

PMR STUDY OF GROUP REORIENTATION IN SOLID VANILLIN

S. C. MISHRA, S. C. GUPTA and K. D. PANDEY

Department of Physics, B.S.N.V. College of Lucknow University, Lucknow 226 001, India.

ABSTRACT

Low resolution PMR investigations were carried out on solid vanillin at 7.6 MHz in the temperature range 77°–355°K. The lattice was non-rotating and effectively rigid at 77°K. The sudden drop in the second moment from the rigid lattice value (15.27 G²), obtained by assumed molecular model, in the range 280°–310°K, has been attributed to the hindered reorientation of –OH and –OCH₃ groups. The activation energy for the motion is about 2.03 k. cal/mole.

INTRODUCTION

THE PMR experiments were carried on vanillin (3-hydroxy, 4-methoxy benzaldehyde), a compound of high-medicinal and industrial importance¹, with a view to studying the crystalline lattice and molecular motions present in the solid phase. The study affords a check of the proposed molecular structure. The input of appropriate thermal energy (described—later) provides for group reorientation which is, of course, hindered in nature and fashion instead of free and simultaneous.

HYDROGEN BONDING AND MOLECULAR STRUCTURE

Calvert and Praybyska² and Walker³ have given the preliminary x-ray data of vanillin. The crystal system is orthorhombic and unit cell parameters are; $a = 7.88$, $b = 14.04$ and $c = 13.52$ Å. In the absence of precise data regarding the molecular and crystal structure of the title compound, the molecular model (figure 1) was constructed assuming a reasonable similarity of bond angles and bond distances with those having nearly same composition in character and identical stereo-chemical environment and whose detailed crystallographic and stereo-chemical reportings are available. C–H length has been taken to be uniform with a value 1.08 Å. The analysis of the model was made with the assumptions (a) the OH group is in the plane of the ring, (b) the benzene ring is unsymmetrical and (c) the OCH₃ group had sufficient planar rigidity at room temperature. The space co-ordinates of the constituent protons are given in table 1. I.R. studies⁴⁻⁵ have suggested strong H-bond formation in –OH and –OCH₃ lying at adjacent sites. Lindberg⁶ has observed chelate ring formation in the title compound.

EXPERIMENTAL

The low resolution experiments were performed at T.I.F.R. (Bombay). The experimental second moments were obtained from the derivative recordings using trapezium rule expression, $S = \Sigma h^3 f(h) / 3 \Sigma h f(h)$. High purity sample was obtained by the courtesy of Prof. D. N. Dhar, IIT Kanpur. The variation of second moment and linewidth with temperature are shown in figures 3 and 4. The accuracy in the measurements was about ± 1 G² as measured from standard results.

CALCULATIONS

Rigid Lattice Second Moment: There exist intra and inter molecular contributions; the S_1 and S_2 , former

