heated between 50–60°. Then it is treated with an excess of 1% solution of H_2PB in 10% ethanol till no further precipitation took place. It was heated on a water-bath for half an hour, filtered hot through a sintered glass crucible (porosity 4), washed with water-alcohol mixture (containing 1% EtOH) until free from the reagent, dried at 100–110° and weighed as Pd $(C_{12}H_8N_2O_2)$ (H_2O). The results obtained are given in Table I.

TABLE I

Results of gravimetric estimation of Palladium(II)

Weight of complex mg	Palladium, mg		
	Found	Calcd.	Error %
297·30	97·52	97·74	0·22
272·15	88·32	88·55	0·26
240·65	78·09	78·29	0·25
190·12	61·64	61·86	0·35
160·45	52·04	52·19	0·28

Effect of foreign ions: In order to assess possible analytical applications of the reagent, the effect of some ions which often accompanied palladium was studied. Alkali metal salts were used for the solutions of anions and nitrates, chlorides and sulphates for the solution of cations. For 0·1 gm of the Pd(II) solution, the tolerance limit is 10 mg for Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II), 5 mg for UO_9^{+2} and VO^{+2}, 100 mg for Pt(IV) and 2 mg for Rh(III).

Structure : The molecular weight of Pd(II)-complex in benzene was found by ebulliometry to be 327 ± 12. The elemental analysis and molecular weight data suggest 1 : 1 (metal-ligand) stoichiometry besides the presence of one water molecule. The magnetic susceptibility measurement indicates the complex to be diamagnetic. The electronic absorption spectra of the complex in benzene consist of three bands with their peaks at 22400, 26800 and 30500 cm^{-1} assignable respectively to the transitions $^1A_{1g} \rightarrow {}^1B_{1g}$; $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2u}$ which suggest its square-planar stereochemistry[5].

The i.r. spectra of H_2PB show bands at 3190, 2750, 1690 and 1600 cm^{-1} assignable to bonded νNH, νCOOH, νC=O and νC=N, respectively. In the spectra of the Pd(II)-complex, the bands at 3190 cm^{-1} and 2570 cm^{-1} have disappeared indicating the complexation through imine nitrogen and carboxylate oxygen, respectively. The appearance of three new bands, at 1590, 530 and 565 cm^{-1} can be assigned to the presence of νC=N, νPd–O and νPd–N, respectively. The band observed at 3400 cm^{-1} may be due to the presence of νOH of water molecule.

The very small value (1·5 ohm^{-1} cm^2 $mole^{-1}$) of molar conductance of 10^{-3} M solution of complex in dioxane indicates its non-electrolytic nature.

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COLORIMETRIC METHOD FOR ESTIMATION OF OXYMETAZOLINE HYDROCHLORIDE

THE application of acid-dye[1] method has been extended for colorimetric estimation of oxymetazoline hydrochloride. Bromo cresol green and bromo phenol blue have been applied as reagents. The pH for bromo cresol green is 3·4 and for bromo phenol blue is 2·5. For both reagents λ-maximum is 420 nm, colour stability is one hour. In the case of bromo phenol blue, Beer's law is obeyed between 4 to 16 μg/ml and in the case of bromo cresol green the Beer's law is obeyed between 3 to 15 μg/ml. The results obtained were compared with the N.F.[2] method.

The review article[1] on acid-dye method reveals that acid-dye method is not used for oxymetazoline hydrochloride. National Formulary (N.F.)[2] describes u.v. and non-aqueous titration methods. The Drugs Standards Laboratory, American Pharmaceutical Association[3] has reported qualitative and quantitative tests for oxymetazoline hydrochloride. The quantitative methods are same as N.F.[2]. In qualitative tests one lengthy colour reaction with sodium nitroprusside has been reported but it is not extended for assay procedure. The proposed acid-dye method is the *first colorimetric method for estimation of oxymetazoline hydrochloride.*

Experimental

Standard solution of oxymetazoline was prepared in water to give a concentration of 20 μg/mm. Similarly sample solution of nasal drop was diluted to give concentration of 20 μg/ml. Bromo cresol green and bromo phenol blue solutions were prepared by dissolving 40 mg of each to 100 ml distilled water.

TABLE I

Reagent	Product	Labelled amount of oxymetazoline hydrochloride (mg)	mg found		Recovery %
			Proposed method	N.F. method	
Bromo phenol blue	Nasal drop solution (10 ml)	5	5·05	5·1	99·6
Bromo cresol green	Nasal drop solution (10 ml)	5	5·12	5·1	100·2

Assay Procedure

A solution of bromo cresol green or bromo phenol blue (5 ml) was mixed with 5 ml buffer solution (pH 3·4 for bromo cresol green and pH 2·5 for bromo phenol blue) and 3 ml of standard solution. 10 ml of chloroform was added and mixture was shaken for one minute. Sample solution was treated in the same way. Phases were allowed to separate for 15 minutes. Chloroform phase was collected and the absorbance was measured at 420 nm against chloroform blank.

Results

A comparative data of results obtained by proposed as well as N.F.[2] method is reported in Table I.

Discussion

The described method is advantageous because this is the first colorimetric method for the estimation of oxymetazoline hydrochloride. The method can be applied to dilute solutions. Measurement of colour complex is much more convenient than the official titration method. The method is simple and less time consuming as compared to u.v. method. It was observed that bromo cresol green is more sensitive than bromo phenol blue in the estimation of oxymetazoline hydrochloride.

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LCAO-MO METHOD FOR THE EVALUATION OF SPECTRAL SHIFT DUE TO ELECTRON-REPELLING SUBSTITUENTS IN BENZOIC ACID

LCAO-MO method has been utilised for the evaluation of spectral shifts in *p*-band transition of benzoic acid by electron-repelling substituents such as methoxy, chloro and hydroxy groups. In all the cases except in 2-chloro benzoic acid a bathochromic shift is observed. The observed shifts are found to be in agreement with the experimental results.

Introduction

Of all the approximate M.O. theories, LCAO–MO method proved to be a satisfactory and simple device for calculating the spectral shifts observed in the ultraviolet spectrum when an electron repelling group is introduced in organic compounds. D. Peters[1] has successfully applied LCAO–MO theory in alternant hydrocarbons and calculated the effect of methyl-substitution on *p*-, *α*- and *β*-band transition of ultraviolet spectra. Chandra *et al.*[2–3] have calculated the spectral shift in methyl pyridines and phenol with the aid of this theory. A M.O. calculation of ultraviolet absorption spectra of 1 : 5 and 1 : 8 naphthyl pyridine was made by T. E. Peacock[4]. Due to non-availability of experimental data, the $\pi - \pi^*$ transition frequencies in case of organic compounds containing heteromolecules could not be calculated theoretically. In recent years with the help of high precision spectrometers various workers[5–8] have studied the ultra violet spectrum of large number of organic compounds thus making a wide scope for theoretical work. The present method deals with LCAO·MO method for calculating the spectral shift due to some electron-repelling substituents in benzoic acid.

Method

The directing power of substituents in an aromatic ring with regard to further substituent can be very well explained by inductive and hyperconjugative effects. When an electron-repelling substituent replaces a hydrogen atom in an aromatic ring the value of the coulomb integral changes. The net change in transition energy due to inductive effect is given by:

$$(\Delta E_{mn})_{\text{induc.}} = (C_{nr}^2 - C_{mr}^2)\,\delta\alpha_r$$

where C_{mr} and C_{nr} refer to the atomic orbital coefficient at the r-th carbon atom of the m-th highest filled and n-th lowest vacant molecular orbital respectively. $\delta\alpha_r$ is the change in coulomb integral and has