

LETTERS TO THE EDITOR

THE CRYSTAL STRUCTURE OF ZINC MALONATE, DIHYDRATE $Zn C_3H_3O_4 \cdot 2H_2O$

Synthesis: The crystals were prepared by taking malonic acid and zinc carbonate in the ratio of 2:1; water being used as solvent. The concentrated solution was left for slow evaporation till the crystals began to appear. The mother liquor was removed by decantation and the crystals were washed with distilled water.

Crystal data: Monoclinic with $a = 13.86$, $b = 7.36$, $c = 7.20$ Å, $\beta = 126.7^\circ$, $D_{obs.} = 2.26$, $D_{calc.} = 2.28$ gm/cc. This gives 809.5 a.m.u. for the total unit cell content.

The empirical chemical formula for the entire unit cell content could be written as $4[Zn(C_3H_3O_4) \cdot 2H_2O]$.

Space group absences lead to either Cm or C2 or C2/m. 5.45 X-ray reflexions were collected by Weissenberg photography and intensities estimated visually.

Crystal Structure: We propose a structure (view looking down [001] is in Fig. 1) for the crystal structure based on the space group C2/m which we consider to be the most probable one and which explains everything satisfactorily and which appears to satisfy packing and stereochemical consideration. There are

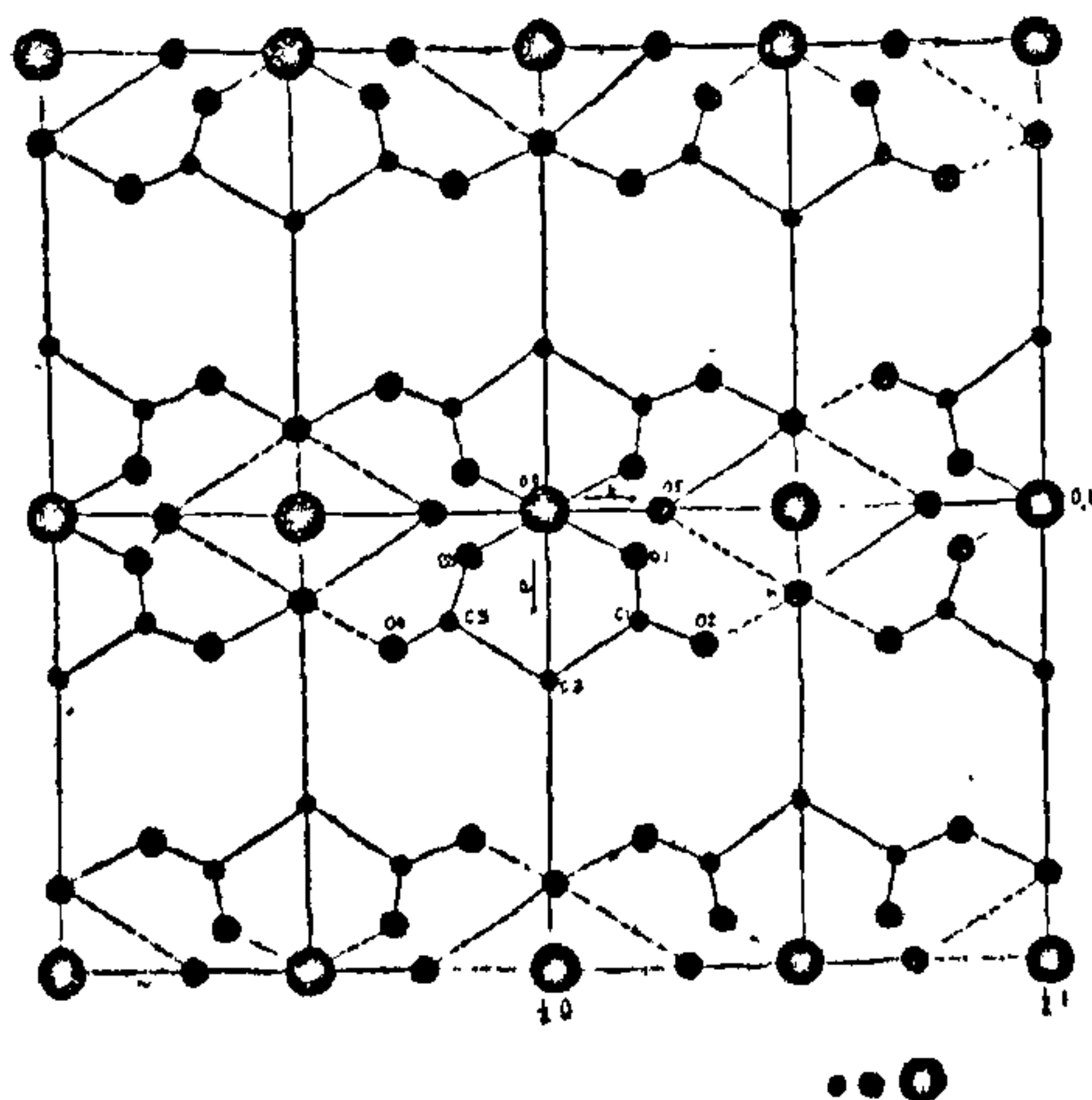


FIG. 1

two sets of zinc atoms occupying positions $(0, 0, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$. The water molecule W1 binds the

malonate anions through hydrogen bonds (shown by dashes and dots in Fig. 1) of 2.89 and 2.86 Å. The zinc atoms are six fold co-ordinated Zn-O distances ranging from 2.01 to 2.06 Å.

Considerable interest lies in establishing the exact chemical configuration of the species in the crystal lattice and work is currently in progress to refine the X-ray single crystal data by full-matrix least squares analysis.

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2-(N- α -METHYL, 2-HYDROXYBENZYLIDENE-IMINO) ETHANESULPHONIC ACID AS A GRAVIMETRIC REAGENT FOR COPPER(II)

