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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 $r_g = 1.759 \pm 0.002$ Å and a Cl–N–Cl angle of $107.1 \pm 0.5°$. The bond angle is larger than that found in NF_3, consistent with the (recently revised) trends displayed by the trihalides of phosphorus and arsenic, but much lower than the 120° angle reported for the isoelectronic molecule $N(SiH_3)_3$. 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 SiH_3 groups. Mean amplitudes of vibration of 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 $N(SiH_3)_3$[1], 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[2]. Indeed, the VSEPR postulates call for bond angles smaller than tetrahedral and smaller, even, than those in 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[3–5], in which the compound was diluted by inert substances. These investigations revealed that NCl_3 is pyramidal rather than planar. They have also suggested that the bond angle is in the vicinity of 108°. It looked possible to extend the dilu-