

The sign for ν_i is chosen positive or negative depending on the angle μ_i being acute or obtuse, respectively.

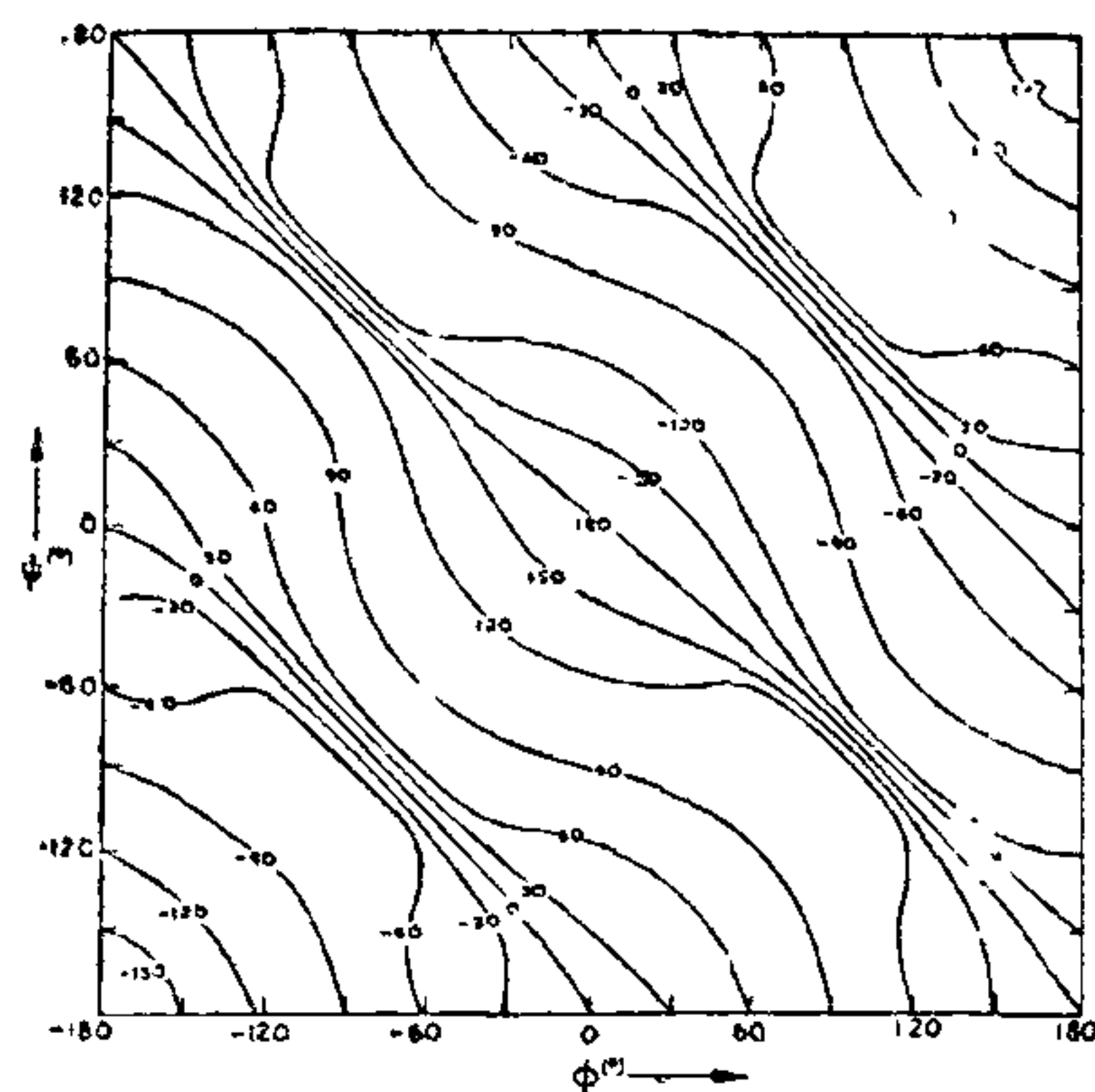


FIG 2

FIG. 2. Equi ν_i -contours (see text for definition) in the (ϕ, ψ) plane.

