

LETTERS TO THE EDITOR

NMR STUDY OF INTRA-MOLECULAR MOTION
IN SOLID 2-5 DICHLOROANILINE

THE crystal of 2-5 dichloroaniline is very useful for the study of the intramolecular mobility of the NH_2 group as there is no evidence of a hydrogen bond which may hinder such motion. The present study is directed towards examining the feasibility of the free rotation of the amino-group.

Crystal Data

The crystals of 2,5 dichloroaniline are monoclinic, with space group $P_{21/c}$. The cell dimensions are $a = 13.237 \pm 0.007$, $b = 3.892 \pm 0.006$, $c = 18.803 \pm 0.02 \text{ \AA}$, $\beta = 135^\circ 13' \pm 11'$, $V = 682 \pm 3 \text{ \AA}^3$ with four molecules in the unit cell. The crystal structure¹ has been determined with the combined application of nuclear quadrupole resonance and X-ray diffraction. Excluding the NH_2 group, the molecule has a Pseudo centre of symmetry. Since there is no evidence of a N-H...Cl hydrogen bond there is a possibility of the rotation of the amino-group about the C-N bond connecting it to the phenyl ring.

Experimental Details

The NMR spectrogram of the sample was recorded at Tata Institute of Fundamental Research (Bombay) with the help of 12" magnet, Varian associates variable frequency spectrometer and variable temperature probe assembly. Temperature variations were obtained by suitably regulating the flow of cooled or heated nitrogen gas over the sample. The resonance frequency was 7.5 MC/S. Our sample of 2-5 dichloroaniline was obtained by courtesy of the Central Drug Research Institute, Lucknow, and was highly pure.

Second Moment Calculations

Theoretical.—The rigid lattice second moment consists of two parts (i) intra-molecular contribution S_1 and (ii) intermolecular contribution S_2 . The former is due to the interaction between the protons of the same molecule and may be evaluated by Van Vlecks² formula for powder samples

$$S_1 = \frac{716.15}{N} \sum_{j > k} r_{jk}^{-6} \quad (1)$$

where N is the number of protons in the molecule and r_{jk} is the internuclear distance between the j^{th} and the k^{th} nuclei. The calculation of S_1 , therefore, involves the construction of a molecular model. In our model of the molecule (Fig. 1)

we have assumed a planar hexagonal benzene ring with C-C, C-H and C-Cl bonds of 1.38, 1.07 and 1.70 Å respectively. The N-H bond length³ and $\angle \text{HNH}$ were taken as 1.015 Å and 106.6° respectively. This molecular model yielded the value of S_1 as 10.83 gauss².

