sub>C-SiH<sub>3</sub></i> <sup>a</sup>	<i>N(SiH<sub>3</sub>)<sub>3</sub></i> <sup>c</sup> <i>planar</i>	<i>P(SiH<sub>3</sub>)<sub>3</sub></i> <sup>c</sup> <i>pyramidal</i>
<i>r<sub>0</sub></i> = 1.867(1) Å	<i>r<sub>g</sub></i> = 1.735(2) Å	<i>r<sub>g</sub></i> = 2.248 Å
<i>H<sub>3</sub>C-Cl</i> <sup>b</sup>	<i>NCl<sub>3</sub></i> <sup>d</sup> <i>pyramidal</i>	<i>PCl<sub>3</sub></i> <sup>e</sup> <i>pyramidal</i>
<i>r<sub>0</sub></i> = 1.781 Å	<i>r<sub>g</sub></i> = 1.759(2) Å	<i>r<sub>g</sub></i> = 2.043 Å
$\Delta$ = +0.086 Å	$\Delta$ = -0.024 Å	$\Delta$ = +0.205 Å

<sup>a</sup> R. W. KILB AND L. PIERCE, *J. Chem. Phys.*, 27 (1957) 108.<sup>b</sup> C. C. COSTAIN, *J. Chem. Phys.*, 29 (1958) 864.<sup>c</sup> B. BEAGLEY, private communication.<sup>d</sup> This work.<sup>e</sup> See ref. 17 of text.

The bond length as well as the bond angle reveal how different the Cl ligand is from its isoelectronic counterpart, SiH<sub>3</sub>. The planarity of the skeleton of N(SiH<sub>3</sub>)<sub>3</sub> has been attributed to *p*<sub>π</sub>-*d*<sub>π</sub> delocalization of the nitrogen lone pair into *d* orbitals of the SiH<sub>3</sub> groups. Such an interaction should shorten the N-Si bonds. Table 3 compares the derivatives of N with analogous phosphorus and carbon compounds. Carbon provides a useful comparison case having no central atom lone pair to delocalize. The analogy between the isoelectronic compounds H<sub>2</sub>CHCl and H<sub>2</sub>NCl (where N-Cl is nearly the same as in NCl<sub>3</sub>) improves the comparison. It is seen that the N-Si bond length is relatively much shorter than the N-Cl length, consistent with a greater *p*<sub>π</sub>-*d*<sub>π</sub> delocalization in N(SiH<sub>3</sub>)<sub>3</sub> than in NCl<sub>3</sub> and, accordingly, a stereochemically more repulsive lone pair in the latter compound. It is also clear that nitrogen is markedly different from phosphorus, for the bonds in P(SiH<sub>3</sub>)<sub>3</sub> are pyramidal and longer than those in PCl<sub>3</sub>.

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## REFERENCES

1 K. HEDBERG, *J. Amer. Chem. Soc.*, 77 (1955) 6491.

- 2 N. V. SIDGWICK AND H. M. POWELL, *Proc. Roy. Soc. (London)*, A176 (1940) 153; R. J. GILLESPIE, *J. Chem. Educ.*, 40 (1963) 295; *Angew. Chem.*, 79 (1967) 885; *Angew. Chem., Int. Ed. Engl.*, 6 (1967) 819; *J. Amer. Chem. Soc.*, 82 (1960) 5978.
- 3 J. C. CARTER, R. F. BRATTON AND J. F. JACKOVITZ, *J. Chem. Phys.*, 49 (1968) 3751.
- 4 P. J. HENDRA AND J. R. MACKENZIE, *Chem. Commun.*, (1968) 760.
- 5 L. BAYERSDORFER, U. ENGELHARDT, J. FISCHER, K. HÖHNE AND J. JANDER, *Z. Anorg. Allg. Chem.*, 366 (1969) 169.
- 6 T. C. CLARK, *Ph.D. Thesis*, University of London, 1969; T. C. CLARK AND M. A. A. CLYNE, *Trans. Faraday Soc.*, 65 (1969) 2994; T. C. CLARK AND M. A. A. CLYNE, *12th Symposium on Combustion*, (1968), in press.
- 7 L. S. BARTELL, K. KUCHITSU AND R. J. DE NEUI, *J. Chem. Phys.*, 35 (1961) 1211.
- 8 H. R. FOSTER, private communication.
- 9 T. G. STRAND AND R. A. BONHAM, *J. Chem. Phys.*, 40 (1964) 1688.
- 10 L. BEWILOGUA, *Phys. Z.*, 32 (1931) 740; W. HEISENBERG, *Phys. Z.*, 32 (1931) 737.
- 11 R. A. BONHAM AND T. UKAJI, *J. Chem. Phys.*, 36 (1962) 72.
- 12 L. S. BARTELL AND K. KUCHITSU, *J. Phys. Soc. Jap.*, 17 (Suppl. B-II) (1962) 20.
- 13 L. S. BARTELL, in A. WEISSBERGER AND B. W. ROSSITER (Editors), *Physical Methods in Chemistry*, 4th Ed., Interscience, New York, in press; *Acta Crystallogr.*, A25 (1969) S76.
- 14 J. OVEREND AND J. R. SCHERER, *J. Chem. Phys.*, 32 (1960) 1289; J. H. SCHACHTSCHNEIDER AND R. G. SNYDER, *Spectrochim. Acta*, 19 (1963) 117; J. ALDOUS AND I. M. MILLS, *Spectrochim. Acta*, 18 (1962) 1073.
- 15 a Y. MORINO, K. KUCHITSU AND T. SHIMANOUCI, *J. Chem. Phys.*, 20 (1952) 726; Y. MORINO, K. KUCHITSU, A. TAKAHASHI AND K. MAEDA, *J. Chem. Phys.*, 21 (1953) 1927.
- 15 b S. J. CYVIN, *Molecular Vibrations and Mean Square Amplitudes*, Universitets Forlaget, Oslo, and Elsevier, Amsterdam, 1968, p. 118 and p. 196.
- 16 M. Otake, C. MATSUMURA AND Y. MORINO, *J. Mol. Spectrosc.*, 28 (1968) 316.
- 17 Y. MORINO, K. KUCHITSU AND T. MORITANI, *Inorg. Chem.*, 8 (1969) 867.
- 18 F. B. CLIPPARD, JR. AND L. S. BARTELL, *Inorg. Chem.*, 9 (1970) 805.
- 19 Y. MORINO, K. KUCHITSU AND S. YAMAMOTO, *Spectrochim. Acta*, A24 (1968) 335.
- 20 D. P. STEVENSON AND V. SCHOMAKER, *J. Amer. Chem. Soc.*, 62 (1940) 1913.
- 21 H. A. SKINNER AND L. E. SUTTON, *Trans. Faraday Soc.*, 40 (1944) 164.
- 22 G. E. MOORE AND R. M. BADGER, *J. Amer. Chem. Soc.*, 74 (1952) 6076.
- 23 D. J. MILLEN, private communication.