CHAPTER II

SYNTHESIS OF N-ARYLHYDROXAMIC ACIDS

RESUME

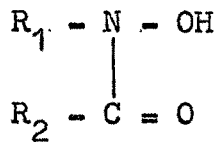
The synthesis and properties of five new N-arylhydroxamic acids is described. The preparations are made by reacting hydroxylamine with acid chloride at low temperature in diethyl ether containing aqueous suspensions of sodium bicarbonate.

These acids are characterized by elemental analysis, mp, ultraviolet, infrared, nmr and mass spectra.

These compounds were prepared under a broad project of our laboratory which dealt with several aspects of the chemistry of hydroxamic acids.

SYNTHESIS OF N-ARYLHYDROXAMIC ACIDS

In the present investigation the preparation and properties of new hydroxamic acids, represented by the general formula (I), have been described.



(I)

Where R_1 is phenyl or p - Cl - phenyl

R_2 is alkyl, aryl and substituted aryl etc.

The ultraviolet, infrared, nuclear magnetic resonance and mass spectra of the hydroxamic acids were determined primarily for their characterization. However, the salient features of these spectra have been briefly discussed.

METHOD OF SYNTHESIS - A REVIEW

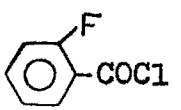
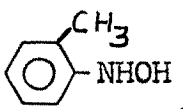
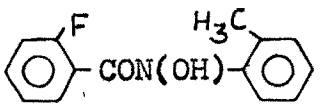
A tremendous progress in the chemistry of the synthesis and analytical applications of the hydroxamic acids has been made since five decades. The general methods of preparation of various types of hydroxamic

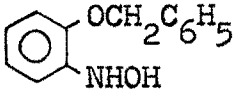
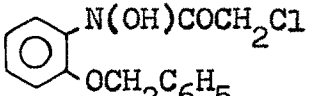
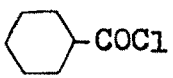
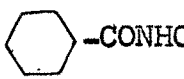
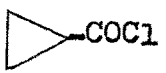
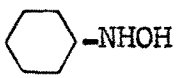
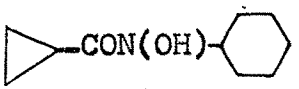
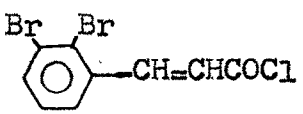
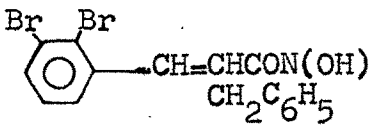
acids are summarised by Yale (1) in a well documented review article. The other useful reviews are those by Sandler and Karo, Henecka and Kurtz, Metzger, Mathis, Smith, Coutts and Katritky (2-8).

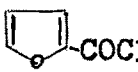
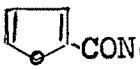
The synthesis of N-arylhydroxamic acid is generally based on Schotten-Bauman reaction (9). N-Phenylbenzohydroxamic acid (PBHA), the parent compound was first synthesised by Bamberger (10) by reacting the N-phenylhydroxylamine, dissolved in hot water, with benzoyl chloride. Shome (11) modified the reaction condition and carried out the acylation reaction at room temperature. Ryan and his co-workers (12,13) dispensed with the aqueous medium and used diethyl ether, rendered basic with pyridine as the reaction medium. Tandon and Bhattacharyya (14) carried out the benzoylation at low temperature (8C or lower) in diethyl ether medium. Hydrochloric acid liberated during the reaction was neutralized by pyridine. Baumgarten (15) recommended a 5% aqueous solution of sodium hydroxide in place of liquor ammonia for extraction of hydroxamic acid. A brief review on the method of synthesis as summarised in Table 1. Tandon and Bhattacharyya's method (14) was radically modified by Priyadarshini and Tandon (16) and Agrawal and Tandon (17-19). In the modified procedure both the N-arylhydroxy-

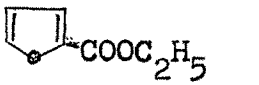
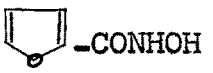
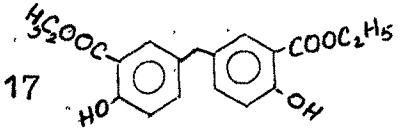
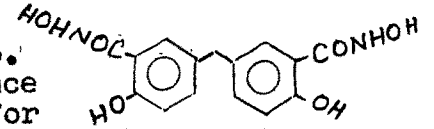
TABLE 1

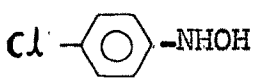
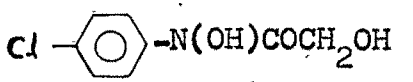
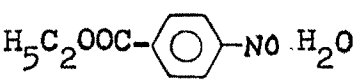
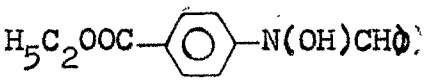
METHODS FOR SYNTHESIS OF HYDROXAMIC ACIDS

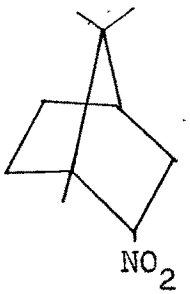
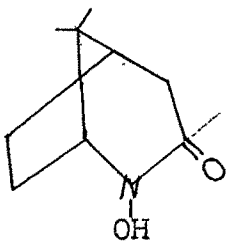
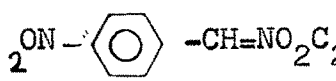
Sl. No.	Acylating Agent	Hydroxylamine Derivative	Solvent	Reaction Conditions	Product	Yield (%)	mp (°C)	Ref.
I	II	III	IV	V	VI	VII	VIII	IX
	Acid Chlorides							
1	C_6H_5COCl	C_6H_5NHOH	H_2O	Steam temp. in presence of $NaHCO_3$	$C_6H_5CON(OH)C_6H_5$	-	121	10
2	C_6H_5COCl	C_6H_5NHOH	H_2O	Room temp. in presence of $NaHCO_3$	$C_6H_5CON(OH)C_6H_5$	-	121	11
3	C_6H_5COCl	C_6H_5NHOH	Ether	Low temp. in presence of pyridine	$C_6H_5CON(OH)C_6H_5$	-	121	14
4	C_6H_5COCl	C_6H_5NHOH	"	0°C-5°C in presence of $NaHCO_3$	$C_6H_5CON(OH)C_6H_5$	-	121	16
5			"	Low temp. in presence of $NaHCO_3$		70	130	19