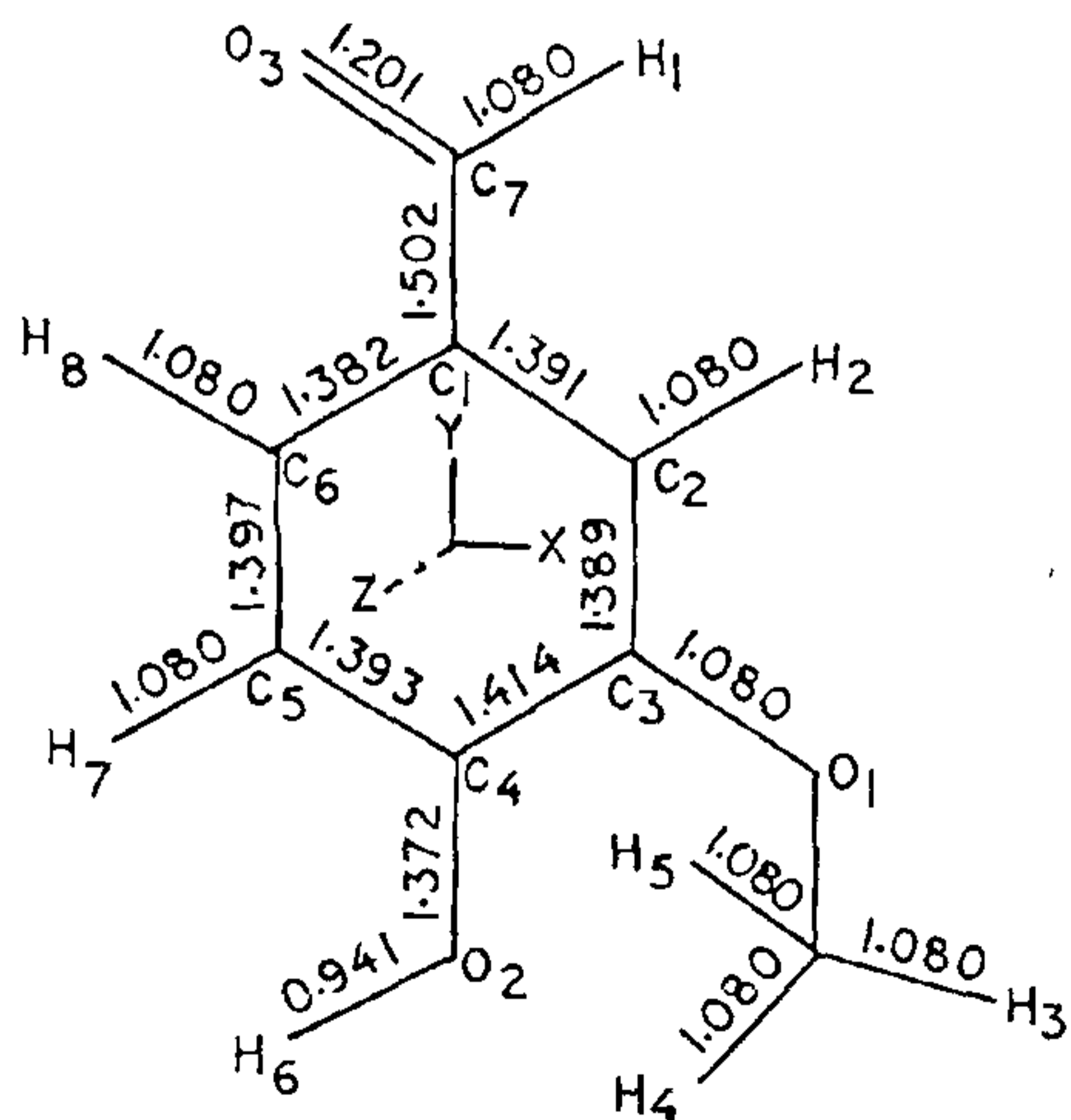


Figure 1. Molecular model of vanillin

Table 1 Position co-ordinates of constituent protons in vanillin

Protons	X	Y	Z
H ₁	0.8802	3.5107	0
H ₂	2.1209	1.2611	0
H ₃	3.4711	-2.9708	0.9479
H ₄	1.8607	-3.7111	0
H ₅	1.6911	-1.9712	-0.9479
H ₆	-0.8907	-2.9907	0
H ₇	-2.2106	-1.2212	0
H ₈	-2.1912	-1.2502	0