No systematic study^{1,2} seems to have been made on the Schiff base 2-(N- α -methyl, 2-hydroxybenzylideneimino) ethanesulphonic acid (H_2NE) which forms solid metal complexes³ with a number of bivalent metal-ions including Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), $UO_2(II)$ and Pd(II). The copper(II) complex is insoluble in water, and can thus form the basis of a quantitative separation procedure.

H_2NE was synthesized by the procedure reported earlier⁴, m.p. $143^\circ C$. It gave satisfactory C, H, N and S analysis results. A 10% solution of this reagent in aqueous ethanol was prepared. Copper sulphate, 24.97 g, was dissolved in a litre of distilled water to give a copper(II) solution, which was standardized iodometrically.

Gravimetric Estimation of Copper(II)

The pH of an aliquot of the copper(II) solution was adjusted between 7.20-7.60 with sodium phosphate and phosphoric acid buffer. The reagent was added gradually with constant stirring till no further formation of the apple green precipitate took place. It was heated between $90-95^\circ C$ for ten minutes, cooled, filtered and washed with warm aqueous alcohol till it was free from the reagent and sulphate. It was dried at $100^\circ C$ and weighed. Analyses gave its formula as $[Cu(C_{10}H_{11}NSO_4)(H_2O)_3]$. The results

obtained from the above determinations are summarized in Table I.

TABLE I
Results of gravimetric estimation of copper(II)

Weight of complex mg	Copper, mg		
	Found	Calcd.	Error%
329.4	58.19	58.31	0.20
298.6	52.76	52.89	0.24
268.0	47.35	47.46	0.23
228.8	40.41	40.50	0.23
199.3	35.21	35.29	0.24

Effect of foreign ions.—Interfering ions like Fe^{3+} and V^{5+} were masked with help of sodium potassium tartarate and Ti^{4+} by potassium fluoride. Anions like SO_4^{2-} , PO_4^{3-} , Cl^- , F^- , NO_3^- and cations like Co^{2+} , Ni^{2+} did not interfere in the pH range 7.20–7.60.

