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SOLID ELECTRONIC ABSORPTION, VIBRATIONAL AND FROTON MAGNETIC RESONANCE SPECTRA OF ARYLIDENE DERIVATIVES OF OXALIC AND SUCCINIC HYDRAZIDES

By

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SOLID ELECTRONIC ABSORBTION, VIBRATIONAL AND RROTON MAGNETIC RESONANCE SPECTRA OF ARYLIDENE DERIVATIVES OF OXALIC AND SUCCINIC HYDRAZIDES

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ABSTRACT

The electronic absorption spectra of some arylidene oxalic and arylidene succinic hydrazides are studied in organic solvents of different polarities. The absorption bands are assigned to electronic transitions, vibrations and band shift with changed solvent and substituent and discussed. The main bands in the ir spectra due to the carbohydrazone part are assigned and discussed in relation to substituent effect. The signals in the ^{1}Hnmr spectra of some compounds are considered and explained in relative to molecular structures.

INTRODUCTION

Hydrazides of organic acids, their arylidene derivatives and metal chelates drew the attention of many workers in the last decades. The interest in such studies arise from the antituberculous compounds[1-3] based on their tendency to form stable metal chelates [4,5] and to exhibit as well antimalerial activities[6]. It was also reported that metal chelates of hydrazides and their derivatives display fungicidal effects[7].

Based on the importance of metal chelates of hydrazides several studies have been aimed out in this connection[8-12] which contain, however, much conflicting knowledge due to the various structures prepared, for chelates of a given metal ion with the some ligand, by different authors. Thus, despite the importance of such metal chelates a final conclusion concerning their structure have not been given.

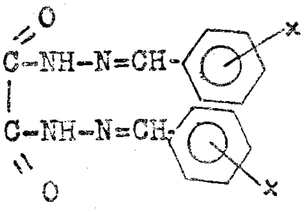
A clear understanding of the chelating properties of organic ligands readily achieved using spectroscopic methods, mainly ir, mnr, electronic and esr methods. Based on this, it is important to have knowledge about the spectral behaviour of the ligands in order to achieve correct informations about the structure of the metal chelates.

Although many studies delt with the ir spectra of hydrazides of organic acids and their derivatives [13-16] yet few studies delt with their electronic spectra [17,18] and acid base properties [19,20]. Also, these studies delt with hydrazides of monocarboxylic acid.

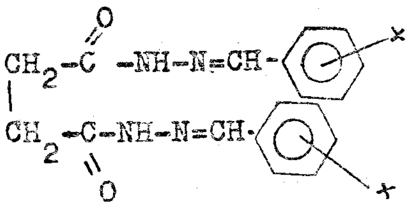
The present investigation is devoted to study the electronic, ir and ^{1}Hnmr spectra of oxalic hydrazide, succinic hydrazide and some of their arylidene derivatives which would be of good help in studying their metal chelates by spectroscopic methods.

EXPERIMENTAL

The compounds used were pure laboratory BDH products. Oxalic and succinic hydrazides were prepared by a method similar to that of Slnve for hydrazides of monocarboxylic acid. The methods involves the reflux of the diester (one mole) with two moles of hydrazine hydrate (96 %). The arylidene derivatives were obtained by condensation of the hydrazides with benzaldehyde or its derivatives in the usual way used for hydrazones[21]. The compounds prepared were purified by repeated crystallisation from ethanol. The purity of the compounds was checked by elemental analysis. The compounds used in the present investigation have the general structural formulae:



(I)



(II)

in which x=p-OH(a), p–OCH$_3$(b), p–CH$_3$(c), m–CH$_3$(d), o-OH(e), H(f), p–Br(g), p–Cl(h), m–Cl(i), o–NO$_2$(j), m–NO$_2$(k) and p–NO$_2$(l).

The solvents used were BDH spectroscopic grade, the deutrated solvents were obtained from Alderich.

The electronic absorption spectra were recorded within the wavelength range 200–450 nm on the Unicam SP-8000 n.v. specrtophotometer using 1.0 cm matched silica cells. The ir spectra were obtained in the solid state as KBr discs using the SP-1000 infrared specrtophotometer. The ^{1}Hnmr spectra were obtained by the aid of the Varian T60 nmr spectrometer in D^6 DMSO or $CDCl_3$ using dimethylsilane as internal standard.