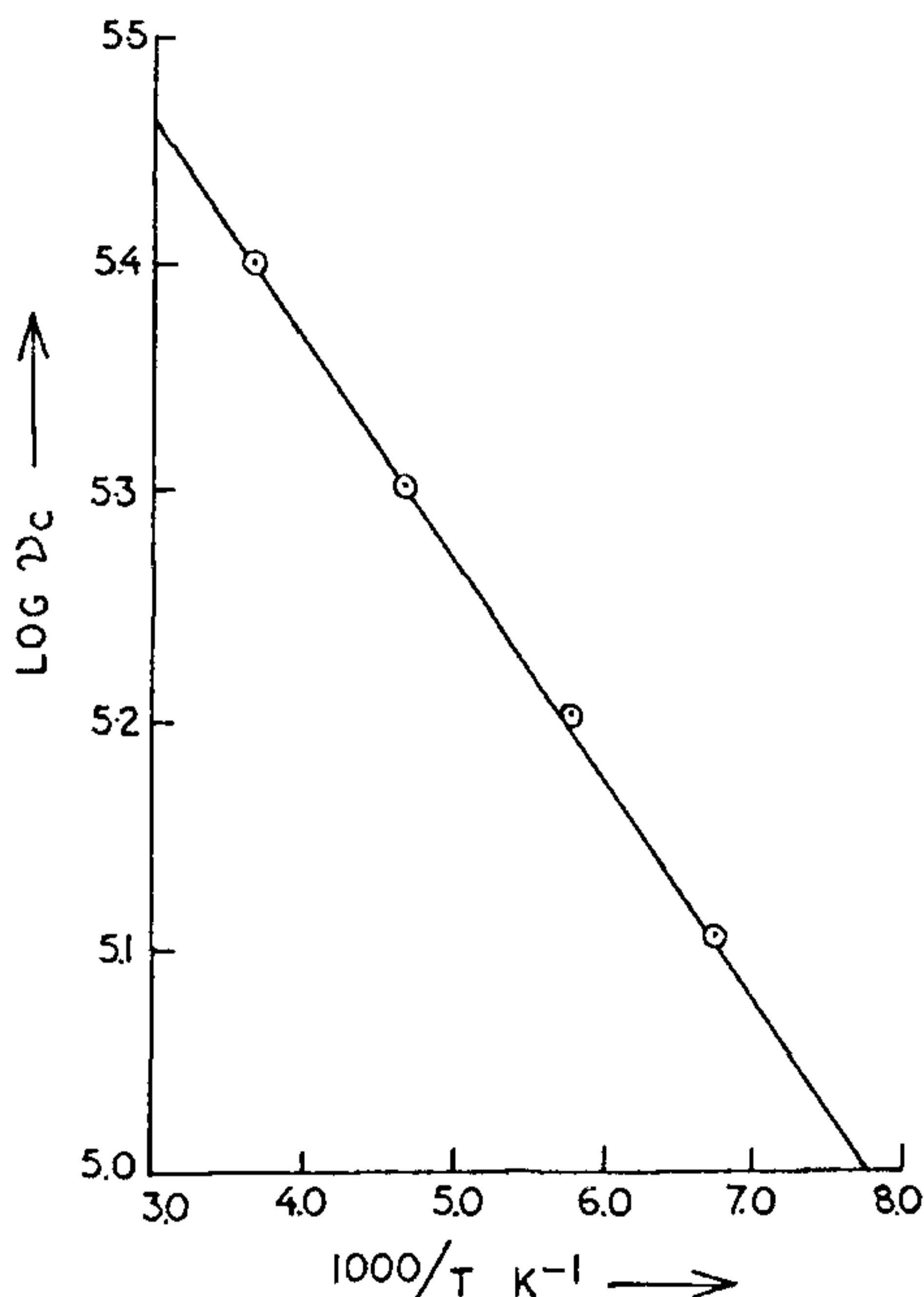


Figure 2. Log τ_c versus $1/T$ curve

arising due to protonic interactions within the same molecule and later due to protonic interactions with the neighbouring molecules. The S_1 was evaluated using van Vleck's formula⁷,

$$S_1 = \frac{715.9}{N} \sum_{j>k} r_{jk}^{-6} G^2$$

The term $\sum_{j>k} r_{jk}^{-6}$ in the formula was obtained with the help of the model and the proton position co-

