LETTERS TO THE EDITOR

MAGNETO OPTIC ROTATORY DISPERSION CURVES OF BENZENE

Introduction

THE conformation of polymers and biopolymers are studied by physical techniques such as X-ray diffraction NMR, ORD, CD, etc. Recently Murthy and Naidu[1] have attempted to see if magneto optic rotatory dispersion could be used in conjunction with ORD in conformation of macromolecules and derived an expression for magneto optic rotation (MOR) (Verdet constant) in terms of refractive index. In the present investigation, MORD curves for benzene are drawn from evaluations of MOR from measurements on refractive indices at various wavelengths. The details of the method are given below.

The Method

Rao and Murthy[2] developed a method of evaluating mean molecular polarizability (a_M) from Verdet constant starting from Mallemann's principle and the expression for a_M reads as

$$a_M = \left[\frac{9e\lambda^2}{8\pi^3 N} \cdot \frac{nM\, p\delta}{p\,(n^2+2)^2 \left(1 - \frac{\Delta^*}{2}\right)^2} \right]^{1/2} \qquad (1)$$

The significance of various terms in equation (1) is given in reference (2). On rearranging terms and substituting a for a_M and making use of Lorentz-Lorenz equation for a and simplifying, we get

$$\delta = \left[\frac{KM}{p} \frac{(n^2-1)^2}{n\lambda^2} \right] \qquad (2)$$

The significance of various terms in equation is explained in reference (1). δ is given in minutes/gauss/cm. This equation is used to get δ at various wavelengths from a measurement on refractive index, n.

Pure analar sample of benzene is taken and is further purified and distilled in accordance with specifications of Weissberger[3]. The refractive indices of benzene are measured at various wavelengths of cadmium, mercury and sodium sources, using Pulfrich refractomerer (ASCO make) having an accuracy of 6″ and giving refractive index to an accuracy of 1 in 10^4. Using these refractive indices, the Verdet constants are calculated at different wavelengths and a graph is drawn between magneto optic rotation (MOR) *versus* wavelength (λ). In order to have comparison for this MORD curve, values of Verdet constants (MOR) for benzene are taken at different wavelengths from *International Critical Tables*, Vol. VI[4] and a curve is drawn between MOR *versus* λ. The experimental MORD curve along with the curve drawn for literature values are given in Fig. 1 and the values are given in Table I.

TABLE I

Wavelength $\lambda \times 10^6$ cm	Magneto optic rotation (δ) $\times 10^4$ mts/gauss/cm	
	$\delta_{cal.}$	$\delta_{rep.}$
31·00	..	174·279
33·06	..	138·551
36·31	..	102·587
40·46	..	75·144
43·58	55·401	..
45·29	..	55·791
46·78	48·471	..
48·00	45·991	..
50·86	40·897	..
54·61	35·098	..
57·80	31·207	..
58·93	30·273	30·60
64·38	25·397	..