RESULTS AND DISCUSSION

A) Electronic Absorption Spectra (Table I)

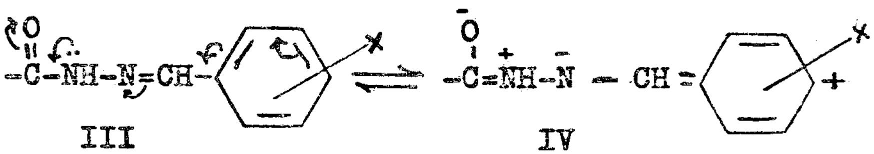
The electronic absorption spectra of the compounds under investigation are recorded in organic solvents of varying polarities. The results obtained were found to depend on the nature of the solvent used and as well on molecular structure.

The spectra of the hydrazides display one broad band at 270–290 nm which corresponds to an overlap of the absorption due to the π-π^* of the C=O groups and the intramolesular charge transfer interaction[18]. The spectra of the arylidenes in ethanol or cyclohexane display 3–4 bands depending on the molecular structure (Table I).

Table 1. Electronic Absorption Spectral bands (nm) of Some Arylidene Derivatives of Oxalic and Succinic Hydrazides.

Compound	Arylidene Oxalic Hydrazides							Arrylidene Succinic Hydrazides						
	Ethanol				Cyelohexane			Ethanol				Cyclohexane		
	A	B	C	D	A	B	C	A	B	C	D	A	B	Z
a	220	255	287	325	220	260	275	225	270	290	300	220	248	270
b	212	—	288–298	337	222	255	283	225	—	278–287	320	220	252	273
c	218	—	—	310	225	273	280	222	250	282	300	220	255	270
d	230	255	280	325	225	257	283	220	260	280	295	220	220	278
e	223	—	—	312	222	255	280	225	252	283	303	220	250	273
f	218	255	—	305	222	260	283	215	—	283	295	220	260	280
g	230	245	—	310	220	267	277	220	247	287	307	220	248	272
h	220	—	—	310	220	267	277	225	—	287	302	222	250	275
i	218	—	288	312	220	265	282	223	248	287	295	225	250	273
j	218	255	290	325	220	255	295	220	225	285	337	220	255	275
k	220	225	292	330	220	255	277	220	248	275	305	220	250	285
l	225	250	295	325	220	262	285	230	260	—	320	220	252	277

The first band within the 215–230 nm region can be assigned to the the π–π^* transition of the phenyl group (^1L_a–^1A state) while the second one at 245–295 nm results from an overlap of the π–π^* transition of the C=O groups and the low energy π–π^* transition of the phenyl group (^1L_b–^1A state). The composite nature of the band is gathered from its splitting by changes of the electronic nature of the substituent or the solvent polarity. The third band at 300–320 nm is assigned to intramolecular charge transfer involving the location of an n-electron from the α-hydrogen atom to the antibonding π-level on the C=O group. This interaction is enhanced by charge migration from the phenyl group influenced by the substituent on it. Such interaction is represented as follows:



III IV

Besides these common bands, the spectra, of j, k and 1 display a new band with high extinction at 300–340 nm which corresponds to the $\alpha \rightarrow NO_2$ interaction. The spectra of compounds I_e and II_e display a new band with λ_{max} at 320–340 nm due to the π–π^* transition within the chelate ring formed through the intramolecular hydrogen bonding.

The spectra obtained in solvents of different polarities show that only the CT band displays obvious solvent shifts. The other bands are slightly influenced. For compounds I_e and II_e the band due to the transition within the hydrogen bond chelate ring shows some variations in its position with changed solvent polarity. This reflects changes in the strength of the intramolecular hydrogen bond in the different solvents. In this case the position of the hydrogen bond will be distributed between the azomethine nitrogen and solvent molecules. The magnitude of shift will depend on the ability of the solvent to accept the proton from the solute molecule alternatively its basicity. As the basicity of the solvent molecule increases, the strength of the intramolecular hydrogen bond decreases and the band is shifted to high energies[22] i.e. is blue shifted. The energy of the band was in the order >4.06—4.46 eV which is in accordance with increased solvent basicity.