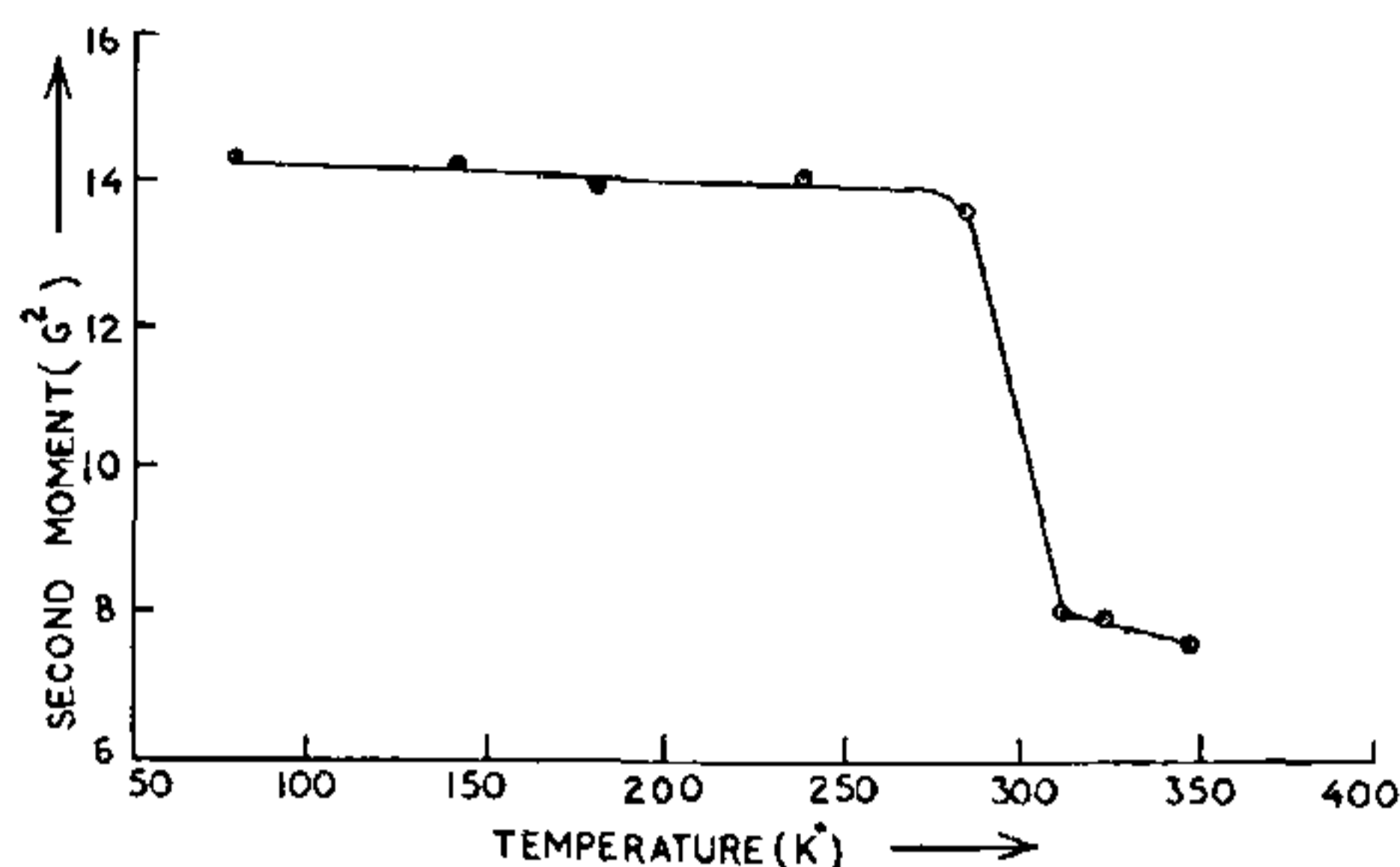


Figure 3. Variation of second moment with temperature

ordinates and comes out to be $0.117 G^2$. The inter part S_2 was found to be $4.4 G^2$ approximately employing Andrew and Eades⁸ method whereas Smith's theory⁹ yielded a value $5.08 G^2$ and in the present discussion the mean $4.74 G^2$ is used.

The total rigid lattice second moment is, thus, $S = S_1 + S_2 = 10.53 + 4.74 = 15.27 G^2$.

Reorientational computations for OH and OCH₃ groups: The group rotation brings about a reduction in the second moment through a modification in the time varying field of the resonance spectrum. The reduction in S_1 caused by group rotation can be calculated from the theory of Gutowsky and Pake¹⁰. Reduction in S_1 on account of reorientation of OH group about C-O bond was obtained to be $2.86 G^2$ and that due to reorientation of OCH₃ group, the reduction was $6.41 G^2$. The reductions for various possibilities were individually obtained and are contained in table 2.