I	II	III	IV	V	VI	VII	VIII	IX
6	$ClCH_2COCl$		Ether	0°C-5°C in presence of $NaHCO_3$		-	99	20
7	$(C_4H_9)_3COCl$	NH_2OH	Pyridine	0°C	$(C_4H_9)_3CONHOH$	82	132	21
8	$(C_6H_5)_3COCl$	NH_2OH	Benzene	25°C	$(C_6H_5)_3CONHOH$	81	175	22
9		NH_2OH	Ether	-5°C in presence of $NaHCO_3$		61	134	23
10			"	-5°C in presence of $NaHCO_3$		33.5	105	23
11		$C_6H_5CH_2NHOH$	"	0°C in presence of $NaHCO_3$		48	165	24

I	II	III	IV	V	VI	VII	VIII	IX
12	CH_3CH_2COCl	$(Me_3Si)_2N\text{-}O\text{-}SiMe_3$	Hexane	Room temp. hydrolysis	$CH_3CH_2CONHOH$	90	91	25
13	Poly(acryloyl chloride) copolymer	C_6H_5NHOH	DMF	5°C for 14 days	N-acylhydroxamic acid resin	-	-	26
14	Chloroformyl XAD - 4	C_6H_5NHOH	Ether	Room temp. in presence of $NaHCO_3$ for 90 min.	N-hydroxy-N-phenyl carbamoyl-XAD-4	-	-	27
15	 -COCl	CH_3NHOH	Meth-anol	5°C in presence of Na_2CO_3 and nutralize with AcOH	 -$CON(OH)CH_3$	-	-	28

I	II	III	IV	V	VI	VII	VIII	IX
	Acid Esters							
16		NH_2OH	Methanol	Room temp.		80	119	29
17		NH_2OH	H_2O	Room temp. in presence of NaOH for one day		90	170	30
18	$(CH_3)_3CCOOCH_3$	NH_2OH	Methanol	In presence of KOH at room temp. for 48 hr.	$(CH_3)_3CCONHOH$	98	164	21
19	Poly N-methacrylo-succinimide	CH_3NHOH	DMF	Room temp. in presence of triethylamine	Poly N-methylmethacrylohydroxamic acid	-	-	31
20	$C_{11}H_{23}CH(OH)-[CH_2-CH(COOCH_3)]_m-H$	NH_2OH	Benzene	At 0°C in sodium methoxide (in methanol) for 1 hr. and 7 days at room temp.	$C_{11}H_{23}CH(OH)-[CH_2-CH(CONHOH)]_m-H$	-	-	32

I	II	III	IV	V	VI	VII	VIII	IX
21	Ethyl nicotinate	NH_2OH	Ethanol	Sodium ethoxide(in ethanol) room temp. for 12 hr.	Nicotinohydroxamic acid		185	33
	Carboxylic acids							
22	Oxalic acid	m-toluidine	-	An hydrous condition for 1 hr.at 120°C and hydrolyse	m-toluidinyloxamic acid	-	140	34
23	$HOCH_2COOH$		Ether	In presence of dicyclohexyl carbodimide		-	124	35
24	OHC-COOH		H_2O	At pH 6.0 and 40°C for 2 hr.		75	122	36
25	Asparagine monohydrate	NH_2OH	H_2O	At 100°C for 20 min and treated with AcOH	N-(β-Aspartyl) hydroxylamine	45	179	37

I	II	III	IV	V	VI	VII	VIII	IX
	Misclaneous							
26.	$(C_6H_5)_2POCl$	NH_2OSiMe_3	Methanol	In presence of triethyl-amine	$(C_6H_5)_2PONHOH$	-	-	38
27.		-	Ethanol	In presence of sodium ethoxide and hv at 240 nm for 4.5 hr.		76	212	39
28.	$C_8H_{17}NO_2$ (1-nitro octane)	-	CH_2Cl_2	0°-5°C in presence of SeO_2 in CH_2Cl_2 and triethylamine	N-octanohydroxamic acid	15	73	40
29.		-	H_2SO_4(31N)	Addition at 0°-5°C and kept at room temp. for 15 min.		98	176.5	41

lamine and acid chloride were taken in just equimolar proportions and were reacted at 0°C or below in diethyl ether. Solutions were made alkaline with aqueous suspension of sodium bicarbonate. It was found that under these conditions the product obtained contained negligible amount of diderivative and was readily purified by two to three crystallizations from suitable solvent.

E X P E R I M E N T A L

CHEMICALS

All the chemicals used were of G.R. and AnalaR grades of E. Merck and B.D.H., respectively, unless otherwise specified.

SOLVENTS

Ethyl Alcohol

The spectroscopic grade ethyl alcohol was prepared by twice distilling 95% ethyl alcohol over silver nitrate and potassium hydroxide (42).

Chloroform

The ethyl alcohol free chloroform was used. Ethyl alcohol was removed by washing the commercial chloroform five or six times with about half of its volume of water and distilling it after drying over fused calcium chloride.

APPARATUS

N.P.L. certified grade 'A' graduated apparatus (Gallenkamp Technico Brand) was used for measurements.

The ultraviolet and visible spectra were scanned on Beckman recording spectrophotometer and measurements at constant wavelength were performed on a C.Z. Jena, VSU2-P spectrophotometer with 10 mm matched silica cells.

The infrared spectra were recorded on Perkin Elimer Model-221 spectrophotometer in nujol or as KBr pellets.

The NMR spectra were recorded on a Varian T-60 spectrophotometer operating at 60 MHz for protons, in $CDCl_3$ with tetramethylsilane as internal standard.

The mass spectra were recorded on a AEI (UK) mass spectrophotometer Model No. MS 3074 at 70 eV.

