

LETTERS TO THE EDITOR

STUDY OF AMINO GROUP ROTATION IN 2, 4, 6-TRIBROMO-ANILINE BY PROTON MAGNETIC RESONANCE

THE Proton Magnetic Resonance study on 2, 4, 6-tribromo-aniline has been made to check the crystal structure previously determined and to study the molecular orientations. The results have been interpreted by comparing the observed second moments with the theoretically calculated value of second moments. Theoretical second moments have been calculated for the motion of amino group round its bond with benzene ring and for the rigid lattice. Well defined changes were observed in the second moment for the intra-molecular motion (Fig. 1.).

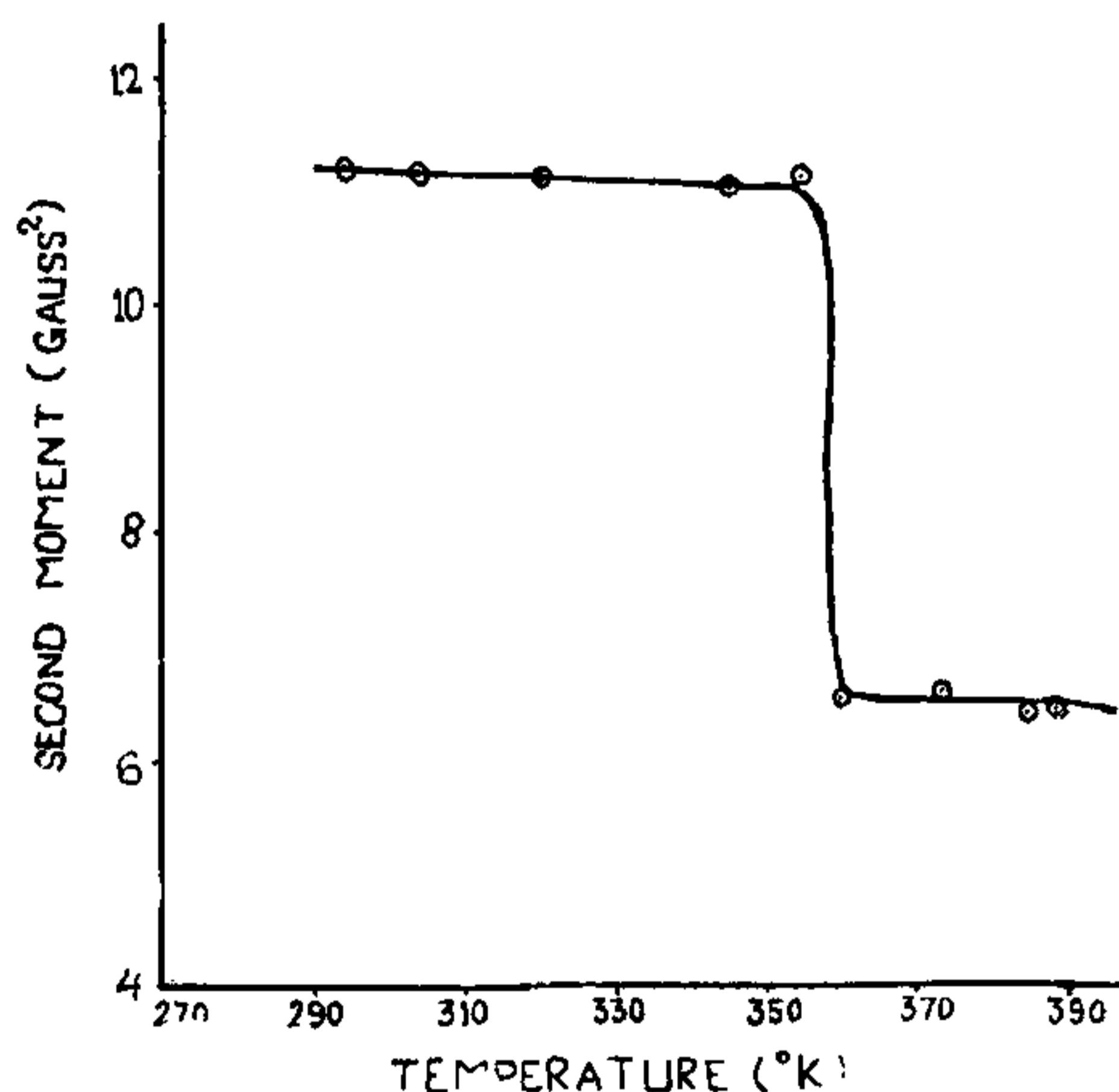


FIG. 1

X-ray structure of 2, 4, 6-tribromo-aniline was previously determined by Cristensen and Stromme¹. The crystals were orthorhombic, having four molecules per unit cell. Unit cell dimensions are $a = 13.441 \pm .004$ Å, $b = 14.623 \pm .008$ Å, $c = 4.263 \pm .002$ Å.

