

Determination of some imines structures derived from salicylaldehyde with phenylene diamines by physical methods

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Abstract

The project is concerned with the preparation of four imines derived from salicylaldehyde with some aromatic primary amines, namely, o,m and p-phenylene diamine. These imines were identified by physical means available, namely the melting points, UV and IR spectra . The study led to the investigation of intra and inter molecular hydrogen bondings in these imines . Finally, the influence of intermolecular hydrogen bonding on association (polymerization) in imines was included and its effect on the melting points of imines was also discussed .

Keywords : Aromatic imines, structures, physical methods.

Introduction

A varieties of imines whether were aliphatic, aromatic or a mixture of aliphatic – aromatic ones were prepared during the last two decades (Patai, 1960) . This was for their wide importance and applications in the fields of chemistry (Azzouz *et al.*, 2002, 2005), biological (Abushad, *et al.*, 1989), medical (Rao *et al.*, 1978) sciences and industrial (Papenfuhs, *et al.*, 1975) applications .

Azomethines derived from various carbonyl, β – keto esters, benzoyl – acetone and 2,4 – dihydroxy benzaldehyde, had previously been studied extensively (Saeed *et al.*, 1983, Azzouz *etal* 2008-2009) .

The present work deals with synthesis of imines derived from salicylaldehyde with ortho, meta and p – phenylene diamine . The existence of hydrogen bonding in these imines was confirmed from the measurements of UV and IR spectra, as well as, melting points . Association studies in these imines by the aid of hydrogen bonding and their influence on melting points of imines were also discussed . Honestly

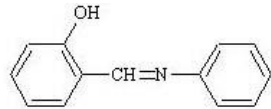
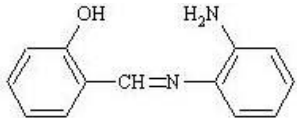
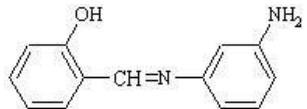
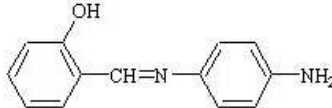
, this synthetic work opened the way to other accepted work dealing with kinetic and thermodynamic studies on tautomerism of imines under study (Azzouz *et al* 2010) .

Experimental

All chemicals used through out this work were of Fluka or BDH origin . They were used as supplied without any further purification .

All imines were synthesized using a standard method (Patai, 1960) . This was accomplished by mixing equimolar amounts of freshly distilled salicylaldehyde with o, m, or p – phenylene diamine . Add 10ml of absolute ethanol . The mixtures were refluxed for about one hour . Solid imines were collected and recrystallized from absolute ethanol and dried .

Table (1) Shows some physical property and nomenclature of imines

Comp.No.	Symbol of imine	Nomenclature	Colour	m.p °C	Structure
1	SA	Salicylidine aniline	Yellow	50-52	
2	S-o-AA	Salicylidine-o-amino aniline	Brown	163-165	
3	S-m-AA	Salicylidine-m-amino aniline	Brown	98-99	
4	S-p-AA	Salicylidine-p-amino aniline	Orange	217-220	

Instrumentation

All UV absorption measurements were carried on a computerized double beam Shimadzu UV – 1650 pc . A matched silica cells of dimensions 1×1×3cm³ were used .

The IR of imines were measured by using FTIR Tensor – 27 manufactured by German Bruker company . Solid IR imines were measured by KBr disk . Similarly, the liquid of imines solutions of concentrations 10^{-3} M in benzene solvent were measured in the same instrument in a range of $400 - 4000\text{cm}^{-1}$.

Melting points of solid imines were measured by using Electrothermal melting points apparatus .

Results and discussion

Spectroscopic method used in identification of hydrogen bond

1. The electronic spectra.

Actually, the electronic UV spectra were used previously for the investigation of hydrogen bonding of oximes(Azzouz etal 2004) and Schiff bases (Azzouz etal 2004, 2010) . In this method, the UV spectra for all imines under study, were measured in ethanol (polar solvent) and benzene (non polar solvent) . The type of transition, was measured by calculating ϵ_{max} values for all imines as shown in Table (2) .