HYDROXYLAMINES

N-Phenylhydroxylamine

This was freshly prepared by the reduction of nitrobenzene with zinc dust and ammonium chloride from aqueous solutions and recrystallized from benzene and petroleum ether mp 81°C (reported 81-82°C) (43) is obtained in 65% yield as white needles.

N-p-Chlorophenylhydroxylamine

This was prepared by the reduction of N-p-chloronitrobenzene from alcoholic media with zinc dust as described by Agrawal (44).

A mixture of 30 g of p-chloronitrobenzene, 60-ml of ethyl alcohol, 40 ml of water and 6 g of ammonium chloride was stirred mechanically and treated with 30 g of zinc dust in a small lot of 1-1.5 g during the course of 25-30 min. The reaction temperature was maintained between 60 and 65°C throughout, and stirring was continued for another 15 min. While hot, the zinc oxide was filtered and washed with 6 x 5 ml of hot ethyl alcohol. On addition of about 400 g of ice to the filtrate, a light yellow product was obtained which on crystallization from benzene and petroleum ether gave white falks in 80% yield, mp 90°C (reported 90°C) (45).

GENERAL PROCEDURE FOR THE SYNTHESIS OF N-ARYLHYDROXAMIC ACIDS

Freshly prepared and crystallized N-phenyl or N-p-chlorophenylhydroxylamine (0.1 M) is dissolved in 75 ml of diethyl ether and mixed with aqueous suspension of sodium bicarbonate (0.2-0.3 M). The mixture is stirred mechanically and cooled externally to bring the temperature to 0° ± 5°C. To this a solution of the acid chloride in 50 ml of diethyl ether is added dropwise during a course of about 30-40 min. The precipitated product is filtered at the pump and the ether layer separated and the solvent is removed under vacuum. Any solid product thus obtained is

combined with the bulk and titurated with saturated sodium bicarbonate solution to remove the acidic impurities. The solid product is filtered off, washed with water and dried. Further it is purified by crystallization with appropriate solvent.

PREPARATION OF N-p-CHLOROPHENYL-3,4,5-TRIMETHOXYCINNAMO-HYDROXAMIC ACID (PTCHA)

In a 500-ml conical flask fitted with a dropping funnel taken 5 g (0.035 M) freshly prepared and crystallized N-p-chlorophenyl hydroxylamine dissolved in 50 ml of pure benzene. An aqueous suspension of 5 g (0.058 M) sodium bicarbonate in 30 ml of water is added and stirred with a magnetic stirrer. After the mixture was externally cooled to 0° ± 5°C, 7.5 g (0.03 M) of 3,4,5-trimethoxy-cinnamoyl chloride in 20 ml of pure benzene was added through the dropping funnel over a period of 30 min and the stirring was continued for another 15 min. Almost the entire amount of hydroxamic acid formed was precipitated as a yellowish granular solid. The solid is filtered off, washed with water and the etherial layer is discarded. The vacuum dried product is recrystallized from pure benzene or ethyl acetate twice to yield a pale yellow compound having a mp 169°C (yield 75%).

The other hydroxamic acids reported here are prepared by coupling the respective acid chloride and hydroxylamine in ether medium and the products were crystallized from benzene or a mixture of benzene and petroleum ether; as per the general procedure described above. Since compounds IV and V are highly soluble in ether the etherial layer has been evaporated in vacuum and the solid residue was mixed with the bulk obtained by filteration.

RESULTS AND DISCUSSION

PREPARATION

The method adopted here for the preparation of hydroxamic acid is very simple and of general applicability. It gives better yield. It may be stated that the use of stoichiometric proportion of N-arylhydroxylamine and the acid chloride was most satisfactory. The excess of acid chloride results in increasing amount of diderivative. Similarly, an excess of hydroxylamine leads to a product which is impure, probably due to decomposition of the hydroxylamine (14-19) or due to well known acid catalysed rearrangement of N-arylhydroxylamine and its decomposition to the complex product (15). The hydroxamic acids are listed in Table 2.

PROPERTIES

The properties of the synthesised hydroxamic acids are given in Table 2. The salient features are briefly discussed below.

Colour and crystallinity

All the synthesised hydroxamic acids are white in colour except N-p-chlorophenyl-3,4,5-trimethoxycinnamo-hydroxamic acid which is light yellow in colour. All these acids are crystalline compound.

TABLE 2

PREPARATION AND PROPERTIES OF N-ARYLHYDROXAMIC ACIDS

Compd. No.	Hydroxamic acid	Molecular formula	Molecular weight	mp (°C)	Yield (%)	Colour	Elemental Analysis (%) C	H	N
I	N-p-Chlorophenyl-3,4,5-trimethoxy-cinnamo-	$C_{18}H_{18}NO_5Cl$	363.80	169	75	Pale yellow	59.21 (59.43)	4.91 (4.99)	3.89 (3.85)
II	N-p-Chlorophenyl-p-butoxybenzo-	$C_{17}H_{18}NO_3Cl$	319.80	164	70	White	63.80 (63.85)	5.70 (5.67)	4.40 (4.38)
III	N-Phenyl-p-butoxybenzo-	$C_{17}H_{19}NO_3$	285.34	136	75	White	71.51 (71.56)	6.70 (6.71)	4.86 (4.91)
IV	N-p-Chlorophenyl-p-chlorophenoxy-isobutyro-	$C_{16}H_{15}NO_3Cl_2$	340.21	144	50	White	56.51 (56.49)	4.40 (4.44)	4.15 (4.12)
V	N-Phenyl-p-chlorophenoxy-isobutyro-	$C_{16}H_{16}NO_3Cl$	305.76	125	50	White	62.80 (62.85)	5.30 (5.27)	4.50 (4.58)

The theoretical values are given in parenthesis

Solubility

These hydroxamic acids are readily soluble in dioxan, chloroform, carbon tetrachloride, benzene, alcohol, dimethyl formamide etc. but very sparingly soluble in water.

Stability

The hydroxamic acids are stable to heat, light and air. The author stored these acids in stoppered ambur bottles for two years.

ULTRAVIOLET SPECTRA

The characteristics of the ultraviolet spectra of the newly synthesised hydroxamic acids, in spectroanalysed 95% ethanol are given in Table 3. The representative spectra of the hydroxamic acids synthesised are shown in Fig. 1.

