

SYNTHESIS AND CHARACTERIZATION OF SOME NEW COMPOUNDS DERIVED FROM SEMICARBAZIDES AND 2-AMINO OXADIAZOLE (MONOMERS AND POLYMERS) AND STUDY THEIR LIQUID CRYSTALLINE PROPERTIES.

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Abstract:

A series of new compounds derived from semicarbazides containing azomethane linkage which found to be liquid crystals.

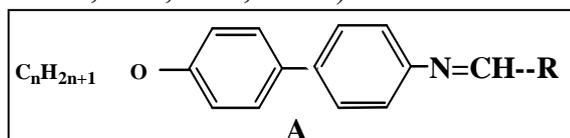
These Schiff's bases resulted from the reaction between substituted semicarbazide [I] and different substituted benzaldehyde in presence of few drops of glacial acetic acid as a catalyst and absolute ethanol as a solvent.

These derivatives exhibited thermotropic liquid crystalline properties. This semicarbazide then cyclized to 2-amino oxadiazole which converted to allylic monomers by reacting it with acryloyl and methyl methacryloyl chlorides.

These monomers were polymerized free radically with AIBN or benzoyl peroxide as initiator. The monomers and its polymers were characterized by IR and H^1NMR spectra. These new compounds show mesomorphic properties were discussed with relation to chemical structure of these molecules. The structures of these compounds were characterized by IR, H^1NMR spectra for some of them, C.H.N. analysis, melting points and transition temperatures were checked.

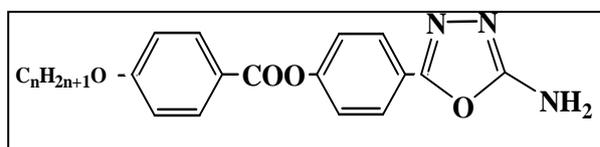
Introduction:

A large number of mesomorphic compounds containing Schiff's bases (azomethine linkage) have been synthesized (1-4). This is because of the effect of considerable change in polarity, polarizability and geometry of the molecules (5). Many compounds which form liquid crystal mesophases contain a para-substituted benzene ring as central group. The contribution of benzene ring to mesophase stability appears to lie in its rigidity, linearity and polarizable π -electron density (6). It was demonstrated that π -density in the central group is no a necessary condition for mesophase formation (7). Hence, a variety of central groups have been reported (e.g. $CH=N$, $C=C$, $N=N$, ... etc) A.

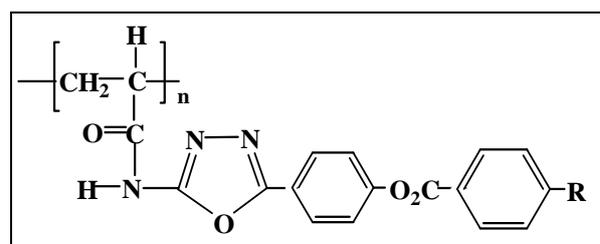


Others (8), have synthesized a number of semicarbazides of 4-(4-n-alkoxy benzoyloxy) benzaldehydes, they cyclized to

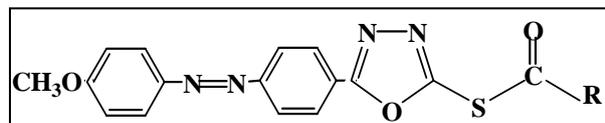
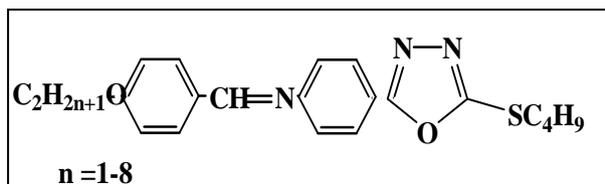
respective amino-oxadiazoles, 2-amino-5-[4-(4-n-alkoxy benzoyloxy)phenyl] 1,3,4-oxadiazoles.



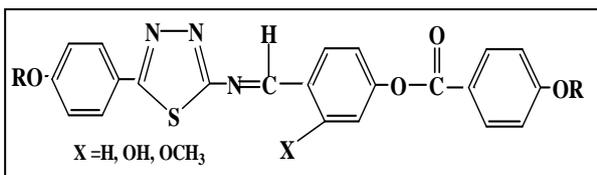
This series of amino-oxadiazole compounds exhibit nematic mesomorphism. Also, Salih (9) has prepared a group of semicarbazides, 2-amino oxadiazole, its cyclized monomers with polymers and found that all these compounds exhibited liquid crystalline properties.



Other workers (10-11), have synthesized homologous series of liquid crystalline Schiff bases 1,3,4-oxadiazoles and having azo linkage.



Hamed(12), also synthesized series of compounds having heterocyclic rings and found that these compounds exhibited liquid crystalline properties .