Physically it may be seen that the above method of assigning the sign is equivalent to projecting the point C^{α}_{i-1} and C^{α}_{i+1} on to the line of intersection of the two planes as given by the vector r_i , and comparing the projected vector of $\overrightarrow{C^{\alpha}_{i-1}-C^{\alpha}_{i+1}}$ with r_i . While

it might be possible to adopt for the above comparison any vector other than $\overrightarrow{C^{\alpha}_{i-1}-C^{\alpha}_{i+1}}$, we have chosen this here, since, as far as backbone atoms are concerned C^{α} atoms act as convenient reference points and also the progress of the chain is readily reckoned by tracing their path.

Figure 2 gives the equi- ν contours in the (ϕ, ψ) plane. The 'centrosymmetric' pattern of the contours is also readily understood. For example, the conformation $\phi = -120^\circ, \psi = -60^\circ$ and $\phi = +120^\circ, \psi = +60^\circ$ have ν values of -60° and $+60^\circ$ respectively.

A more detailed application of these ideas along the lines of our earlier analysis, including statistical distribution of the angle ν_i , is in progress and will be reported in due course.

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FIVE COORDINATE OXOVANADIUM(IV) COMPLEXES

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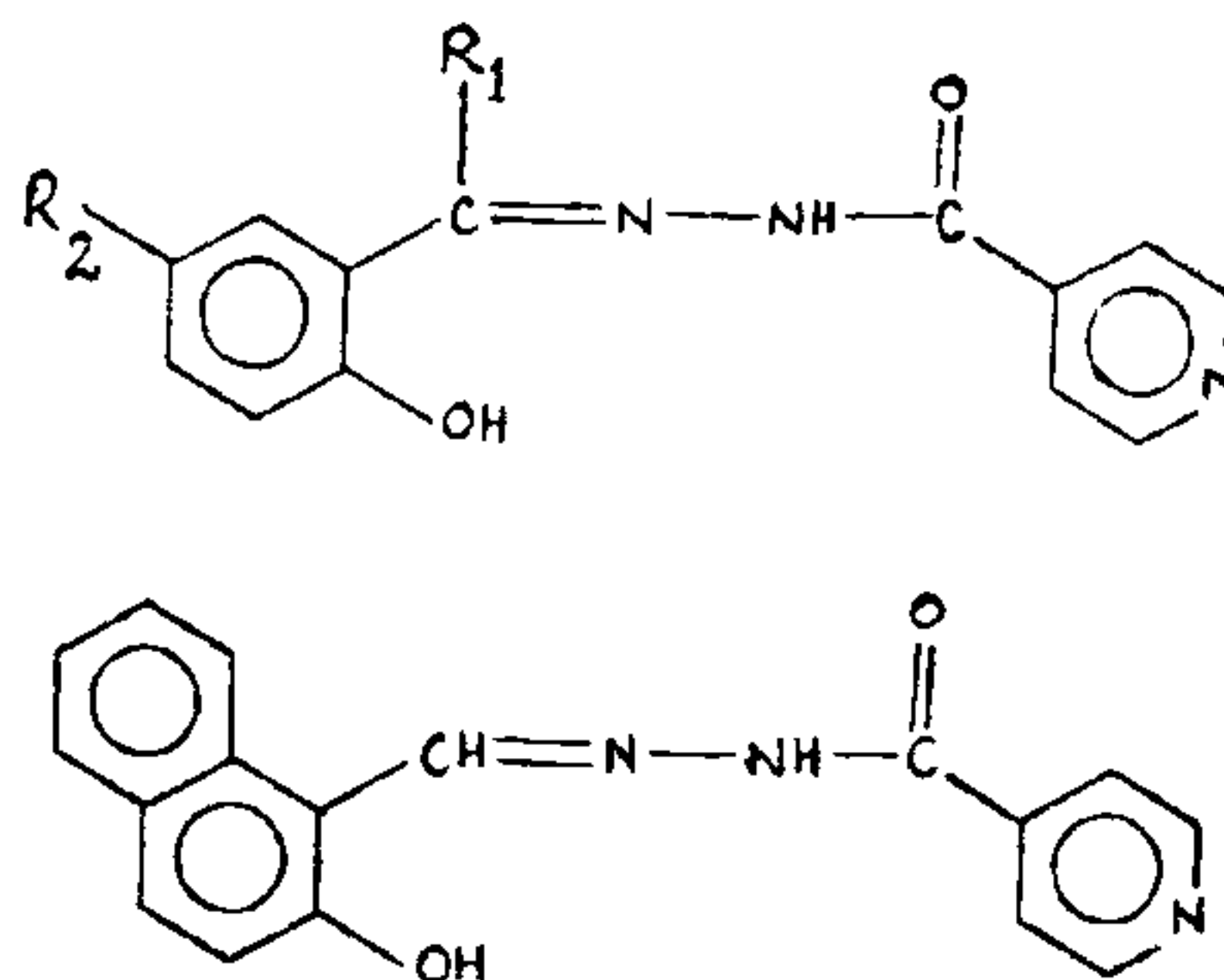
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INTRODUCTION