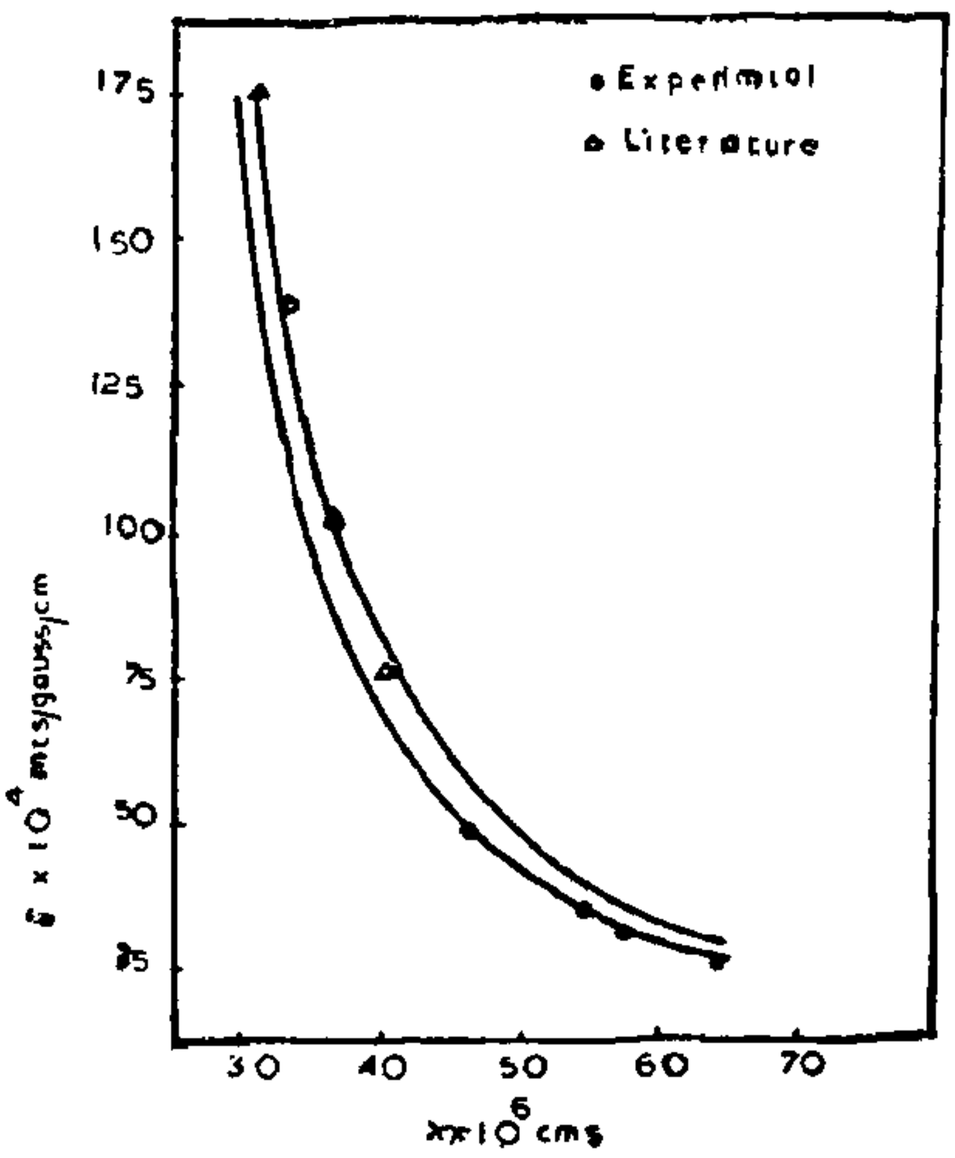

FIG. 1. MORD curves of benzene.

Results and Discussion

From Fig. 1, it can be seen that there is fairly good agreement between the experimental MORD curve and MORD curve drawn for literature values. The small deviation in the values is explained due to the

fact that a_M is replaced by a in equation (1) and this approximation results in an error of 2 to 3%. Lack of accuracy in visual measurements of δ in those days (prior to 1952) may also contribute to this variation. Thus, within this limitation, the experimental and literature curves are agreeing very well. This, in turn, suggests general applicability of the method with reasonable accuracy. The chief advantage of this method is that MORD curves can be drawn theoretically for any system available in solid or liquid or liquid crystalline form without recourse to instrumentation of MORD. This involves less expensive equipment compared Magneto optic spectropolarimeter. The MORD is seen to have common origin of ORD by Dawber[5], and this suggests the utility of MORD for conformations (like ORD). Attempts to utilise MORD for conformations is in progress.

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Molecular Biophysics Laboratory,
Department of Physics,
Autonomous Post-Graduate Centre,
Anantapur 515 003, (A.P.), India,
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V. R. MURTHY.
Y. C. RANGASWAMY.

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X-RAY ANALYSIS OF THE MONOPOTASSIUM SALT OF ADENOSINE-5′-DIPHOSPHATE-DIHYDRATE $C_{10}H_{14}N_5O_{10}P_2K.2H_2O$

THE ADP–ATP system plays a vital role in the energy transfer processes of a cell. Enzymatic reactions involving this system require the presence of various metal ions as cofactors. For example, the phosphorylation of ADP to ATP by the enzyme pyruvate kinase specifically demands the presence of monovalent K^+ ions along with Mg^{2+}. Detailed geometry of these coenzymes, when they are bound to K^+ and Mg^{2+} ions will therefore be of interest. We report here the molecular structure of the monopotassium salt of adenosine-5′-diphosphate (ADP–K) (Fig. 1) as obtained from the single crystal X-ray analysis.