Semicarbazones on heating exhibit biphasic region and decomposition tendencies as the temperature increases. The biphasic region (crystalline + nematic) turns into homogenous nematic phase at higher temperature but decomposition and the final transformation of semicarbazone to the product is being studied in detail(8).

Also, semicarbazides and thiosemicarbazides have been reported to possess antibacterial (13), antifungal (14) antitubercular(15) and anticonvulsant(16) properties and so as for oxadiazole (17-19). Keeping this in view , we have synthesized some derivatives of semicarbazides with different substituents.

Experimental:

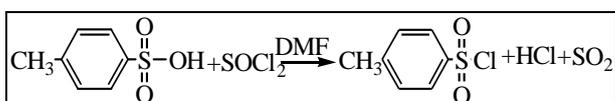
Materials:

DMF was refluxed over P_2O_5 for three hours ,then distilled under nitrogen atmosphere and was stored over freshly activated molecular sieve. All other chemicals employed were of analytical reagent grade and were used without further purification .IR spectra were performed on a Pye Unicam spectrophotometer sp1025 spectrophotometer at a rang between $625-3800\text{ cm}^{-1}$ as KBr film .Melting points were determined by using a calibrated mettler FBS melting apparatus. Optical observations were performed by a leitz microscope (laborlux 12 pol.) equipped with heating

stage (leitz 350), and photographic camera (Vario orthmate 2)in Baghdad.

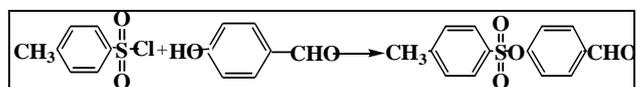
1H NMR spectra were recorded on FT-EX 90 JEOL type NMR spectrophotometer using $(CDCl_3)$ as a solvent and TMS as internal reference .Microanalysis of the compounds were carried out on Perkin-Elmer 240C elemental analyzer .The abbreviation str. and bend. are used to indicate stretching and bending bands ,respectively

1-Preparation of p-Toluene sulphonyl chloride (Tosyl chloride) :



Tosyl chloride was prepared by treating 4-toluene sulphonic acid with thionyl chloride ,one drop of (DMF) and heating till evolution of hydrochloric acid ceases. Excess of thionyl chloride is distilled off . (M.P= $67-69^{\circ}C$)(20).

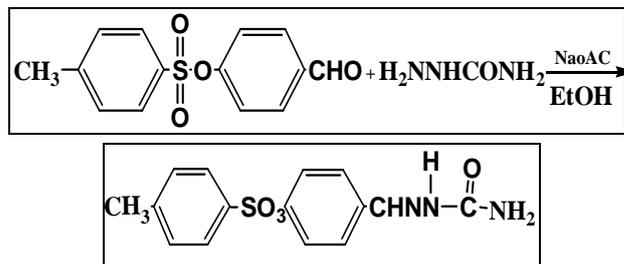
2-Preparation of p-Toluene sulphonyl benzaldehyde:



(0.1Mole) of tosyl chloride in (5ml DMF) was added dropwise to the solution of 4-hydroxy benzaldehyde and (13.5ml)of triethyl amine in (10ml.of DMF) with stirring.After additionl, stirring continuous at room temperature for 24 hour .Then filtered and re-crystallized from 95% ethanol).White crystals m. p.= $68-70^{\circ}C$,Yield 72%)(21).

IR (KBr): ν 1730 ($-C=O$), ν 2695-2830 (C-H st.), ν 1390 ($C=O$ bend.) cm^{-1} .

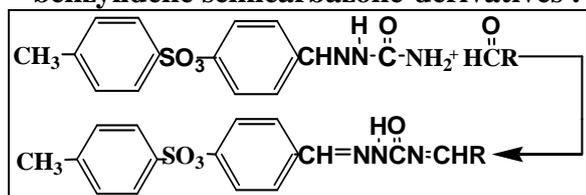
3-Preparation of 4-(4-Toluene sulphonyl) benzaldehyde semicarbazide.



(3m mole) of (p-toluene sulphony benzaldehyde in (10ml.) ethanol was added to a mixture of (18 mmole) of semicarbazide hydrochloride and fused sodium acetate . The mixture was refluxed for (40) minutes .Cooled, diluted with distilled water and filtered, re-crystallized from glacial acetic acid. White precipitate, Yield 90% (m.p =196-212⁰ C.(22).

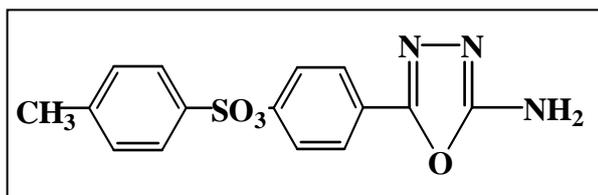
IR(KBr):v3500-3300(-NH₂),3150(-CONH), 1665 for C=O in(-CONH₂) cm⁻¹.

4-Preparation of 4-(4-Toluene sulphony benzylidene semicarbazone derivatives .