IT is well known that the hydrazone residue in the hydrazones can react with metal ion either in keto or in the enol form¹. Hydrazones derived from isonicotinoyl hydrazide have been used as chelating agents². Complexes of oxovanadium (IV) and oxovanadium (V) with benzimidazoles³ and Schiff bases⁴ have been studied. It is apparent from the literature that there are quite a few scattered examples of vanadium complexes with hydrazones⁵. It is therefore appropriate to study complex formation of oxovanadium (IV) with the following hydrazones.

EXPERIMENTAL

Vanadyl sulphate, isonicotinic acid hydrazide were of reagent grade. The substituted salicylaldehyde



	R ₁	R ₂		R ₁	R ₂
I	H	H	V	CH ₃	H
II	H	Cl	VI	CH ₃	Cl
III	H	CH ₃	VII	CH ₃	CH ₃

* For correspondence.

hydrazones and acetophenones were prepared by standard methods^{6,7}. Hydrazones were prepared by mixing equimolar mixture of hydrazide and aldehyde or ketone in the absolute ethanol. The solid products obtained were recrystallised from ethanol.

The complexes were prepared by mixing the alcoholic solution of vanadyl sulphate (0.1 mole) with alcoholic solution of ligand (0.2 mole). The mixture was heated on a water bath for an hour. The precipitated complex was filtered and washed successively with small portions of warm aqueous alcohol to remove the excess of the ligand. The complexes are then dried in a desiccator over phosphorus pentoxide.

Vanadium in the complexes was estimated as V_2O_5 by precipitating vanadium hydroxide and igniting it to pentoxide. Nitrogen was estimated by the microanalytical method.

The elemental analysis is shown in Table I.

Perkin-Elmer 337 spectrophotometer in the region 4000–650 cm^{-1} .

RESULTS AND DISCUSSION

The complexes are dark brown in colour and are amorphous in nature. These are sparingly soluble in DMSO, DMF and pyridine. However the satisfactory electronic spectra were not obtained with solution. Limited solubility of these complexes in common organic solvents did not permit the determination of molecular weights.

The results of elemental analysis shown in Table I agree well with 1:2 stoichiometry. Oxovanadium (IV) sulphate loses its sulphate ion during the course of reaction with hydrazones. The proton of the *o*-hydroxy group is replaced by vanadium. The solution of these complexes in DMF do not show measurable conductance, hence the complexes are non-electrolytes.