All the hydroxamic acids studied here possess the benzene and carbonyl chromophore in their molecule. These are having two distinct bands, around 208-240 nm and 254-326 nm (Fig. 1). These two bands are assigned as the primary and secondary, bands of the benzene (46,47). The well assessible spectra of benzene gives distinct absorption bands arise from the $\pi - \pi^*$ transitions.

TABLE 3

UV SPECTRAL CHARACTERISTICS OF HYDROXAMIC ACIDS IN ETHANOL

Comp. No.	Hydroxamic acid	λ max (nm)	E ($\times 10^4$)	$\frac{\lambda_{II}}{\lambda_{I}}$
I	N-p-Chlorophenyl-3,4,5-trimethoxycinnamo-	326 (240)	3.1	1.3
II	N-p-Chlorophenyl-p-butoxybenzo-	280 (215)	2.9	1.3
III	N-Phenyl-p-butoxybenzo-	274 (208)	2.1	1.3
IV	N-p-Chlorophenyl-p-chlorophenoxy-isobutyro-	262 (228)	1.2	1.1
V	N-Phenyl-p-chlorophenoxyisobutyro-	254 (225)	0.7	1.1

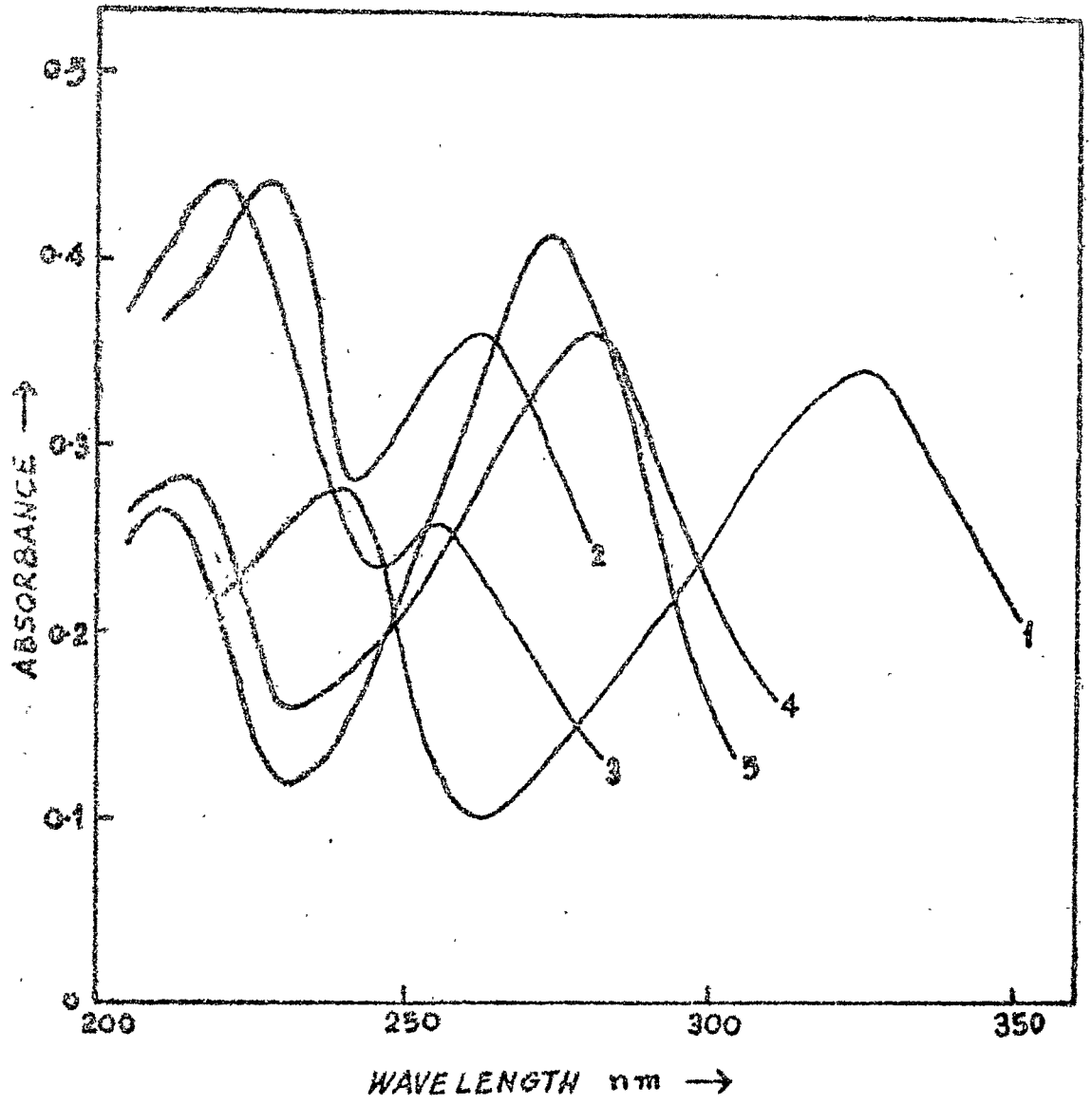


Fig. 1. Ultraviolet spectra of :
1. N-p-Chlorophenyl-3,4,5-trimethoxycinnamohydroxamic acid
2. N-p-Chlorophenyl-p-butoxybenzohydroxamic acid
3. N-Phenyl-p-butoxybenzohydroxamic acid
4. N-p-Chlorophenyl-p-chlorophenoxyisobutyrohydroxamic acid
5. N-Phenyl-p-chlorophenoxyisobutyrohydroxamic acid.

These bands are designated as bands I, II and III (46,48).

	Band I nm	Band II nm	Band III nm
Benzene	183(50,000)	204(~8000)	230(300)

These bands are designated as primary and secondary or as bands I, II and III (46-48). The absorption band due to carbonyl group, originates from the weak $n - \pi^*$ transition is presumed to be eclipsed in the strong secondary band of the benzene; as evident from the spectra (Table 3, Fig. 1).

It is infered from the spectral data that the changes in the substitution in the molecule, usually produces the change in the position and intensity of the absorption bands, but there is no evidence of new bands. The correlation of the spectral data of the hydroxamic acids and the characterization of their absorption bands are possible from the position, magnitude and intensity of the bands.