To test the effect of solvent polarity on the CT band, the Gati and Sralay[23] equation was applied in the form:

$$\Delta\upsilon = (a-b)\,\frac{(n^2-1)}{(2n^2+1)} + b\,\frac{(D-1)}{(D+1)}$$

in which a — b are constants, n and D are the refrective index and dielectric constants of the solvent used.

The plot of $\Delta\upsilon$ as a function of the factor $\left(\frac{D-1}{D+1}\right)$ does not give a proper linear relation. Also the application of the dielectric constant functions given by Suppan[24] $f(D) \frac{2D-1}{2D+1}$, and $(D) = \frac{D-1}{D+2}$ gave nonlinear relation for the plots of λ_{max} as a function of $f(D)$ or $\varnothing(D)$. This behaviour denotes that the dielectric constant of the medium is not the main factor governing solvent shift and the solute-solvent interaction through hydrogen bonding and solvation of solute molecules in the ground and excited states contribute to some extent to the energy of electronic excititation. However, the plots of λ_{max} as a function of the Z or ET[25] solvent values are not good linear relations indicating that the solvent shift should be considered as combined effects of the dielectrinc constant and solvation changes.

As a general trend, the bands due to the $\pi-\pi^*$ transition of the aromatic rings display small shifts with changed electronic nature of the substituent X. The CT band on the other hand is shifted to red as the donor character of the substituent X increases or its acceptor property decreases. This behaviour promotes to investigate the applicability of the Hammett equation to the system under investigation. The plot of λ_{max} as a function of the σ-Hammett is a more or less linear relation with a negative slope (Fig. 1) denoting that the Hammett linear free energy relationships hold for the intramolecular CT interaction in the form

$$\lambda X = \lambda H + \rho\sigma X$$

A similar behaviour is observed on using the plot $\sigma^* \varnothing_x$ values instead of σ_x. Then, it seems plausible to accept that the charge migration from the arylidene ring to the amide linkage would influence both the ground and excited states of the molecule.

B) The ir spectra (Table II).

The bands in the ir spectra of the compounds under investigation are assigned applying a method similar to that of Looker[26] and considering the bands for substituted benzene reported by Katritzky[27]. The bands due to the carbohydrazone part are depicted in Table II. From these results it is obvious that the position of the various bands are influenced by the position and electronic nature of the substituent x.

Table 2. Band Assignment of ir spectra for C-NH-N=CH part of some Arylidene Oxalic and Succinic Hydrazides.

Comp.	Arylidene of oxalic Hydrazide						Arylidene of Succinic Hydrazide					
	ν_{NH}	$\nu_{C=O}$	$\nu_{C=N}$	ν_{NH}	ν_{C-N}	ν_{N-N}	ν_{NH}	$\nu_{C=O}$	$\nu_{C=N}$	ν_{NH}	ν_{C-N}	ν_{N-N}
a	3260	1660	1630^{sh}	1540	1240	1165	3280	1665^{sh}	1620	1525^{sh}	1265	1175
b	3260	1660	1625^{sh}	1515	1240^{sh}	1165^{sh}	3210	1663	1618	1514^{sh}	1265	1180
c	3260	1660	1630^{sh}	1535	1235	1163	3240	1665	1620	1525	1263^{sh}	1175
d	3250	2662	1635^{sh}	1520	1235	1162	3230	1668	1625	1530^{sh}	1263	1170
e	3280	1670	1620^{sh}	1540	1246^{sh}	1155	3230	1675	1615	1540^{sh}	1250	1180
f	3250	1665	1635^{sh}	1525	1230^{sh}	1160	3200	1670	1625	1530	1260	1170
g	3240	1668	1640	1530	1230	1185^{sh}	3200	1670	1635^{sh}	1540	1255	1165
l	3240	1670	1645^{sh}	1530	1230	1155^{sh}	3190	1675	1630^{sh}	1545	1255	1165
i	3240	1670	1645^{sh}	1525	1225	1130	3230	1668	1625	1530^{sh}	1263	1170
j	3180	1670	1650^{sh}	1550^{b}	1235^{sh}	1155	3190	1683	1645	1550	1250	1160
k	3210	1675	1650^{sh}	1555	1225	1150	3190	1677	1640	1540	1250	1165
l	3220	1675	1650^{sh}	1548^{b}	1220^{sh}	1150	3220	1672	1640	1530	1235	1160

The bands due to the C=O (Amide I at 1680–1660 cm^{-1}) C=N (at 1650–1620 cm^{-1}) and σNH (Amide II at 1555–1515 cm^{-1}) are shifted to lower wave numbers with increased donor properties of the substituent x while the C=N (at 1260–1225 cm^{-1}) and N–N (at 1180–1150 cm^{-1}) display a counter shift. This reveals that the polarising influence of the substituent on the carbohydrazone part of the molecule leads to a decrease in the band order of the C=O and C=N linkages, while these of the N–N and C–N bands is increased which is in accordance with the formulation given above.