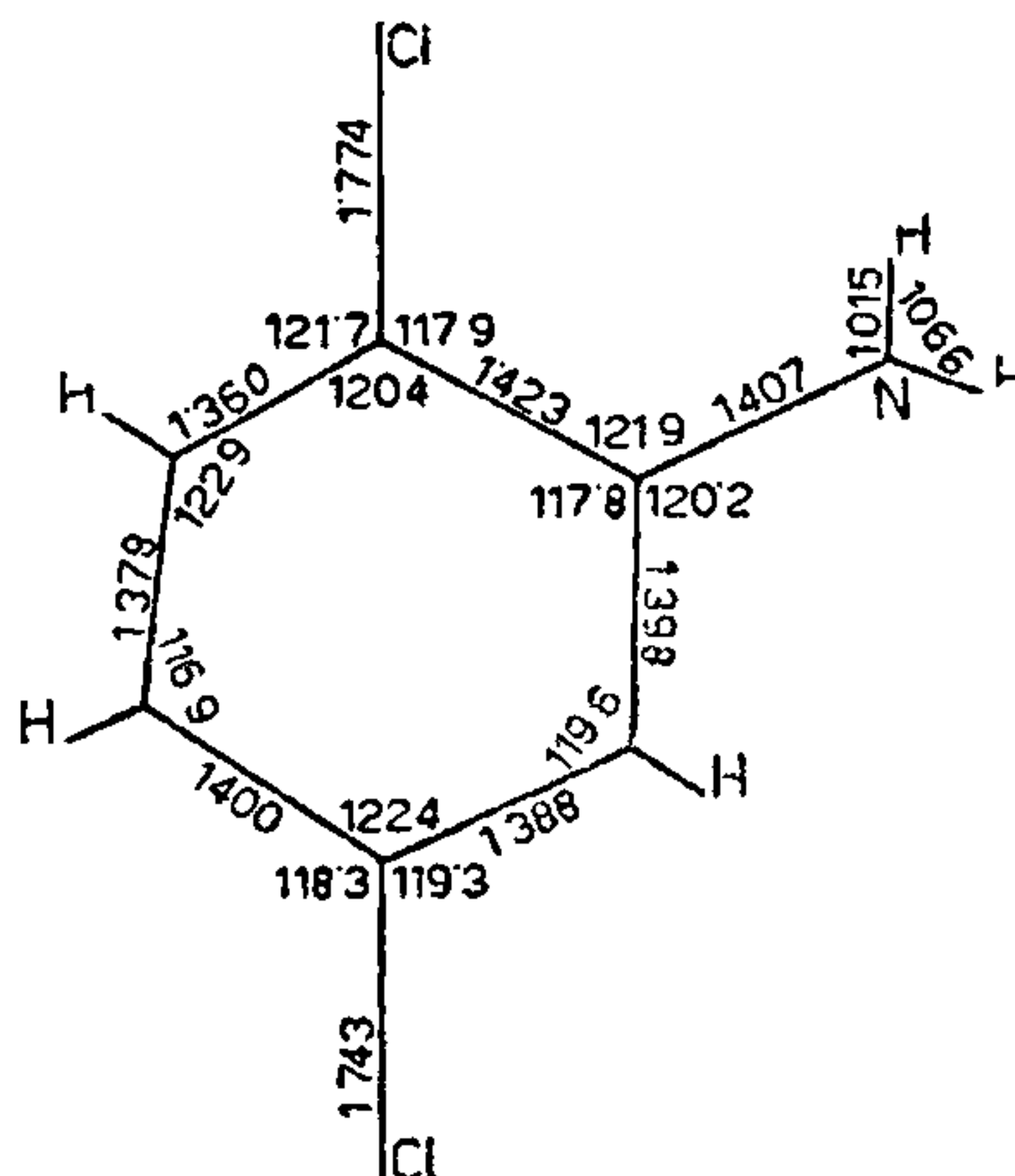


FIG. 1. Molecular structure of 2,5-dichloroaniline.

The inter-molecular contribution S_2 arises out of the interaction between the protons of the different molecules situated at the various lattice sites. The calculation of this part is very tedious but a rough estimate⁴ may be made from the expression

$$S_2 = 358.1 \times 4\pi N_p (3R^3 V)^{-1} \quad (2)$$

where N_p is the number of protons in the unit cell, R is the molecular radius and V is the lattice volume. Substitution of $R = 3.56$, $N_p = 20$ and $V = 682 \text{ \AA}^3$ yields $S_2 = 12.70 \text{ gauss}^2$.

The value of the rigid lattice second moment is, therefore, $10.83 + 12.70 = 23.53 \text{ gauss}^2$.

Experimental.—The experimental value of the second moment may be calculated from the trace with the help of the expression

$$S = \frac{1}{3} \left[\int_0^\infty g'(H) (H - H_0)^3 dH / \int_0^\infty g'(H) (H - H_0) dH \right] \quad (3)$$

where H_0 is the resonance field value. This expression may be simplified to the form

$$S = \frac{\sum h^3 f(h)}{3 \sum hf(h)} \quad (4)$$

by applying the trapezium rule to the integrals. A graph is plotted between the experimental values of the second moment obtained at different temperatures.

Discussion

The fairly good agreement between the theoretical value (23.53 gauss²) and the experimental (21.91 gauss²) as values at 77° K indicates that the lattice is effectively rigid at the liquid nitrogen temperature. From Fig. 2 we observe that between 77° K