The ultraviolet spectra of the hydroxamic acids can be very well correlated with that of the substituted amides and anilides due to their structural similarity.

The secondary band of benzene is observed at 243 nm in the absorption spectra of acetanilide but in benzanilide the band has been shifted to 267 nm. The same pattern is observed in the hydroxamic acids also. The secondary band of the hydroxamic acids derived from aliphatic carboxylic acids is around 250 nm, but N-phenylbenzo-hydroxamic acid (PBHA), the band is observed at 268. Substitution of the benzene ring displaces the primary and secondary bands.

In compound I, the primary and secondary bands of benzenes are obtained at 240 nm and 326 nm, respectively. The bathochromic shift in the absorption band with respect to the other compounds, can be explained by the presence of the conjugation in the molecule. The increase in length of conjugation (R-C = C-C = O, R = phenyl) by the two alternate multiple bonds, have shown pronounced increase in the absorption spectrum, both in wavelength and intensity. In this case the $\pi - \pi^*$ and $n - \pi^*$ transition provides the absorption bands, which is supported by the presence of methoxy groups in the C-phenyl ring.

Examining the absorption spectrum of compounds II and III, a noticeable shift in the wavelength and intensity of the band is seen which can be due the presence of a

bulky alkoxy group in the C-phenyl ring. This change can be detectable if we examine the ultraviolet spectrum of N-phenylbenzohydroxamic acid (PBHA) (268 nm).

In compounds IV and V, though the primary band is prominent like the other compounds, a conspicous diminish in the wavelength and magnitude of the secondary absorption band of the benzene of the molecule is noted unlike the other compounds. This shadowing of the secondary band can be explained on the basis of the breaking of conjugation in the molecule (R-$\overset{|}{C}$-C = O instead of R-C = O) by the introduction of a tertiary carbon atom between the carbonyl chromophore and the phenyl ring.

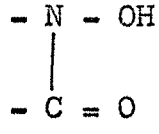
Comparing the absorption bands of the examined hydroxamic acids, it can be infered that the secondary band of the benzene is mainly contributed by the C-phenyl ring rather than the N-phenyl ring.

Doub and Vandenbelt (49) has correlated the spectra of substituted benzenes and the bands are discriminated by their position, magnitude of intensity and ratio of wavelength of bands λ II/ λ I. The ratio of λ II/ λ I in hydroxamic acids is around 1.1 (Table 3) in agreement with reported earlier (50).

INFRARED SPECTRA

The frequencies of absorption bands of the newly synthesised N-arylhydroxamic acids examined here are listed in Table 4. Absorption spectra of a few representative acids are given in Figs. 2-3. No attempt has been made to do a complete analysis of the spectra, only those bands which are associated with the hydroxamic acid functional group (II) and those are prominently displayed have been assigned.

Of the principal bands associated with the hydroxamic acid functional group (II) are due to the (O-H)



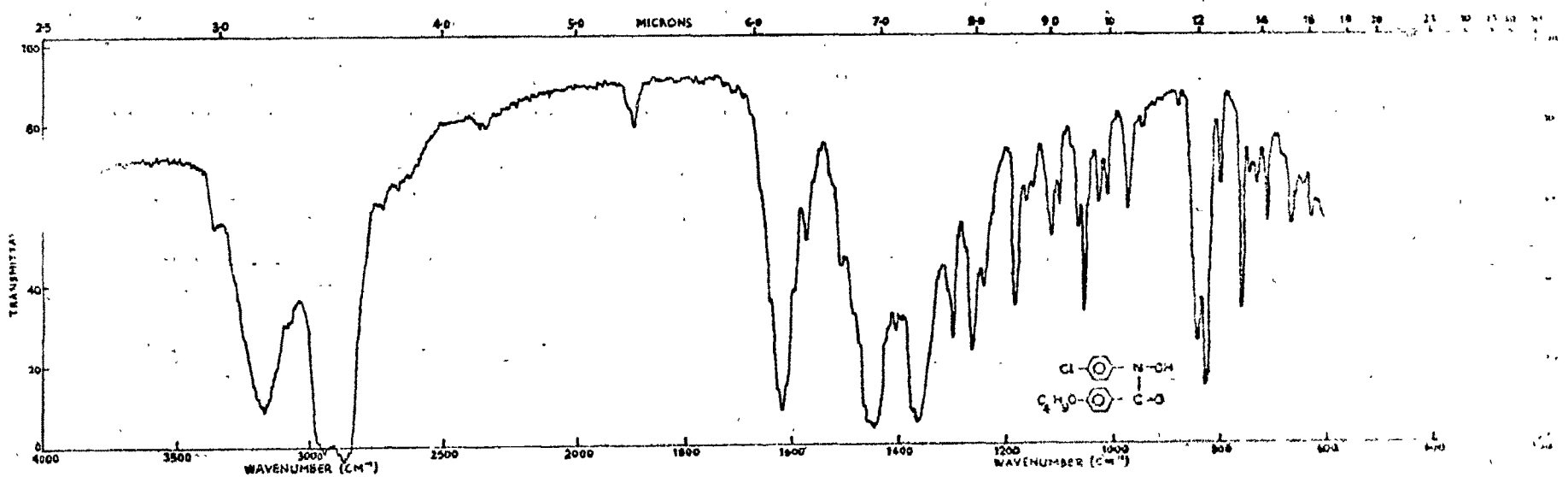
(II)

and (C=O) stretching vibrations and these can be assigned unambiuously. The (N-O), (C-N) and (C-Cl) stretching vibrations are assigned with less confirmity because of the overlapping with several other modes of vibrations and also the non-availability of systematic data on the assignment of the bands in infrared spectra of these hydroxamic acids.