The plot of the wave number for the C=O, C=N, N–N and C–N bands as a function of the σ_x-Hammett constant is a more or less linear relationships (Fig. 2) indicating the validity of the Hammett relations in the form

$$\gamma_X = \gamma_H + \rho\sigma_x$$

The linearity is also gathered from the resonably high values of the correlation coefficient (r) as given in Table II. Similar results are obtained on using $\sigma^* \varnothing_x$ values instead of σ_x supporting the opinion that the intramolecular charge transfer with the amide linkage is affected by the arylidene ring with the substituent as one unite.

The CH_2-bands in the spectra of arylidene succinic hydrazides are also influenced but to smaller magnitude and not in a very regular manner with changed subtitution on the arylidene ring which indicates that the polarising influence of the substituent on the O=O group would influence the adjacent CH_2 groups. This leads to the premise that charge transfer interaction in the arylidene derivatives of organic acid hydrazides would involve the whole molecule. This conclusion is similar to that obtained in case of arylidene derivatives of monocarboxylic aromatic acids[18,20].

c) The ^{1}Hnmr Spectra (Table III):

Table 3. Hnmr spectra of some Arylidene oxaiic and Succinic Hydrazides.

Compounds	CH:	Aromatic	CH=	-NH	—OH
Benzylidene oxalic hydrazine	—	7.3 –7.6	8.5	11.92–12.2	—
Salicylidene oxalic hydrazine	—	6.8 –7.3	8.6	10.85	12.4^b
Benzylidene succinic hydrazide	2.9	7.3 –7.6	8.9	11.14–11.33	—
Salicylidene succniic hydrazine	3.2	6.83–7.35	8.26	10.97–11.1	9.93 11.47

sp = splitting, b=broad

The ^{1}Hnmr spectra of oxalic hydrazide display two sets of signals; a singlet with integration equivalent to two protons at 9.7 ppm due to the NH group and a doublet intigration equivalent to four protons at 4.7–4.3 ppm corresponding to the -NH_2 groups. The spectra of succinic hydrazide shows the NH_2 signals at more or less the same position while the NH signal is shifted to higher fields (8.9 ppm). This is due to the decreased deshielding effect of the C=O groups on the NH linkage in virtue of the donating character of the methyl group.

The ^{1}Hnmr spectra of the arylidene derivatives are deprived of the signals due to the NH_2 protons. They display a singlet at 8.9–8.5 ppm. (equivalent to two protons) due to the -N=CH- protons. The NH signal is shifted down fields to the range 12.2–10.85 ppm. This shift can be explained by the increased contribution of the polar form IV to the total structure. The protons of the aromatic rings lead to the group of signals at 7.6–6.8 ppm; the signals shift down field with increased acceptor properties of the substituent x. The spectra of the salicylidene derivatives display the OH signal at 12.4–11.1 ppm being shifted down fields in the spectrum of salicylidene oxalic hydrazide.