Table (2) Showed a UV band referred to hydrogen bondings in all imines

Comp. No.	Symbol of Derivatives	Ethanol		Benzene		Wave number $(\nu)(\text{cm}^{-1}) \times 10^{-4}$		$\Delta\nu$ (cm^{-1})	Type of Transition
		λ (nm)	ϵ $\text{l.mol}^{-1}.\text{cm}^{-1}$	λ (nm)	ϵ $\text{l.mol}^{-1}.\text{cm}^{-1}$	Ethanol	Benzene		
1	SA	364	3763	360	4000	2.74	2.77	-300	$\Pi \rightarrow \pi^*$
2	S-o-AA	352	3763	350	3612	2.84	2.86	-200	$\pi \rightarrow \pi^*$
3	S-m-AA	330	3216	322	3200	3.03	3.13	-1000	$\pi \rightarrow \pi^*$

4	S-p-AA	304	3762	302	4000	3.29	3.31	-200	$\pi \rightarrow \pi^*$
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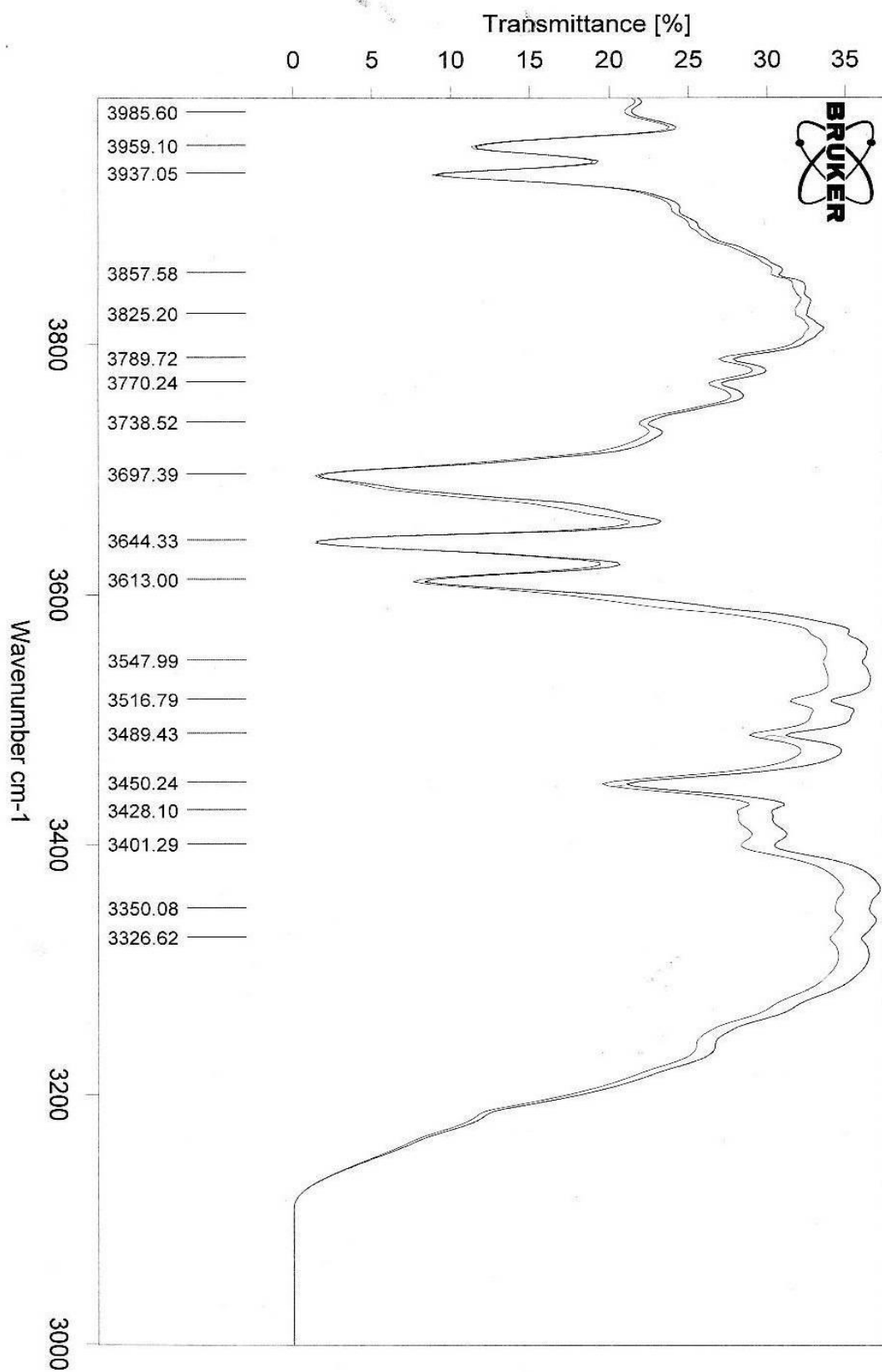


Fig. 1 : IR spectra for S-O-AA before (—) and after dilution (---) .