The present work deals with the measurement of the second moment at different temperatures. The second moments are then corrected for modulation amplitude as suggested by Andrew². Theoretical second moment has been calculated as the sum of intra (S_1) and inter (S_2) molecular contributions. S_1 calculated by VanVleck's³ relation comes out to be 2.92 gauss². S_2 has been calculated follow-

ing Andrew and Eades⁴ and was found to be 6.9 gauss². The experimentally observed second moment at 294° K is 11.3 gauss². The theoretically calculated value of rigid lattice second moment is 9.42 gauss². The difference between the two values has been accounted by assuming a small torsional oscillation (about 5°) of benzene ring about the N-C-C axis. Strong vibrations of hydrogen atoms about their mean positions also contribute toward this disagreement. The possibility of torsional oscillation has also been supported by X-ray studies¹. The consistency of our experimental and theoretical results justify the X-ray structure.

The fall of second moment at about 360° K is due to the presence of molecular motion inside the lattice. Molecule cannot rotate as a whole, as it is a heavy molecule. Therefore, the rotation of amino group has been speculated. The reduction in second moment when the amino group is rotating has been computed by calculating the rigid lattice second moment of the isolated amino group. Taking N-H bond distance of 1.014 Å it was found to be 14.2 gauss². If the amino group rotates about an axis perpendicular to the inter proton line, then the change in second moment would be $\frac{1}{2} (14.2) = 10.6$ gauss². Since NH₂ group has half of the total protons present in the molecule, therefore, the change in second moment for the motion of amino group would be $\frac{1}{2} (10.6) = 5.3$ gauss². Individual decrement in S_1 for amino group rotation was found to be 1.31 gauss². S_2 would reduce by 3.45-4.48 gauss². Therefore the second moment would reduce by 4.76-5.79 gauss². Thus computation of decrement by two different methods comes out to be the same. Second moment falls to 6.5 gauss² at 360° K. The reduction observed (4.8 gauss²) agrees well with our theoretically computed decrement of 4.76-5.70 gauss², for NH₂ group motion. Mehrotra *et al.*⁵ found a possibility of the rotation of molecule as a whole, by studying the decrement of dielectric relaxation time with temperature. Since second moment remains nearly constant after 360° K, hence our study does not indicate about such a possibility. The motion of amino group is considerably hindered by the presence of strong intra-molecular repulsions between the amino group and the adjacent bromine atoms. Fischer⁶ found that the substitution of bromine atoms in aniline increases its dipole relaxation time. The activation

energy for NH_2 group orientation was found to be 20.2 ± 1.0 K cal/mole. The amount of hindrance offered to NH_2 group rotation is evident from the large activation energy required for its motion.

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A NOTE ON THE PLASTIC DEFORMATION OF BISMUTH SINGLE CRYSTALS

A NUMBER of papers have appeared on the growth¹⁻⁴ and defect structure, particularly on dislocations⁵⁻⁸ in single crystals of bismuth. This paper reports our preliminary work on the plastic deformation behaviour of these crystals.

The structure of bismuth is rhombohedral and the atoms in a layer perpendicular to the trigonal axis are held together by covalent bonds and these in turn are held together by van der Waals forces. Single crystals can be cleaved along these planes which are the (111) planes. Slip takes place on these planes along the $[10\bar{1}]$ direction.

Single crystals of bismuth were grown using zone refined metal obtained from M/s. Koch Light Ltd., U.K., in an inert atmosphere of nitrogen by the zone-levelling technique in porcelain boats at 6 cm/hr. The crystals were one square centimetre in cross-section and 6 cm in length. The cleavage was perpendicular to the axis of growth of the crystals. Room temperature deformation was done by placing a load of 10 Kg at the centre of the crystal which was placed on two knife edges 3.85 cm apart. The load was removed after a curvature in the crystal was caused. After deformation the crystal was cleaved at liquid nitrogen temperatures along the (111) planes. To reveal the dislocations an etchant was used which consisted of 4 parts of fuming nitric acid and 5 parts of glacial acetic acid.

This etchant was tried for its reliability to reveal dislocations in the standard manner.

Figure 1 is a photomicrograph of a crystal that was etched before and after the deformation. Triangular point-bottomed pits and flat-bottomed pits were obtained. Etching a specimen from the centre of the rod where the load was applied, pyramidal, symmetrical and asymmetrical pits were observed which were also terraced. These observations are presented in Fig. 2.