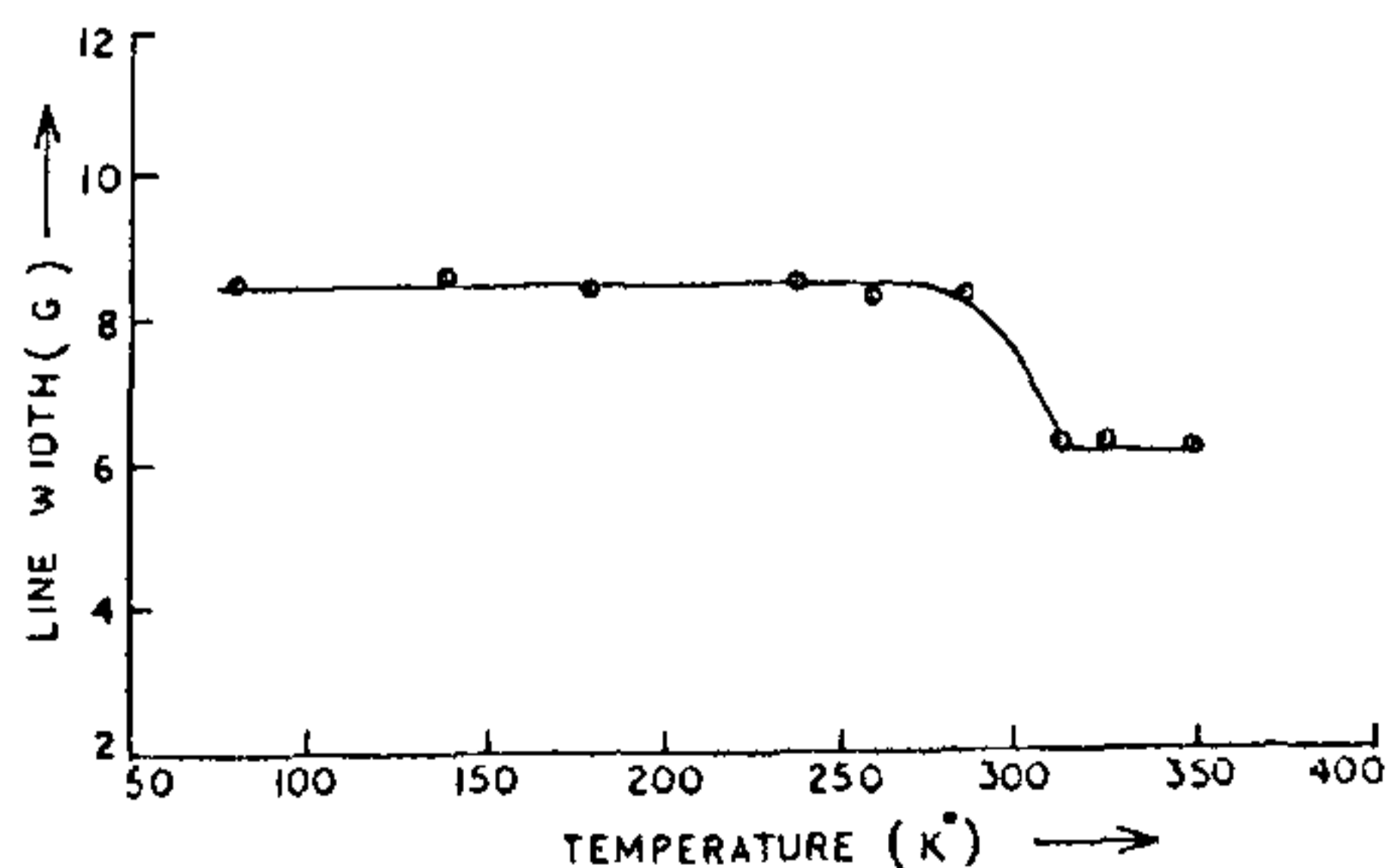


Figure 4. Change of line width temperature

Table 2 Comparison of theoretical reorientational and observed second moment.

Case	Intra part	Inter part	Range	Observed
1. OH and OCH ₃ rotating freely and simultaneously	2.89 G ²	(1.99 to 1.18)G ²	(4.88 to 4.04)G ²	8.12 G ²
2. OH stationary and OCH ₃ rotating	6.41 G ²	(3.08 to 2.37)G ²	(9.49 to 8.78)G ²	8.12 G ²
3. OH rotating and OCH ₃ stationary	6.98 G ²	(3.08 to 2.37)G ²	(10.06 to 9.35)G ²	8.12 G ²

Reduced second moment when molecule as a whole reorients: Gutowsky and Pake¹⁰ method was employed for the reduction of intra contribution. Andrew and Eades⁸ have shown that when molecule as a whole reorients, it reduces the inter contribution by a factor of 0.24. The reduced intra and inter contributions are found to be 2.13 and 1.14 G² respectively and the theoretical reduced second moment for such a case is 3.27 G².