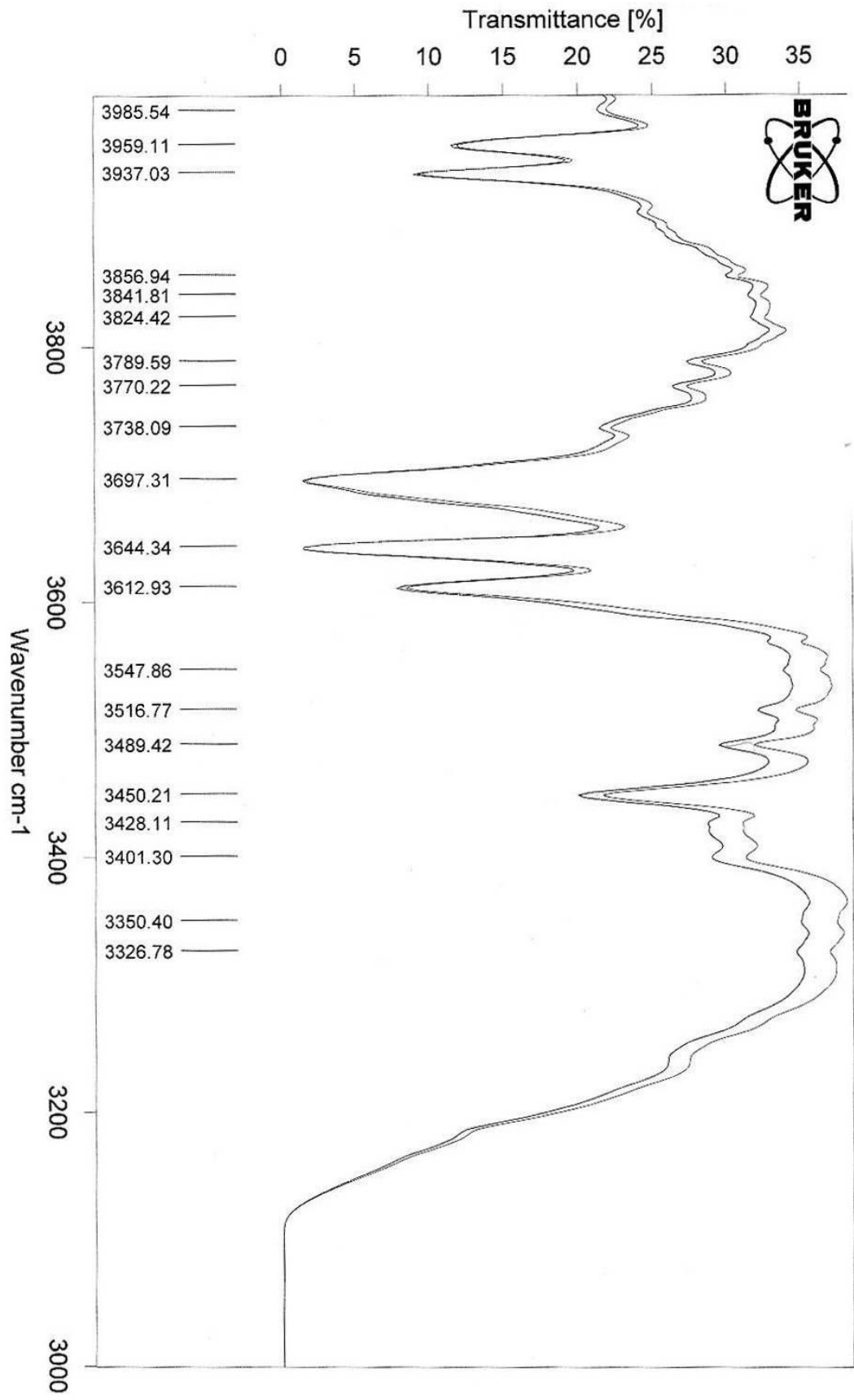


Fig. 2 : IR spectra for S-m-AA before (—) and after dilution (---) .