TABLE 4

INFRARED ABSORPTION CHARACTERISTICS OF N-ARYLHYDROXAMIC ACIDS

Compd. No.	Hydroxamic acid	ir Frequency, (cm^{-1})				
		ν_{O-H}	$\nu_{C=O}$	ν_{N-O}	ν_{C-N}	ν_{C-Cl}
I	N-p-Chlorophenyl-3,4,5-trimethoxycinnamo-	3120	1630	970	1375	720
II	N-p-Chlorophenyl-p-butoxybenzo-	3170	1618	965	1365	720
III	N-Phenyl-p-butoxybenzo-	3180	1620	965	1365	-
IV	N-p-Chlorophenyl-p-chlorophenoxyisobutyro-	3240	1620	955	1380	720
V	N-Phenyl-p-chlorophenoxyisobutyro-	3250	1620	950	1380	730



Infrared spectra of

Fig. 2 N-p-Chlorophenyl-p-butoxybenzohydroxamic acid

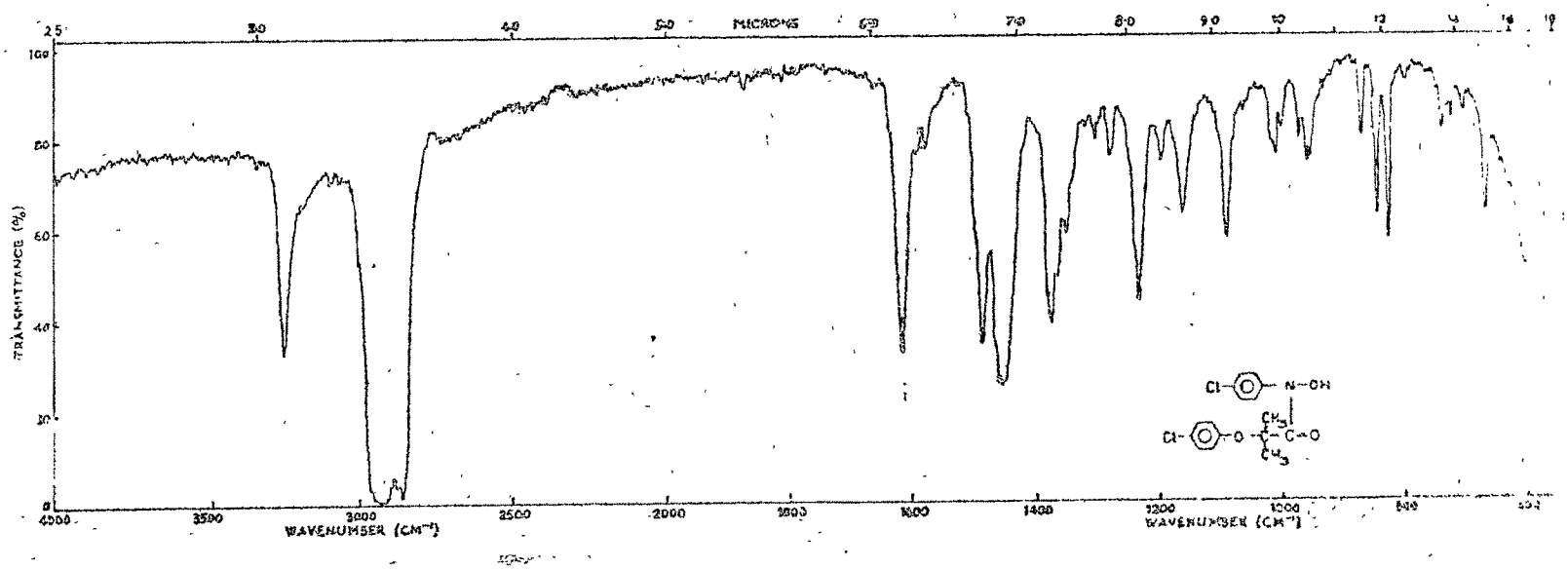


Fig. 3 Infrared spectra of N-Phenyl-p-chlorophenoxyisobutyrohydroxamic acid

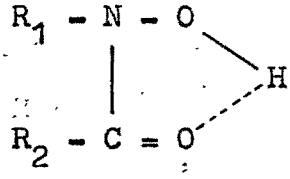
(O-H) Stretching Vibrations

In the N-arylhydroxamic acids examined here the absorption band due to (O-H) stretching vibrations has been assigned in the region 3250-3120 cm^{-1} (Table 4). The shifting of band to the lower frequency compared to the free (O-H) stretching vibration (arround 3600 cm^{-1}) is due to the presence of strong intramolecular hydrogen bonding (51-55). Since in hydroxamic acids the acidic hydrogen of the (O-H) group is in close proximity of the polar carbonyl oxygen (C=O), the possibility of hydrogen bonding is high. Most of the shift in the (O-H) stretching vibration can be due to the change in the ability of the hydroxyl hydrogen to form the hydrogen bond. In compounds II-V, the observed change in the (O-H) stretching frequency (10 cm^{-1}) is due to the presence of the chlorine atom in the N-phenyl ring, which make the hydroxyl group more acidic.

It can be observed that a linear relation is available with the (O-H) stretching frequency and the pK_a of the examined hydroxamic acids. There is a noticeable increase in the vibrational frequency of the (O-H) group with the increase in the ionization constant of the compound. This can be explained on the presumption that, as the acidity of the molecule

increases, the hydrogen bond strengthens and consequently the vibrational energy decreases.

So it can be concluded that the (O-H) stretching frequency is affected mainly by the substitution in the N-phenyl ring and the strength of the intramolecular hydrogen bonding where both are complimentry to each other.



(III)

(C=O Stretching Vibrations)

The (C=O) stretching vibrations are assigned with reference to the spectra of amides and anilides. In unsubstituted amides the band appears between 1690-1650 cm^{-1} and in anilides it comes at 1700 cm^{-1} (56,57). In unsubstituted hydroxamic acids, the band is assigned between 1670-1660 cm^{-1} (5,58-60). The molecular structure of the compound, found to shift the (C=O) stretching vibrations.