DISCUSSION

Within the limits of experimental error, a reasonable agreement in the theoretical rigid lattice second moment (15.27 G²) and the experimental second moment at 77°K (14.36 G²) is seen to exist. This justifies our assumed molecular model and shows the consistency of hydrogen position co-ordinates and also indicates that all molecular motions are virtually frozen at 77°K. The second moment is observed to be practically constant beyond 77° upto 280°K exhibiting the rigid and non-rotating state of crystal lattice as contrasted with a similar¹¹ group of compounds¹²⁻¹⁴, where torsional protonic oscillations are observed to exist, before the onset of group or molecular motion. The behaviour of the title compound appears reasonable in the light of stereo-chemical considerations at the 3 and 4 sites of the ring and the extent and strength of the intermolecular bonding through OH bonds.

Beyond 280°K, an abrupt fall in the second moment indicates the onset of some kind of intramolecular motion or group rotation. The fall should not be attributed to the molecular reorientation as a whole, on the considerations of bulk, size, symmetry and intramolecular linking of the molecule. Again, the calculations also do not support this view (theoretical reduction is 12 G² while the observed reduction is 6.21 G²). The possibility of CHO group rotation can similarly be safely ruled out. Considering the free and simultaneous rotation of the OH and OCH₃ groups, the theoretical, reduced second moment should lie in the range 4.88-4.04 G², as stated earlier, which is too

low a value, even lower than the minimum observed second moment. For the case of OH stationary and OCH₃ rotating, the reorientational second moments lie in the range 9.49 to 8.78 G² and for the reverse case (OCH₃ stationary and OH rotating), the range is 10.06 to 9.35 G². Both these values tally satisfactorily with the observed second moment. Thus we regard that both the groups reorient but their rotation is hindered. Naves *et al*¹⁵ and others^{4,5} have shown that coupling of OH in different vibration modes exists in the title compound; and strong intramol H-bonds have also been observed. Studies of Giuseppe *et al*¹⁶ and Millero *et al*¹⁷ have revealed the possibility of chelate ring formation and the chelate temperature dependent rotational behaviour may be inferred therefrom. Lindberg *et al*¹⁸ have pointed out the potential barrier for the hydroxyl group motion and NMR chemical shifts¹⁹ and Raman studies²⁰ appear to disregard molecular rotation as a whole. The thermodynamic and dielectric studies are also in conformity with the hindered group reorientation.

The activation energy for the group rotation was obtained from the expression;

$$(\Delta H)^2 = \beta^2 + \left(\frac{2}{\pi}\right)C^2 \tan^{-1} \left[\frac{\alpha\gamma\Delta H}{2\pi\nu_c} \right]$$

where the symbols have their usual meaning^{21,22}. The Arrhenius equation of the form $\nu_c = \nu_0 \exp(-E_R/RT)$ was used and a value 2.03 k. cal/mole was obtained for the activation energy employing the variations, as shown in figure 2. This value should be approximate due to comparatively small number of observations in the transition region. The second moment is practically constant in the region 310°-355°K, suggesting non-transitory state which otherwise could have suggested some motion or change in the crystalline structure.

ACKNOWLEDGEMENT

The authors thank Prof. Vijairaghvan (TIFR) for the experimental facility. Thanks are also due to Prof.