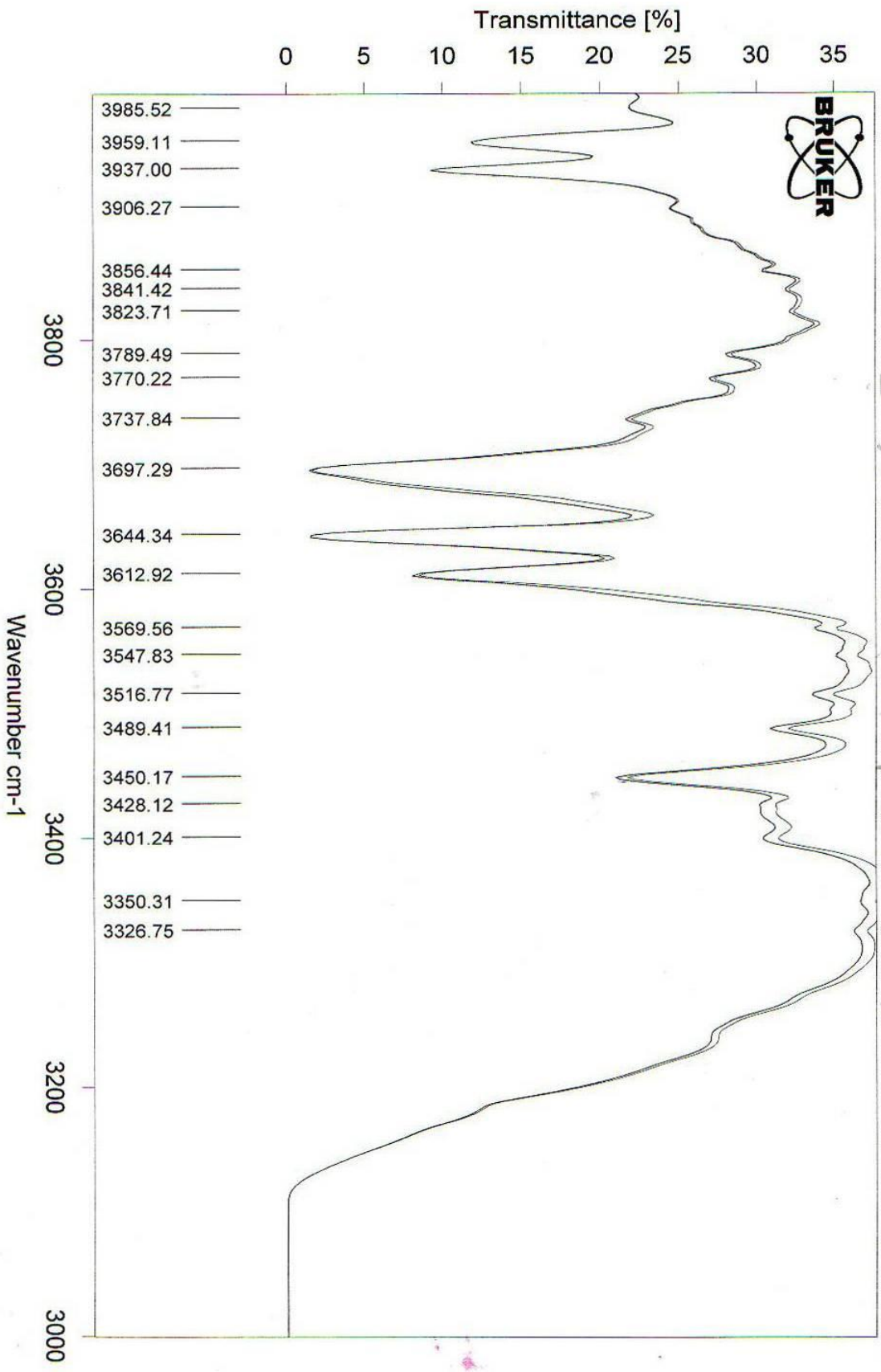


Fig. 3 : IR spectra for S-P-AA before (—) and after dilution (---) .