Since the carbonyl groups in the synthesised hydroxamic acids are conjugated with the other electron systems, a general lowering in carbonyl group stretching

frequency is observed. In the case of compound I (Table 4), the increase in the frequency of carbonyl stretching band is probably due to the partial loss of (C=O) bond character resulting from the delocalization of the π - electrons over the entire unsaturated area in the molecule. Since the electronegativity of the carbonyl oxygen decreases, compared to the other compounds, the hydrogen bond weakens; hence the stretching vibration of the (C=O) group shifts to a high wavenumber (61,62). Examination of the (C=O) stretching bands of all the hydroxamic acids studied here, it can be concluded that the strong intramolecular hydrogen bonding may dominate in suppressing the effect due to the change in substitution in the carbonyl moiety. The (C=O) stretching bands appear between 1618 and 1630 cm^{-1}.

(N-O) Stretching Vibrations

In N-arylhydroxylamines this band appears around 915 cm^{-1} (61). In aromatic hydroxamic acids such as PBHA it appears at 900 cm^{-1} (5,63). In several oximes this band appears around 950 cm^{-1} (64,65). It therefore, appears reasonable to look for this band in the region around 950 cm^{-1}. In substituted hydroxamic acids this band shifts to higher frequency. In PTCHA the (N-O)

band appears at 970 cm^{-1} and in all other compounds the bands were observed between 970 and 950 cm^{-1}.

(C-N) Stretching Vibrations

The fundamental stretching vibration due to (C-N) exist mainly in 1360-1310 cm^{-1} region (51-53). In the hydroxamic acids studied here, the (C-N) stretching vibration are assigned arround 1380-1365 cm^{-1}. The bands appears at higher frequency than the corresponding amines may be because the force constant of (C-N) bond is increased by the resonance with the carbonyl group.

(C-Cl) Stretching Vibrations

The (C-Cl) stretching vibrations for the compound containing chlorine atom attached directly to benzene ring had been assigned between 750 and 700 cm^{-1} (51-53). Two separate (C-Cl) bands are observed in the spectrum of the hydroxamic acid reported here; one at 720 cm^{-1} corresponds to the N-phenyl chlorine atom (compound I, II & IV) and another band at 730 cm^{-1} arise from the (C-Cl) of the phenoxy ring (compound II & IV).

NMR AND MASS SPECTRA

The nmr and mass spectra of the five newly synthesised hydroxamic acids have been discussed here. The PMR spectra were recorded in the range of 0-10δ with off set = in $CDCl_3$ containing TMS as an internal reference. Chemical shifts are expressed in δ- scale. The mass spectra were recorded are given in Tables 5-9.

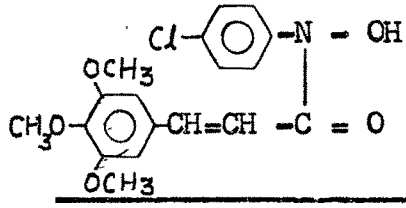
The PMR spectra of the compounds I-V show the signals at 10.8, 10.7, 10.9, 10.5 and 10.5δ, respectively, which disappear on deuteterium exchange and correspond to one proton due to the (O-H) group.

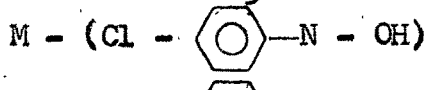
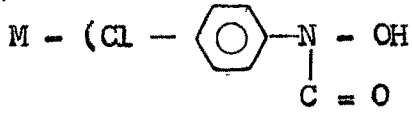
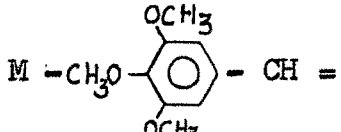
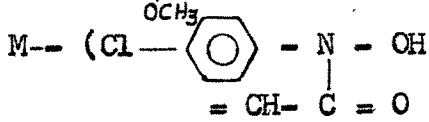
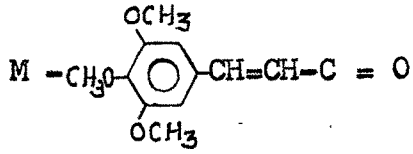
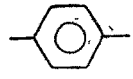
The PMR spectrum of N-p-chlorophenyl 3,4,5-trimethoxycinnamohydroxamic acid (I) is having the chemical shifts at 3.9, 6.7, 7.4δ. The shift at 3.98$\delta$is illdefined doublet for (9 H) and is due to the three methoxy groups ($-OCH_3$), The doublet at 6.7δ is integrating for (2 H) which are originated from the -CH = CH- moiety. A doublet shown at 7.4 δ is accounting for (6 H) arised from the aromatic protons.

The spectrum of N-p-chlorophenyl-p-butoxybenzo-hydroxamic acid (II) showed the signals at 1.0, 1.8, 3.9, 7.2 δ. A triplet observed at 1.0δ is due to (3 H) of the

TABLE 5

MASS SPECTRAL DATA OF COMPOUND I

Structural formula	Molecular formula	Molecular weight
	$C_{18}H_{18}NO_5Cl$	363.8

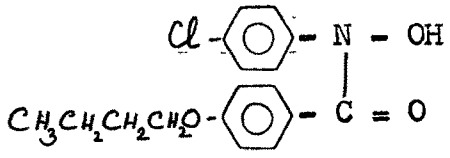
m/z	Relative abundance (%)	Assignment
365	1	M + 2
363	3	M^+
347	16	M - (O)
238	28	M - ($3OCH_3$ + 2O)
221*	1000	
193	30	
183	7	
180	14	
142	20	
76	30	Presence of 

* base peak

TABLE 6

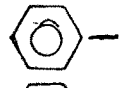
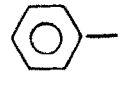
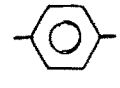
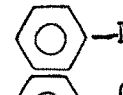
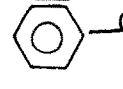
MASS SPECTRAL DATA OF COMPOUND II

Structural formula



Molecular formula $C_{17}H_{18}NO_3Cl$

Molecular weight 319.8

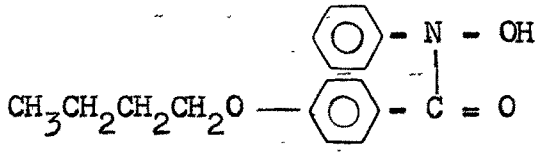
m/z	Relative abundance	Assignment
321	0.5	M + 2
319	1.5	M^+
304	18	M - (CH_3)
303	60	M - (O)
246	7	M - (C_4H_9O)
218	14	M - $(C_4H_9O + O)$
177*	100	M - (Cl -  - N - OH)
149	15	M - (Cl -  - N - OH, C = O)
142	12	M - (C_4H_9O -  - C = O)
76	12	Presence of 
57	20	M - (Cl -  - N - OH, -O -  - C = O)