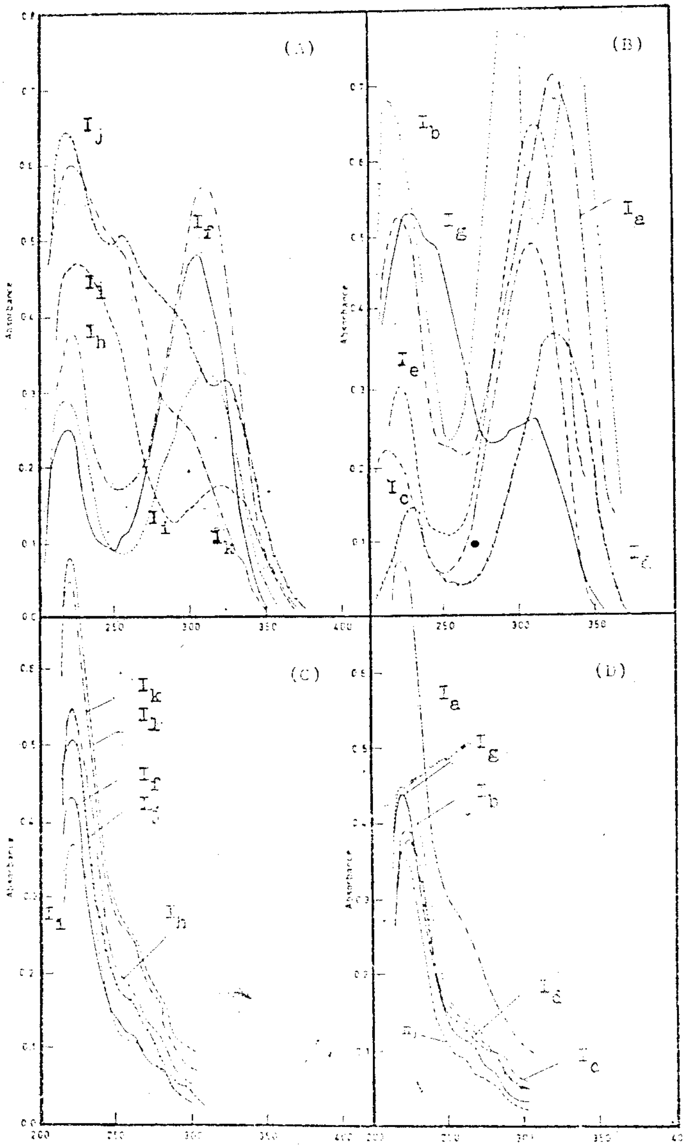


Fig. 1. Electronic Absorption Spectra of Some Aryildene Derivatives of Oxallc Hydrazide in Organic Solvents
A — B — Ethanol, C — D — Cyclohexane

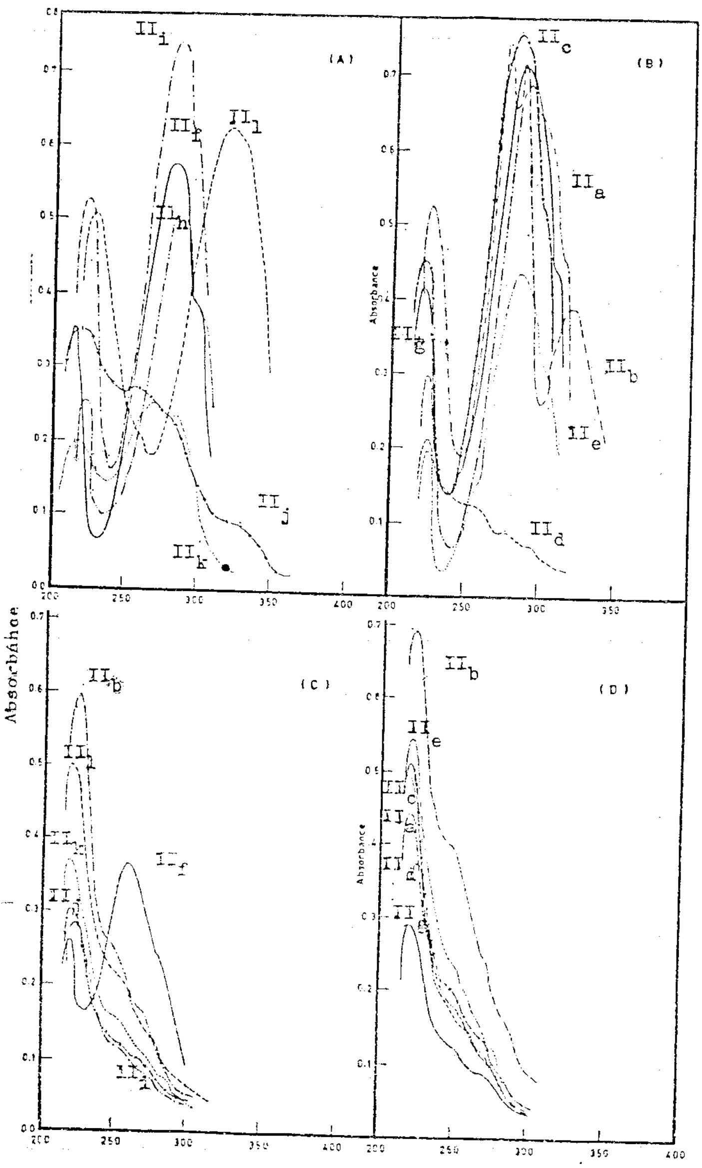


Fig. 2. Electronic Absorption Spectra of Some Aryildene Derivatives Of Succinic Hydrazide in Organic Solvents
A — B — Ethanol, C — D — Cyclohexane