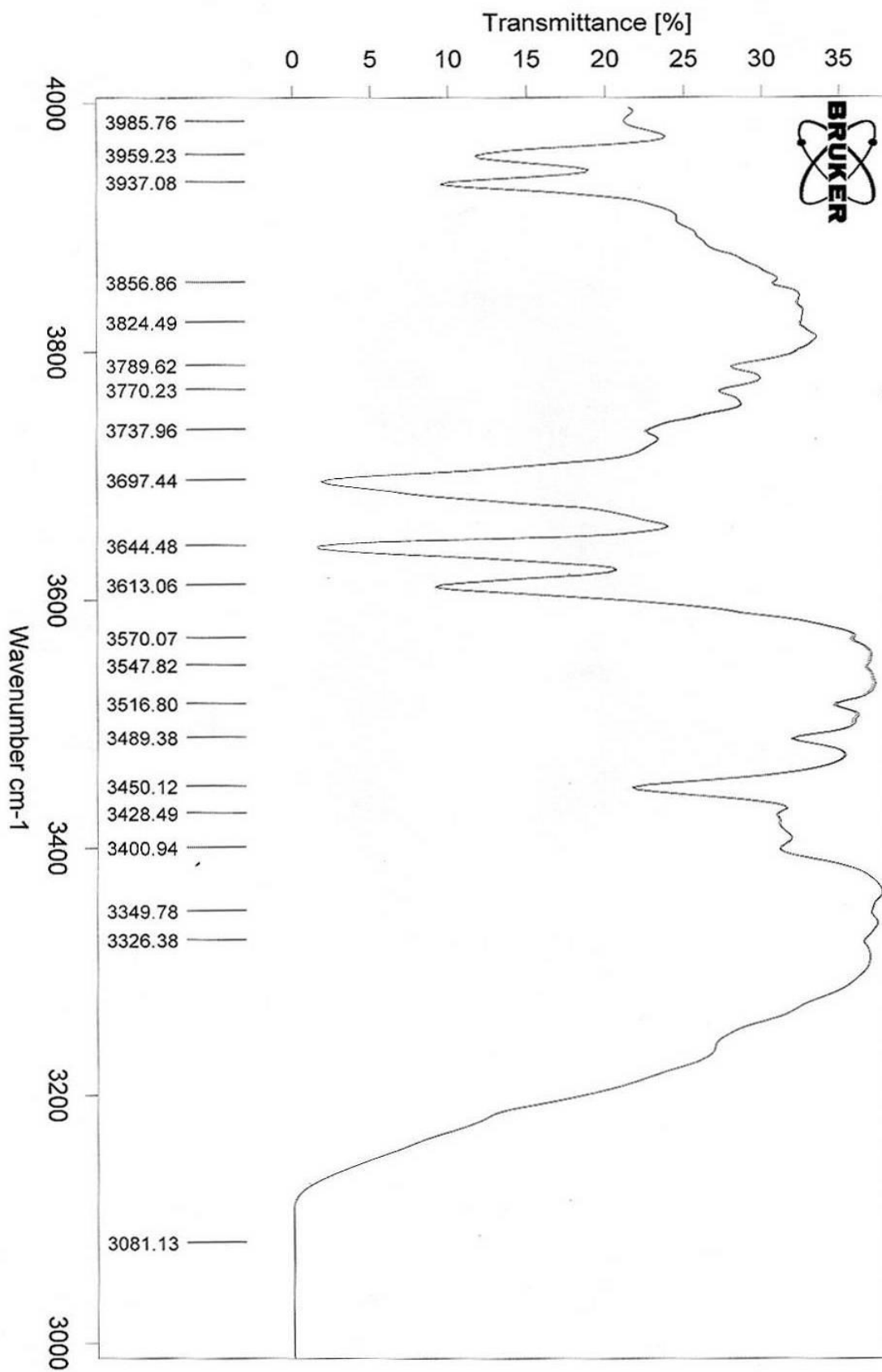


Fig. 4 : IR spectra for S- A before (—) and after dilution (---) .

These IR spectra were summarized in Table (3) .