TABLE I

Ligand No.	Complex No.	Empirical formula	Metal %	Nitrogen %	Magnetic moment at 298° K μ_{eff} B.M.	Important IR frequencies (cm^{-1})
I	VIII	$\text{VO}(\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_3)_2$	9.61 (9.31)	15.86 (15.35)	1.68	1675, 1605, 1285, 895
II	IX	$\text{VO}(\text{C}_{13}\text{H}_9\text{O}_2\text{N}_3\text{Cl})_2$	8.21 (8.26)	13.32 (13.61)	1.70	1675, 1605, 1285, 890
III	X	$\text{VO}(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_3)_2$	8.68 (8.86)	14.00 (14.55)	1.82	1670, 1612, 1275, 980
IV	XI	$\text{VO}(\text{C}_{17}\text{H}_{12}\text{O}_2\text{N}_3)_2$	8.21 (7.88)	12.30 (12.99)	1.77	1670, 1612, 1325, 950
V	XII	$\text{VO}(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_3)_2$	8.90 (8.86)	14.20 (14.55)	1.79	1650, 1595, 1300, 960
VI	XIII	$\text{VO}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N}_3\text{Cl})_2$	8.02 (7.92)	12.82 (13.06)	1.84	1650, 1610, 1295, 960
VII	XIV	$\text{VO}(\text{C}_{18}\text{H}_{14}\text{O}_2\text{N}_3)_2$	8.38 (8.48)	13.80 (13.89)	1.80	1640, 1612, 1290, 960

Values in parentheses are calculated ones.

Physical Measurements.—The conductance measurements in DMF were done on Philips PR 9500 conductivity bridge (cell constant 0.829 cm^{-1}).

The magnetic susceptibilities of the complexes at room temperature were determined on a Gouy balance using mercury cobalt thiocyanate as calibrant.

The infrared spectra of the ligands and the complexes in nujol mull were recorded on a

Magnetic Properties.—The magnetic moments (Table I) corrected for the ligands determined for these complexes are in the range 1.68 to 1.84 B.M. This value is in close agreement with the values reported⁸ for oxovanadium (IV) containing one unpaired electron. It can be concluded that vanadium (IV) has not been oxidised to vanadium (V) state during the course of reaction.

Infrared Spectra.—The IR spectra are interpreted based on the previous assignments^{9,10,11}. In the

spectra of the ligands I-IV and V-VII medium intensity band observed in the region $3200\text{--}3170\text{ cm}^{-1}$ and $3130\text{--}3100\text{ cm}^{-1}$ respectively is assigned to NH stretching. The band observed in the region $2800\text{--}2700\text{ cm}^{-1}$ in ligands I-IV and $3480\text{--}3460\text{ cm}^{-1}$ in ligands V-VII is assigned to intramolecular hydrogen bonded OH. In the complexes the NH band is retained but OH band disappears, indicating the replacement of H of hydroxy group by metal.

The strong band around $1675\text{--}1650\text{ cm}^{-1}$ ($\nu\text{C}=\text{O}$) is present in ligands and is retained in the complexes. Three to four bands of medium to strong intensity are observed in the region $1625\text{--}1500\text{ cm}^{-1}$. These arise from various modes of vibration such as $\nu\text{C}=\text{N}$, $\nu\text{C}=\text{C}$, δOH , $\delta\text{N-H}$, etc., and their conclusive assignment is rather difficult. The band in the region $1625\text{--}1610\text{ cm}^{-1}$ is strong and shows a measurable shift to lower frequency by about $15\text{--}25\text{ cm}^{-1}$ in the complexes. Taking into consideration its intensity, the donor capacity of nitrogen and previous assignments¹⁻⁹⁻¹¹. This may reasonably be assigned to $\nu\text{C}=\text{N}$ and the shift may be due to the coordination of nitrogen to the metal. In the complexes IX, XI-XIV, the strong band observed around 960 cm^{-1} and in the complexes VIII and X the band around 890 cm^{-1} is assigned to $\nu\text{V}=\text{O}$ this probably suggests the monomeric nature of oxovanadium species^{12 13}.

On the basis of above observations it may be concluded that ligands have reacted in keto form and vanadium has coordination number five in the above complexes. Generally five coordinate oxovanadium (IV) complexes have square pyramidal structures.