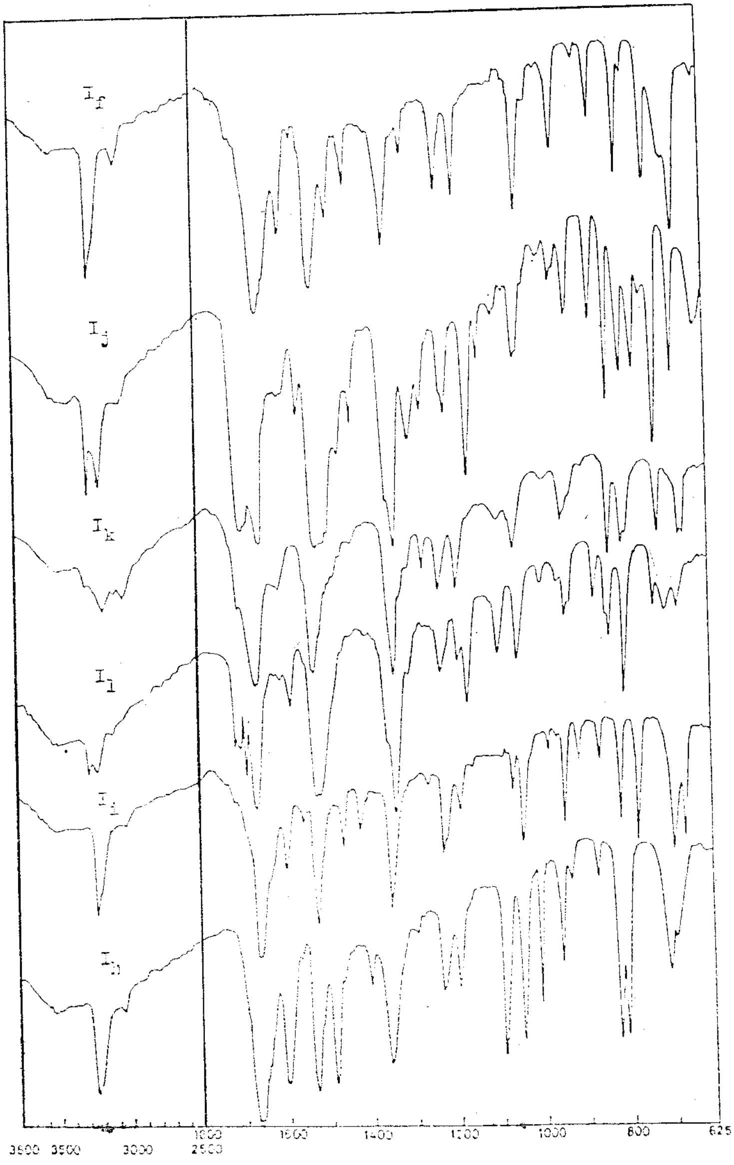


Fig. 4A. Infrared absorption spectra of some arylidene derivatives of oxalic hydrazide.