D. N. Dhar of IIT (Kanpur) and Prof. V. D. Gupta, Head, Physics Department of Lucknow University for encouragement.

21 June 1983; Revised 11 June 1984

1. Kratze, K., *Scientia Pharma*, 1953, **21**, 106.
2. Calvert, L. D. and Prybylska, M., *Appl. Spectroscopy*, 1961, **15**, 39.
3. Walker, C. M., *Anal. Chem.*, 1950, **22**, 200.
4. Sarkanen, H. M. and Ericsson, B., *Tappi*, 1967, **50**, 572.
5. Baire, E. L., Cousin, L. R. and Basilon, M. R., *Anal. Chem.*, 1962, **34**, 824.
6. Lindberg, J. J., *Soc. Sci. Fennica Commun. Phys. Maths.*, 1957, **20**, 66.
7. van Vleck, J. H., *Phys. Rev.*, 1948, **74**, 1168.
8. Andrew, E. R. and Eades, R. G., *Proc. Phys. Soc.*, 1953, **A66**, 415.
9. Smith, G. W., *J. Chem. Phys.*, 1965, **42**, 4299.
10. Gutowski, H. S. and Pake, G. E., *J. Chem. Phys.* 1950, **18**, 162.
11. Gupta, R. C. and Vidula Misra, *Indian J. Pure Appl. Phys.*, 1975, **13**, 404.
12. Banerjee, A. K., Agrawal, P. and Gupta, R. C., *J. Prak. Chem.*, 1973, **315**, 2.
13. Gupta, R. C., Banerjee, A. K. and Agrawal, P., *Indian J. Pure Appl. Phys.*, 1974, **12**, 790.
14. Mirza, P., Banerjee, A. K. and Gupta, R. C., *Curr. Sci.*, 1974, **14**, 440.
15. Naves, Y. R., Guillarmod, A. and Zawesko, C., *Helv. Chim. Acta*, 1967, **50**, 1461.
16. Guesepi, S., *Bol. Sci. Fac. Chim. Indian Bol.*, 1960, 235.
17. Millero, F. J., Ahulwalia, C. J. and Helper, L. G., *Chem. Eng. Data*, 1964, **9**, 319.
18. Lindberg, J. J., *Acta Chem. Scand.*, 1960, **14**, 379.
19. Susumu, Y. and Jadao, I., *Kogyo K. Zasshi*, 1969, **72**, 346.
20. Martin, W. D., Nagh, J. S. and Robert, E. K., *Anal. Chem.*, 1966, **38**, 1479.
21. Bloembergen, N., Purcell, E. M. and Pound, R. B., *Phys. Rev.*, 1948, **73**, 679.
22. Kubo, R. and Tomita, K., *J. Phys. Soc. (Jpn)*, 1954, **9**, 888.

ANNOUNCEMENT

AWARD OF RESEARCH DEGREES

Bangalore University, Bangalore—Ph.D. (Zoology)
—Sri Ch. Narasimha Rao.

Berhampur University, Berhampur—Ph.D. (Physics)
—Sri L. K. Das, Ph.D. (Chemistry) Sri Gopal Krishna Mohanty, Sri Bijaya Kumar Panda, Sri Ramanado Nayak, Ph.D. (Botany)—Sri Sachinanda Padhy, Sri Bipracharan Panigrahi, Ph.D. (Zoology)—Sri Gajendra Kumar Parhi, Sri K. I. Thomas, Sri Sudhansu Sekhar Rath and Miss Syama Kumari Tripathy.

University of Cochin, Cochin—Ph.D. (Electronics)—
Sri G. M. Ajit, Ph.D. (Marine Science)—Smt Ammini Joseph, Smt P. Premalatha.

Karnatak University, Dharwad—Ph.D. (Physics) Sri Kunabenchi Rudrappa Sangappa, Ph.D. (Chemistry) Sri Math Basavaraj Veerupaxayya, (Late) Sri Pujar

Ishappa Bheemappa, Ph.D. (Geology) Sri Neeramanvi Rajashekar Veeranagouda, Ph.D. (Zoology) Sri Pramoda Sumitrappa.

Ranchi University, Ranchi—Ph.D. (Botany) Sri Nandjee Kumar.

Sri Venkateswara University, Tirupathi—Ph.D. (Statistics) Sri K. L. Anantha Padmanabha Sharma, Ph.D. (Physics)—Sri M. Chenchu Munaswami Reddy, Ph.D. (Chemistry) Sri A. Sivarami Reddy, Smt. V. Nirmala, Ph.D. (Zoology) Sri B. Narasimha Murthy, Sri K. Appaswamy Pillai.

Utkal University, Bhubaneswar—Ph.D. (Mathematics)—Sri S. Audinaravana Moorthy, Ph.D. (Chemistry)—Sri Rajendra Prasad Misra, Ph.D. (Botany)—Sri Dipak Kumar Chatterjee, Sri Ramesh Chandra Ray, Smt. Sneha Prava Das.