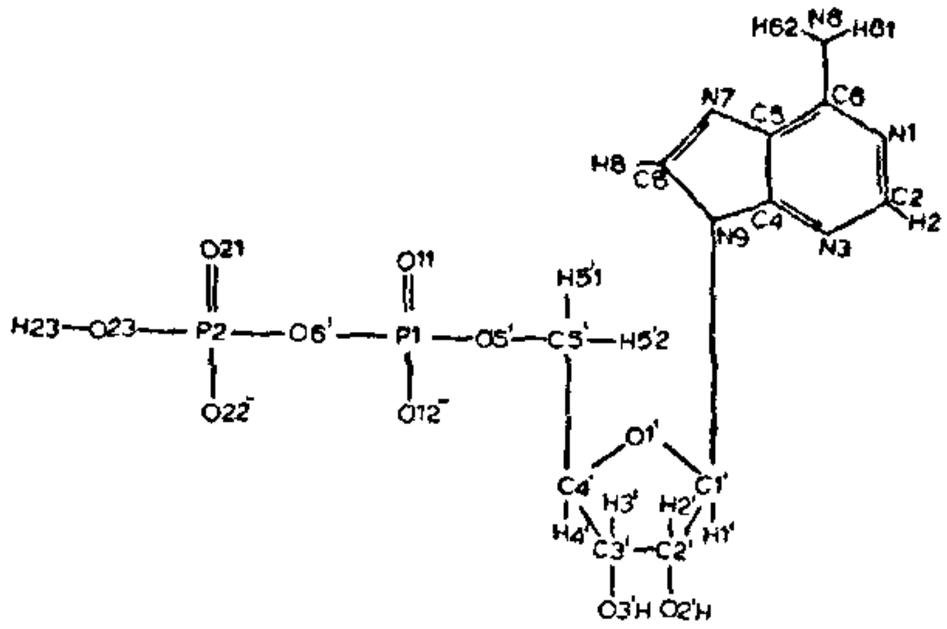

FIG. 1. Atom numbering scheme for ADP–molecule.

Crystal Data

Needle shaped crystals of ADP–K (obtained from Boehringer Mannheim) were grown by diffusion of isopropyl alcohol into its water solutions. The space group is $P2_12_12$ with $a = 28{\cdot}470$ Å, $b = 11{\cdot}449$ Å $c = 6{\cdot}325$ Å, $Z = 4$, $D_m = 1{\cdot}81$ gcm^{-3}, $D_{cal} = 1{\cdot}82$ gcm^{-3}. A crystal (dimensions $0{\cdot}02 \times 0{\cdot}04 \times 0{\cdot}08$ mm^3) sealed inside a Lindemann glass capillary along with a drop of mother liquor was mounted on a CAD–4 automatic diffractometer. Three-dimensional intensity data, to a theta limit of 50° were collected using crystal monochromated copper K_α radiation. Out of the 1190 reflections totally collected, those with $F > 2\sigma(F)$ were treated as observed reflections.

Structure Solution and Refinement

The cell dimensions of ADP–K are found to be very close to those of ADP–Rb in the same space group[1]. Hence the structure was solved using the coordinates of the ADP–Rb crystal structure, as the starting point with K^+ replacing Rb^+ ion. Block diagonal least squares refinement with individual isotropic temperature factors brought the R factor to 26·3%. A difference Fourier map at this stage revealed one water molecule, which again coincided with the one seen in ADP–Rb structure. Refinement including this water molecule and a subsequent difference Fourier showed up two peaks at special positions. These two were treated as water molecules with half the occupancy. During the final cycles of refinement K, P1 and P2 were given anisotropic temperature factors. The present R-factor is 16·6% for the observed reflections. Further refinement is in progress. The positional parameters for nonhydrogen atoms can be obtained from the authors.

Comments

The orientation of the base about the glycosidic C1′–N9 linkage is *anti* (C8–N9–C1′–O1′ = 42·4°). The ribose ring shows C2′-*endo* puckering. The conformation about C4′–C5′ bond is *gauche-gauche* (C3′–C4′–C5′–O5′ = 66·5°, O1′–C4′–C5′–O5′ = −67·4°)