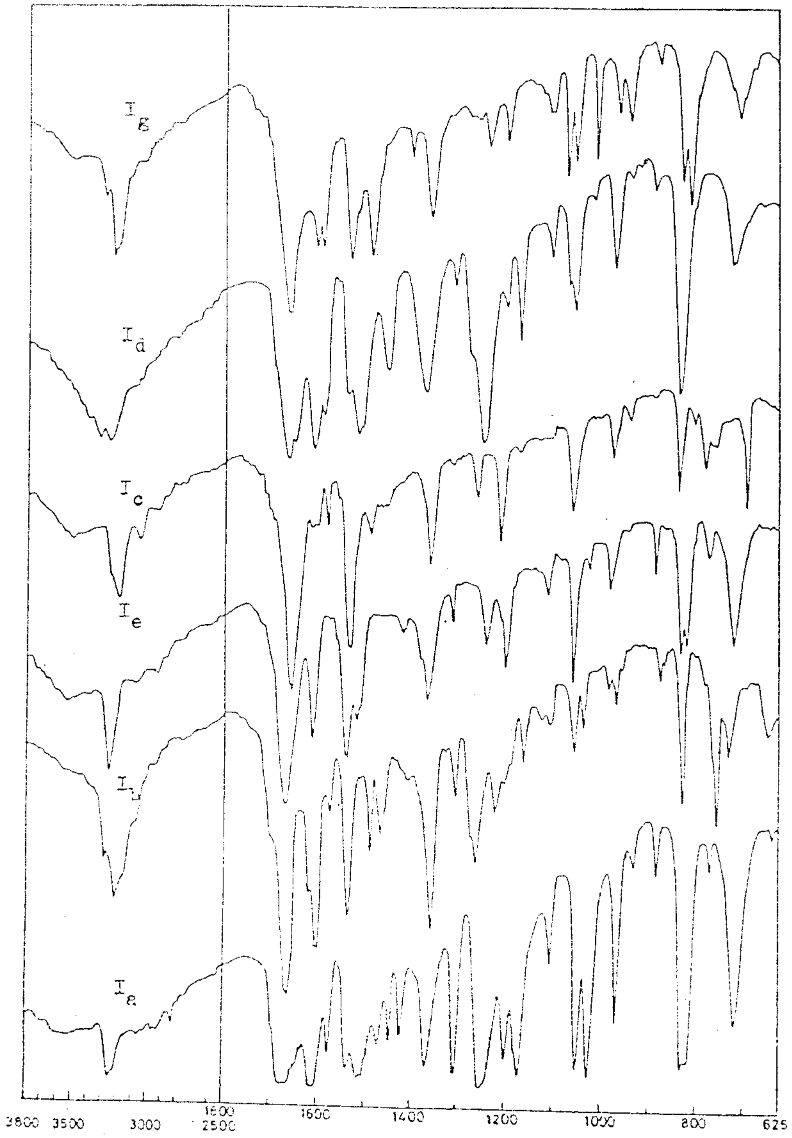


Fig. 4B. Infrared absorption spectra of some arylidene derivatives of oxalic hydrazide.