Structure.—The molecular weight of the copper(II) complex in benzene was found by ebulliometry to be 358 ± 12.0 . Its magnetic moment was found 1.90 B.M. at 298°K . The elemental analysis and molecular weight data suggest 1:1 metal-ligand stoichiometry besides the presence of three water molecules. The electronic absorption spectra of the copper(II) complex in benzene gives one band with its peak located at $11,800 \text{ cm}^{-1}$ which is shifted slightly to $12,200 \text{ cm}^{-1}$ in pyridine and $12,500 \text{ cm}^{-1}$ in picoline. This peak may be assigned to the transition ${}^2E_g \rightarrow {}^2T_{2g}$, suggesting its octahedral structure. The i.r. spectra of H_2NE shows three intense bands at 3647 , 1650 and 1190 cm^{-1} which may be assigned to the presence of νOH , $\nu\text{C}=\text{N}$ and $\nu\text{SO}_3\text{H}$ respectively. In the copper(II) complex the bands at 3647 cm^{-1} and 1190 cm^{-1} have disappeared indicating the complexation of OH and SO_3H . In this spectra three new bands at 1610 , 650 and 615 cm^{-1} appeared which may be assigned to the presence of $\nu\text{C}=\text{N}$, $\nu\text{Cu}-\text{N}$ and $\text{Cu}-\text{O}$, respectively. A new band at 3370 cm^{-1} is also observed which may be due to the presence of νOH of the water molecules confirming its octahedral structure.

The authors are thankful to UGC, New Delhi, for the award of fellowship to one of them (PKK).