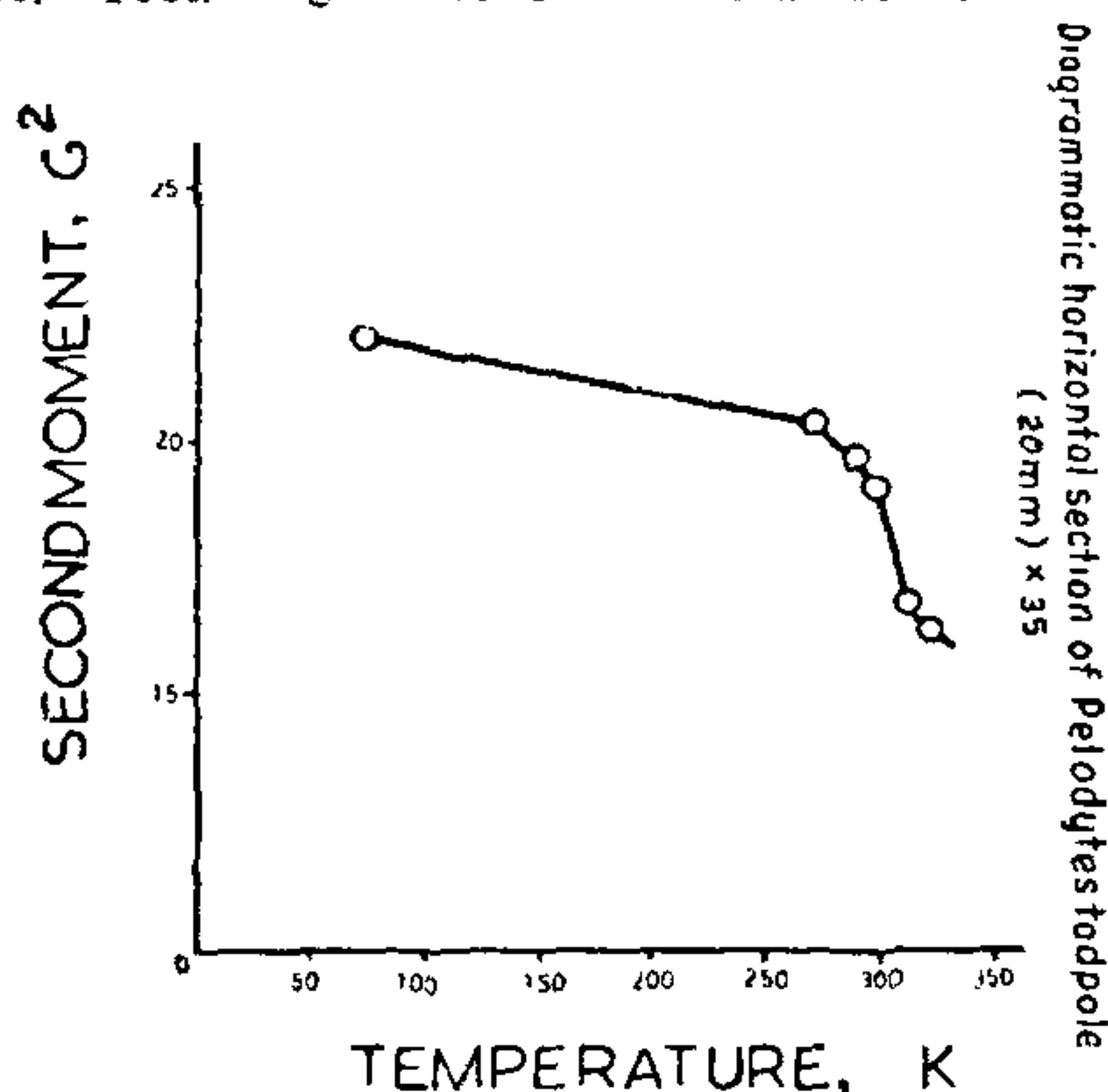


FIG. 2. Second moment vs. temperature curve.

and 294° K the second moment vs. temperature curve possesses a slight downward slope. This slope may be assigned to the torsional oscillations of the NH₂ group which are capable of occurring at such low temperatures. Beyond 294° K there is a rapid fall in the value of the second moment indicating the onset of molecular motion in the crystal lattice.

The molecular motions can take place only after the molecule has been imparted sufficient energy (in our case thermal energy) to enable it to surmount the potential barrier hindering such motion. Two distinct possibilities arise: (i) the molecule may rotate about one of its symmetry axes or, (ii) the amino-group may rotate about the C-N bond joining it to the phenyl ring.

Gutowsky and Pake⁵ have shown that the rotation of the molecule as a whole reduces the value of S_1 to a value $(3 \cos^2 \gamma_{jk} - 1)^2/4$ times the rigid lattice value where γ_{jk} is the angle between the line joining the nuclei j and k and the axis of rotation. The reduced value of the intramolecular contribution comes out to be 2.19 gauss² for the rotation of 2-5 dichloroaniline.

Andrew and Eades⁶ have shown that the rotation of the molecule about one of its symmetry axes reduces the inter-molecular contribution by a factor of 0.24 yielding a value of 2.60 gauss² for the sample under investigation.

The total rotational second moment is, therefore, $2.19 + 2.60 = 4.79$ gauss². This value falls too short of the experimental value of second moment (16.4 gauss²) at about 360° K and therefore, the possibility of the rotation of the 2-5 dichloroaniline about one of its symmetry axes may safely be ruled out.

The crystal structure study of 2-5 dichloroaniline indicates that the lattice is bereft of any hydrogen bonding between the different substituents. Further the dielectric studies of Kramer⁷ reveals that the substitution of the chlorine atoms has little effect on the amino-group. This leads to the conclusion that there is a distinct possibility of the rotation of the amino-group about the C-N bond. The reduction in the value of the second moment due to the free rotation of the NH₂ group taking the N-H bond lengths as 1.015 Å and following the arguments given in a previous publication⁸ should be $19.26 \times 3/4 \times 2/5 = 5.78$ gauss². The reduced value of the second moment due to the rotation of the amino-group should, therefore, be $23.53 - 5.78 = 17.75$ gauss². This value compares favourably, within the limits of experimental error, with the experimental value 16.40 gauss² at 320° K. Hence we conclude that it is possible for the amino-group in solid 2-5 dichloroaniline to execute free rotation about the C-N bond at temperatures higher than the room temperature.

The second moment remains nearly the same as the melting point of the sample is approached. Hence it may be concluded that no other type of molecular motion takes place in the sample.

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