Table (3) : IR spectra of imines in liquid state for identification of hydrogen bond

Comp. No.	Symbol of Derivative	Wavenumber (cm^{-1})							
		OH free	NH ₂ free	Intra H. b	Inter H. b	C=O	Substitute benzene		
1	SA	3516.78 (m)	-	3450.20 (s)	-	1715.20 (w)	3697.20 (s)	3644.33 (s)	3612.92 (s)
2	S-o-AA	3516.79 (m)	3489.43 (m)	3450.24 (s)	3489.43 (m)	1715.20 (w)	3697.39 (s)	3644.33 (s)	3612.00 (s)
3	S-m-AA	3516.77 (m)	3489.42 (m)	3450.21 (s)	3489.42 (m)	1715.19 (w)	3697.31 (s)	3644.34 (s)	3612.93 (s)
4	S-p-AA	3916.77 (m)	3489.41 (m)	3450.17 (s)	3489.41 (m)	1715.20 (w)	3697.29 (s)	3644.34 (s)	3612.92 (s)

Table (3) showed the following absorption bands :-

1. The appearance of a strong absorption bands in imines (1-4) for intra – molecular hydrogen bonding with wavenumbers range between (3450.17-3450.24) cm^{-1} .
2. The appearance of medium intensity bands for the intermolecular hydrogen bonding with wavenumber range (3489.41-3489.43) cm^{-1} . These came in agreement with inter and intra molecular hydrogen bonding studied in imines derived from 2–hydroxyl–1–naphthyl–aldehyde with primary aromatic amines (Azzouz *et al* 2003) .

Physical methods used for identification of prepared imines

Actually, many workers had given a special care and importance to spectral studies of imines (UV , IR , NMR and MS) (Bellamy, 1968,

Silverstein 1967) for imines during the last years . In order to understand this subject, the following details were necessary:

The IR spectra at solid state of imines (1-4)

The IR spectra of imines (1-4) were measured in solid state . and the results were summarized in Table (4) .

Table (4) : IR spectra of imines in solid state

No.	Symbol of derivatives	OH or NH ₂	CH _(str.)	C=N _(str.)	Ph _(str.)	CH _(bend.)
1	SA	3448.47 (b)	3077.11 (w)	1616.48 (s)	1588.07 (m)	1451.65 (m)
2	S-o-AA	3446.07 (b)	3070.00 (w)	1614.77 (s)	1584.93 (m)	1457.31 (m)
3	S-m-AA	3445.91 (b)	3055.83 (w)	1621.38 (s)	1591.60 (s)	1460.45 (m)
4	S-p-AA	3448.44 (b)	2923.20 (w)	1610.97 (s)	1571.14 (s)	1457.98 (m)

This Table shows the following absorptions :-

1. The appearance of a strong stretching absorptions for azomethineCH = N linkage in the range (1610.97-1621.38) cm⁻¹.
2. A strong stretching absorptions for phenyl groups in the range of (1571.14-1591.60)cm⁻¹ for imines (3-4) . These vibrational frequencies were converted to medium absorption for imines (1-2) .
3. A broad stretching absorptions in the range (344.91-3448.47) cm⁻¹, referred to OH or NH₂ groups in imines (1-4), due to their capability to form hydrogen bonding(Pimental, 1960) .
4. The appearance of weak absorptions for CH stretching in all imines and in a range (2923.20-3077.11)cm⁻¹ .
5. The appearance of medium bending absorptions for CH in the range (1451.65-1460.45)cm⁻¹ .

These absorptions shown in Table (4) were in full agreement of the chemical structure of imines (1-4) and with literature (Bellamy 1968, Silverstein 1967, Azzouz *et al* 2007) .

These encouraging results, led to repeat the IR measurements in liquid state . This was carried out for the determination the type of hydrogen bonding in imines (1-4), which have OH and NH₂ groups, (2-4) or OH group only in imine (1) .

IR spectra of imines (1-4) in liquid state

The IR spectra of 10⁻³M imines benzene solvent were shown in Table (3) . This shows the followings absorptions :-

1. The appearance of a triplet stretching absorptions in the range (3612.92-3697.39)cm⁻¹ for di or mono substituted aromatic ring (Silverstein 1967).
2. The appearance of stretching absorption band referred either to OH group in the range (3488.41-3489.43)cm⁻¹ for all imines or NH₂ of primary amine in imines 2-4 .
3. The appearance of stretching absorption for carbonyl group(Azzouz *etal* 2008) group, which seems unlikely in imines (1-4) . Actually, these absorptions were happened by tautomerism reactions (Azzouz *et al.*, 2007) in imines (1-4) or there conversions from enol to keto form .