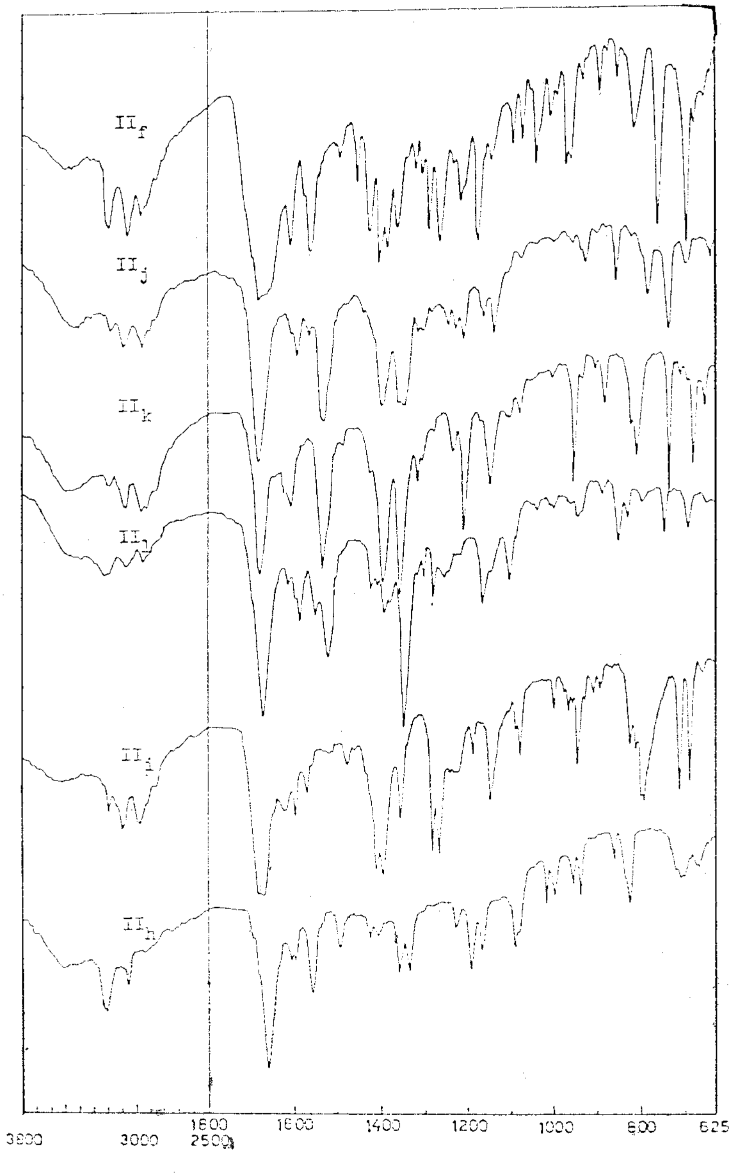


Fig. 5A. Infrared absorption spectra of some arylidene derivatives of succinic hydrazide.

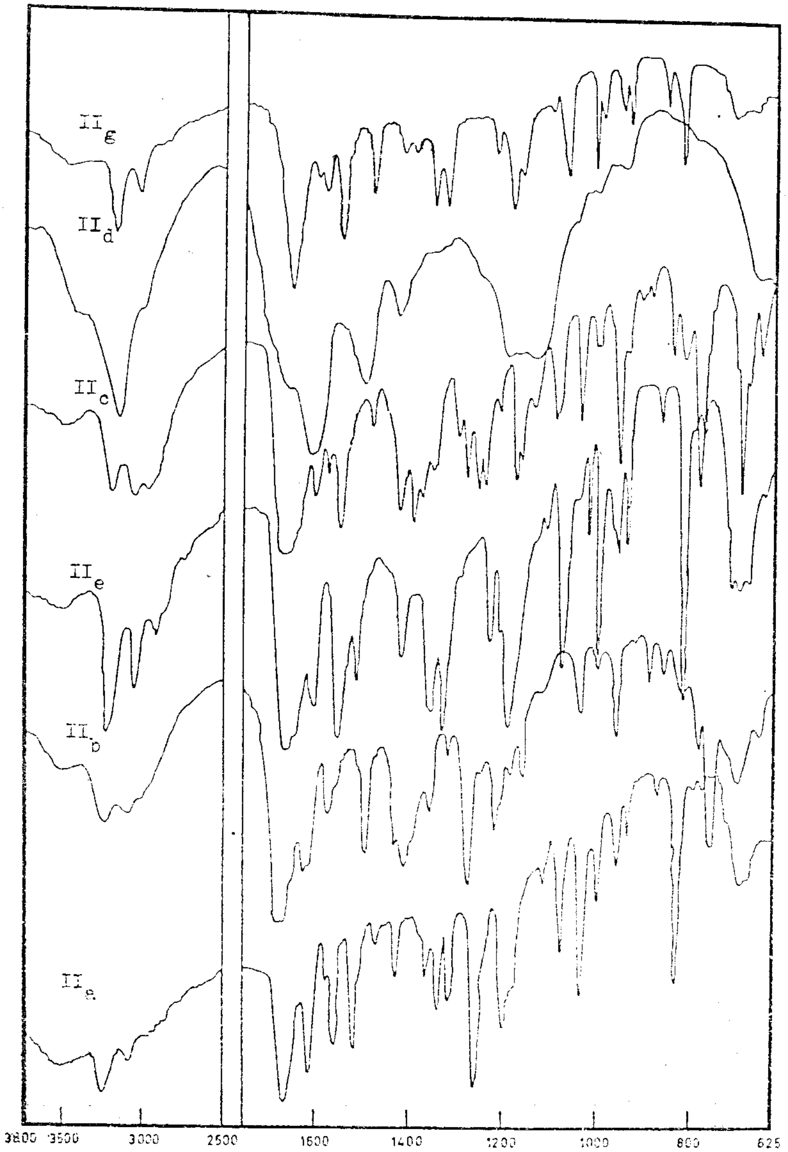


Fig. 5B. Infrared Absorption Spectra Of Some Arylidene Deridatives Of Succinic Hydrazides.

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