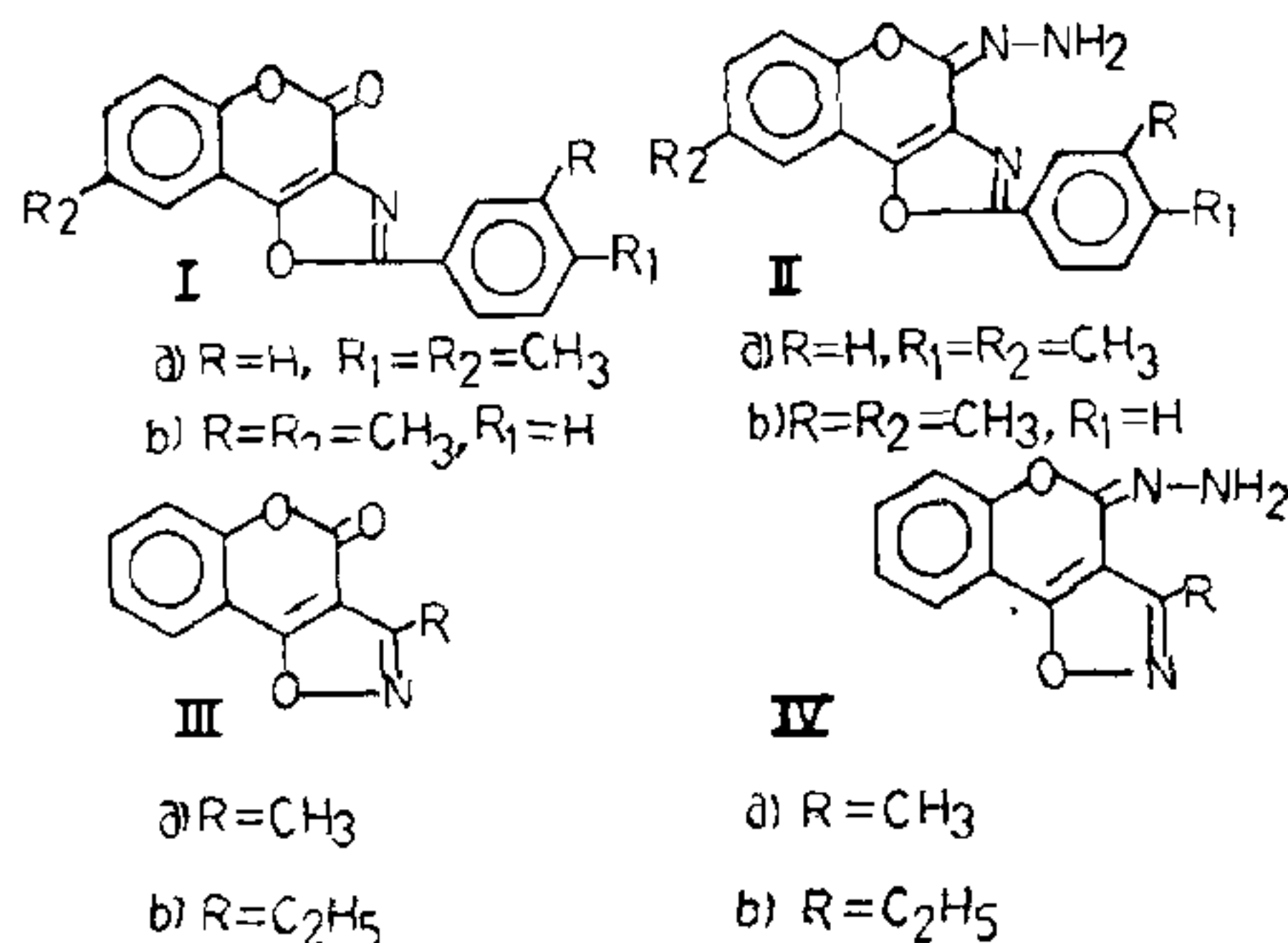
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1. Holm, R. H., Everette, Jr., G. W. and Chakravorty, A., *Prog. Inorg. Chem.*, 1966, 7, 83.
2. Syamal, A., *Coord. Chem. Rev.*, 1975, 16, 309.
3. Singhvi, B. R. and Mehta, R. K., *Indian J. Chem.* (In press).
4. Mehta, R. K. and Singhi, V. C., *Z. Naturforsch.*, 1971, 27 b, 304.

AN INTERESTING REACTION OF 4H-1-BENZOPYRANO (3, 4-d)-OXAZOL- AND ISO-OXAZOL-4-ONES

In a previous communication¹, we have reported the synthesis of 4H-1-benzopyrano(3, 4-d) oxazol-4-one derivatives. With a view to studying some of the reactions of these compounds such as the replacement of the heterocyclic oxygen by nitrogen, we investigated the reaction of (Ia) with hydrazine hydrate. It is pertinent to mention that Baddar *et al.*² have reported the replacement of heterocyclic O by N with Hydrazine hydrate in some α -pyrones to form 1-amino-2-pyridones.



The reaction was carried out by refluxing equimolecular quantities of the reactants, *e.g.*, (Ia) and hydrazine hydrate in alcohol solution for 5 hr. Dilution with water afforded a colourless crystalline compound (IIa), m.p. $147-49^\circ$. Its molecular weight (mass spectrum) was found to be 323 and the elemental analysis corresponded with the molecular formula $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}_3 \cdot \text{H}_2\text{O}$. It u.v. had $\lambda_{\text{max}}^{\text{MeOH}}$ 215 nm ($\log \epsilon 4.39$), 290 nm ($\log \epsilon 4.37$), 320 nm ($\log \epsilon 4.21$). In the i.r. spectrum the lactone band, which in the original compound appeared at 1765 cm^{-1} , was completely absent. Further, the spectrum showed a NH_2 band at 3400 cm^{-1} , whereas the $\text{C}=\text{N}$ band appeared at 1610 cm^{-1} . The n.m.r. spectrum (CDCl_3 , δ) of the compound