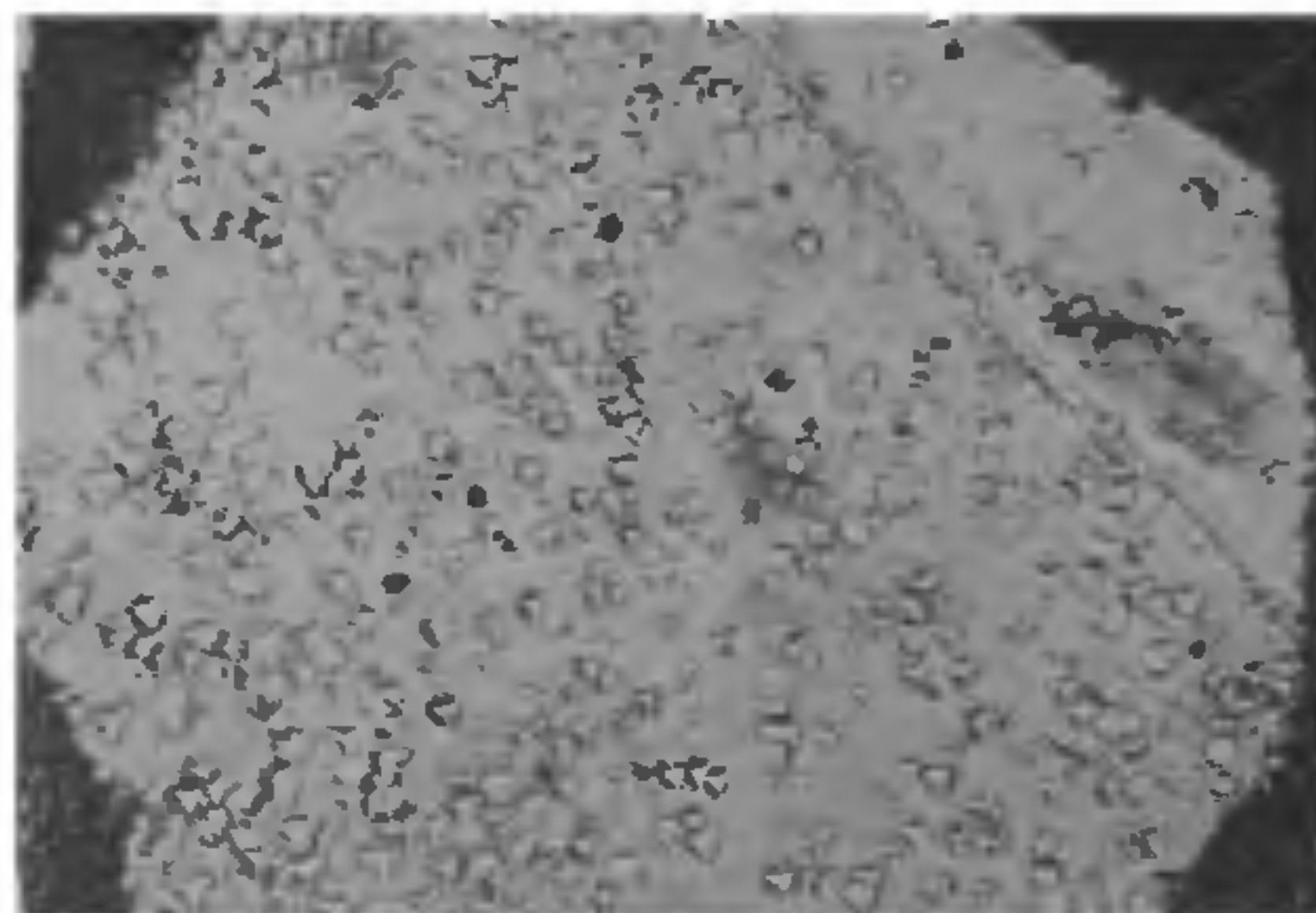


FIG. 1



FIG. 2

Figure 1 shows that motion of dislocations has taken place; where there were point-bottomed pits before the deformation there are flat-bottomed pits. The motion of the dislocations has taken place along the $[10\bar{1}]$ directions. The symmetrical pit in Fig. 2 the apex of which coincides with the base may be a screw dislocation having its axis along the $[111]$ direction. The asymmetrical type of pits the apices of which are deflected towards a side of the base may correspond to linear dislocations which are inclined to the (111) plane. These dislocations are of the type $(112)[10\bar{1}]$.

From the above observations it can be concluded that the motion of dislocations takes place at room