UV spectra of imines (1-4)

The UV spectra of imines (1-4) were measured in ethanol and benzene with concentrations 10⁻³M as in Tables (2 and 5) which show the followings :-

1. A triplet absorption bands with molar extension coefficient values of more than 1000 in unit Liter.mol⁻¹.cm⁻¹ . These were interpreted by $\pi \rightarrow \pi^*$ transition(Pimental 1960) as in Tables (2 and 5) .
2. The first transition band shown in step (1) is referred to hydrogen bonding in imines (1-4) as shown in Table (2) . The other two transitions were due to $\pi \rightarrow \pi^*$ transition of aldehyde with azomethine group(Bayoumi *et al.*, 1971) and primary amine side in all imines as in Table (5) .

Table (5) : UV absorption spectra of imines (1-4) at wavelength (nm) and molar extinction coefficient (€) liter.mole⁻¹cm⁻¹ in ethanol and benzene solvents

No.	Imine abbreviate	Ethanol	Benzene
1	SA	334(3957)	360(4000)
		364(3763)	370(3830)
2	S-o-AA	352(3763)	350(3100)
		376(2635)	388(2937)
3	S-m-AA	317(3100)	360(3311)
		278(2372)	380(2767)
4	S-p-AA	356(3612)	360(4000)
		396(3010)	408(3215)

Melting points

The melting points of imines (1-4) were measured as shown in Table (1) . These imines have similar structures by containing ortho hydroxyl group at the aldehyde part of the molecules . This group was able to form a six membered ring intramolecular hydrogen bond with nitrogen atom (Al-Dilami *et al.*, 1977). This bonding resulted to a planer structure between aromatic aldehyde ring and the azomethine group . This was in contradiction with Al-Bayoum finding in benzylidene aniline(Al-Bayoumi *et al.*, 1971), which confirmed that the aldehyde ring was in one plane and the rest of molecule present in other plane . In other words, the presence of salicylidene aniline (1) in two different planes . Imines (2-4) contain an intermolecular hydrogen bonding of different strengths as evident from IR measurement in benzene solvent seen above

. This bonding was of type N H...N . These variations in intermolecular (Pimental 1960) hydrogen bonding might result in a different degrees of association or polymerization of imines . These produced different melting points for imines . Experimentally imines 3 , 2 and 4 had a melting point values of (98-99) °C , (163-165) °C and (217-220) °C respectively. These indicated that strength of intermolecular bonding in imines were increased in order of 3 , 2 and 4 . This finding was in agreement with earlier work carried out by Majer and Azzouz (Majer *et al.*, 1983) on 2-amino benzaldoxime which showed longer evaporation time from integrated ion current curve by mass spectrometry.

Conclusions

1. Four imines were prepared by standard method of reactions of salicylaldehyde with o , m and p – phenylene diamine .
2. The structure of imines were confirmed by physical methods , namely UV IR spectra and melting points .
3. The study showed the presence of six membered ring in intramolecular hydrogen bonding in all imines as well as the presence of intermolecular hydrogen bonding in imines 2-4 .
4. The intermolecular and intramolecular hydrogen bondings in all imines were of type O H...N and N H...N respectively.
5. These different strengths of intermolecular hydrogen bondings produced a different association or polymerization between molecules of imines in association order of 4 > 2 > 3 .
6. The IR spectra of imines 1-4 in benzene solvent showed the existence of enol \rightleftharpoons keto tautomerism .

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تعيين الهيئات التركيبية للأيمينات المشتقة من سالسائل الدهايد مع

فينايل

ثنائي الامين بالطرق الفيزيائية

د. عادل سعيد عزوز ، د. ثابت سعيد الغبشة ، د. أسيل نمير عبد آغا

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خلاصة

تضمن البحث تحضير اربعة ايمينات مشتقة من سالسائل الدهايد من امينات اولية اروماتية مثل اورثو، ميتا وبارا فينايلين ثنائي امين . شخصل هذه الايمينات بالوسائل الفيزيائية المتاحة مثل درجات الانصهار وأطياف الاشعة فوق البنفسجية وتحت الحمراء . درست الأواصر الهيدروجينية الضمنية والبينية في المركبات، كما اشتمل البحث اخيراً على تأثير الأواصر الهيدروجينية البينية على درجات تكثف (بلمرة) هذه الايمينات وتأثير ذلك على درجات انصهار المركبات والذي تمت مناقشته بشكل مفصل .