* base peak

TABLE 7

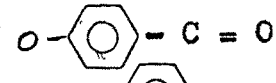
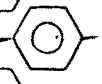
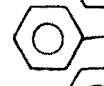
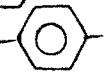
MASS SPECTRAL DATA OF COMPOUND III

Structural formula



Molecular formula $C_{17}H_{19}NO_3$

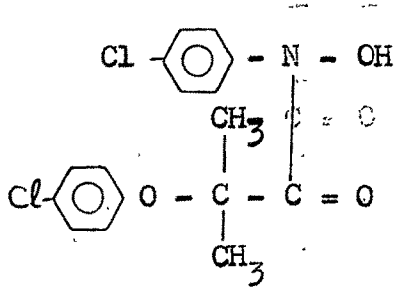
Molecular weight 285.3

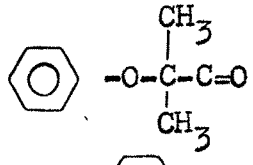
m/z	Relative abundance (%)	Assignment
285	3	M^+
270	20	M - CH_3
269	40	M - O
212	5	M - (C_4H_9O)
196	2	M - $(C_4H_9O + O)$
177*	100	M - ()
120	12	Presence of 
92	30	Presence of 
77	20	Presence of 
76	24	Presence of 
57	35	Presence of C_4H_9

* base peak

TABLE 8

MASS SPECTRAL DATA OF COMPOUND IV

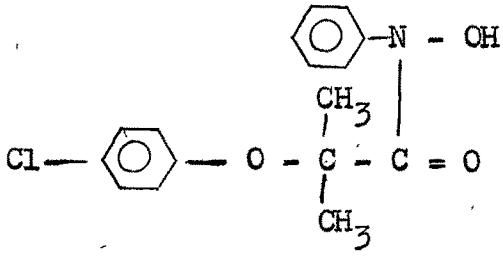
Structural formula	Molecular formula	Molecular weight
	$C_{16}H_{15}NO_3Cl$	340.2

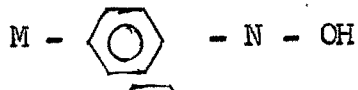
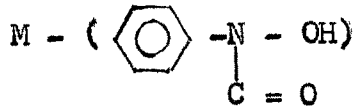
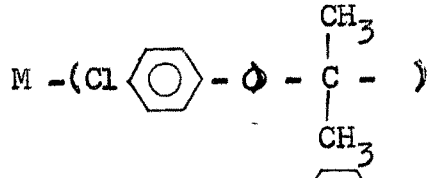
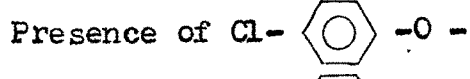
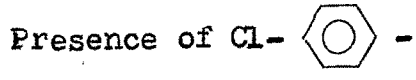
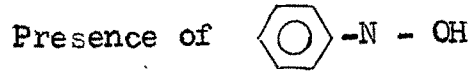
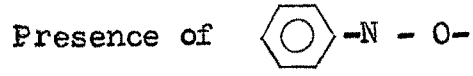
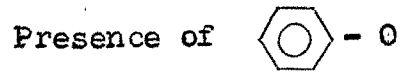
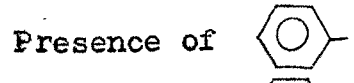
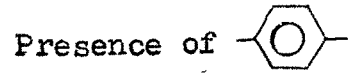
m/z	Relative abundance	Assignment
343	7.5	M + 4
341	48	M + 2
339	75	M^+
323	12	M - O
196	10	M - (Cl -  -N - OH)
169**	100	M - (Cl -  -N - OH, C = O)
142	25	M - Cl - 
141	27	Presence of Cl-  -N-O
134	18	Presence of Cl-  -N-
127	35	Presence of Cl-  -O-
111	60	Presence of Cl- 
76	32	Presence of

** base peak

TABLE 9

MASS SPECTRAL DATA OF COMPOUND V

Structural formula	Molecular formula	Molecular weight
	$C_{16}H_{16}NO_3Cl$	305.7

m/z	Relative abundance	Assignment
307	21	M + 2
305	60	M^+
289	32	(M - O)
196	11	
169**	100	
136	23	
127	14	
111	28	
105	24	
104	21	
92	37	
77	26	
76	17	

** base peak

methyl group ($-CH_3$). A broad multiplet at 1.8δ has been attributed by the (4 H) methylene protons ($-CH_2-CH_2-$) of butoxy group. The triplet observed at 3.9δ is of (2 H), can be assigned to the protons of the $-OCH_2-$ of the butoxy group. The 8 protons of aromatic ring exhibits a multiplet at 7.2δ, which also indicate the para disubstitution in the benzene nuclear.

The PMR spectrum of N-phenyl-p-butoxybenzohydroxamic acid (III) showed the signals at 0.5, 1.1, 3.4, 6.3-7.4δ. A triplet for the 3 H showed at 0.5δ which is arrising from methyl group ($-CH_3$). A multiplet at 1.1δ observed for the (4 H) of the methylene protons while another triplet at 3.4δ attributed by the $-OCH_2-$ moiety. A multiplet between 6.3 and 7.4δ is due to the (9 H) which are originated from the aromatic ring.

The PMR spectrum of N-p-chlorophenyl-p-chlorophenoxy-isobutyrohydroxamic acid (IV) showed the signals at 1.6 and 7.4δ. The signal at 1.6δ is a sharp singlet for (6 H) resonated from the methyl protons. The protons of aromatic region showed an agreeable substitution pattern. The multiplet centred at 7.4δ corresponds to 8 H of the aromatic rings.

The spectrum of N-phenyl-p-chlorophenoxyisobutyro-hydroxamic acid (V) exhibited in sharp singlet for the two methyl groups protons at 1.6δ . The multiplet observed arround 7.4δ is due to (9 H) originated from the two benzene nuclei.

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