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ANALYTICAL REACTIONS OF BARBITURIC ACIDS

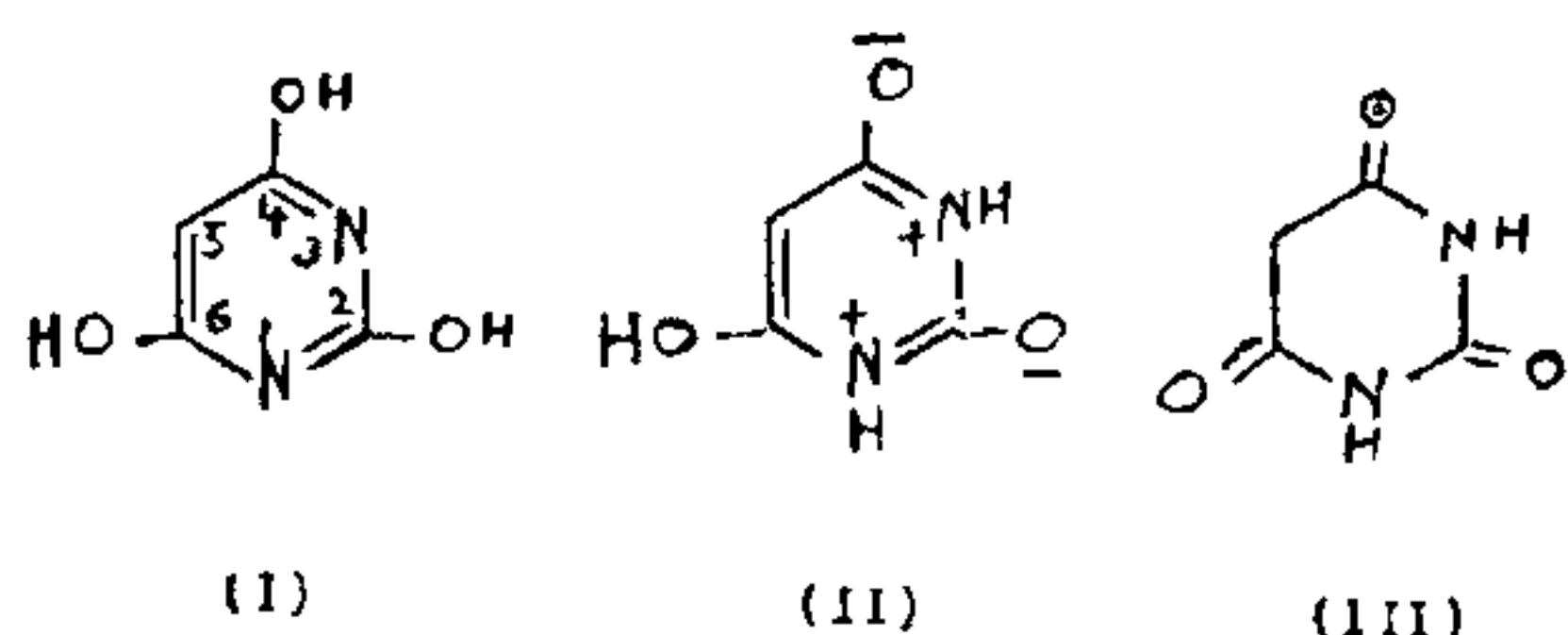
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ABSTRACT

Analytical reactions of barbituric acids used in their identification and also the role of the acids as analytical reagents have been reviewed.

THE name barbituric acid was given to the compound by Alfred von Baeyer who possibly discovered it on St. Barbara's day or wanted to honour his dear friend. It exists in the tautomeric forms, I-III, though the X-ray studies¹ of the solid favour the structure (III). Its preparation involves



the condensation of malonic acid with urea in the presence of POCl_3 . It melts at $248\text{--}252^\circ\text{C}$ (d).

Though the acid itself is not biologically active, substituents especially at 5-C atom make it so. Depressant activity of the compounds increases with heavier substituents. Also the compounds become rapidly more toxic when the molecular weights go beyond 250-300. The most commonly used barbiturates for medicinal purposes contain substituents with 6-10 C-atoms. In a recent article² (incidentally one of the authors is Barbara) the biochemical and physiological aspects of barbiturates have been summarized. It is now proposed to review the subject from analytical standpoint.

Barbituric, thiobarbituric, diphenylbarbituric and diphenylthiobarbituric acids have been used³⁻⁵ to quantitatively precipitate and estimate furfural. The method is superior to that using phloroglucinol. The