A mixture of 4(4-toluene sulphony benzaldehyde semicarbazone (0.9mmole) ,4-substituents benzaldehyde (0.01g) ,1drop of glacial acetic acid and (10 ml) of dry benzene or toluene was refluxed for (3hr) with a Dean stark column.The solvent was removed and the resulting solid was re-crystallized from ethanol (Table 1).

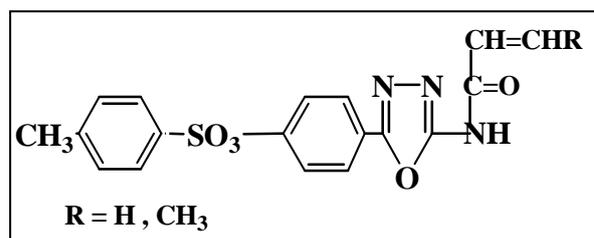
5-Preparation of 2-amino- 5-(4-Toluene sulphony phenyl) 1,3,4-oxadiazole IV.



Bromine (0.6ml) in acetic acid (5ml) was added to a stirred slurry of (6.9mmole) of (IV) and anhydrous sodium acetate (4g) in acetic acid (5ml) contained in a (150ml) flat bottom flask . Due to exothermic reaction, the mixture became warm and rapidly become colorless. The mixture was poured in water, solid which separated was filtered and dried. Re-crystallized from the mixture of alcohol and glacial acetic acid.

6-Preparation of the monomers:

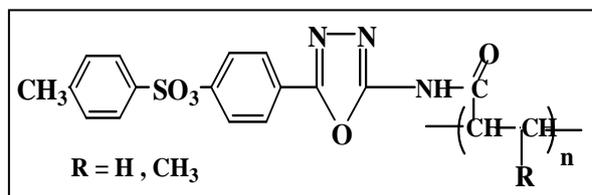
2-[(acryloylamid ,methacryloylamide) 5-(4-Toluene sulphonyphenyl) 1,3,4-oxadiazole V .



(9.8mmole) of IV was dissolved in (40ml)(THF) tetrahydrofuran and (10ml) of Et₃N (tri-ethylamine), to which (5ml) acryloyl chloride in (20ml) THF was added dropwise with stirring at (0⁰C). The reaction was continued at 0C⁰ for 4hrs.The Et₃N-HCl salt was precipitated and filtered The solvent was removed from the filtrate by vacuum. The residual liquid was poured with stirring into (100ml) water to precipitate the product . Re-crystallization was carried out in 95% ethanol.

The Polymerization :

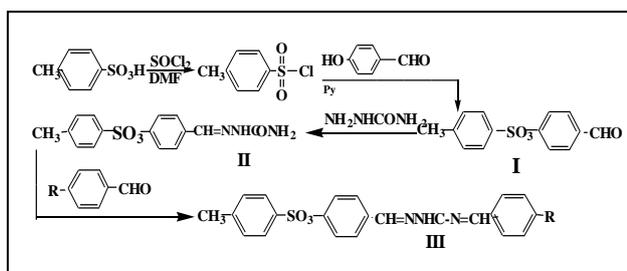
7- Preparation of poly :[(2-acryloylamide, methacryloylamide) 5 - (4 - Toluene sulphonyphenyl)] 1,3,4-oxadiazole VI.



(1mmole) of the monomer was dissolved in 3ml THF,(0.2mmole) AIBN or benzoyl peroxide was added to the solution. The reaction was contained at 70 ⁰ C temperature under N₂ with stirring for 5hrs. The polymer was precipitated in (60ml) methanol. The product was filtered and thoroughly washed with methanol and dried at room temperature under vacuum.

Results and Discussion .

Schiff's bases [III] were synthesized according to Scheme 1.



Scheme

1 Reagents and conditions for prepared compounds .

Compound I was synthesized starting by esterification of tosyl chloride and p-hydroxy benzaldehyde and proceeding condensation with semicarbazide hydrochloride, yielding semicarbazone.

The physical properties of these Schiff bases are given in Table (1).

The Schiff's bases of compounds [III] were synthesized by condensation of the appropriate p-substituted benzaldehyde with the semicarbazone [II] in presence of glacial acetic acid in absolute ethanol as a solvent .

The structure of these compounds were confirmed on the bases of its melting points and spectral data IR and H^1 NMR spectroscopy .

The characteristic IR-absorption bands of these compounds [III] showed the disappearance of two absorption bands due to NH_2 stretching of compound [II] together with the appearance of stretching band in the range (1640-1660) cm^{-1} due to the imine $C=N$ group . It also showed a stretching band in the range (2820-2980) cm^{-1} due to aliphatic (C-H) stretching.

H^1 NMR spectra are in accordance with the formula for each compound of the series. The H^1 NMR spectrum of the compound IIIe is shown in Fig. (2) as an example.

H^1 NMR ($CDCl_3$): δ =2-2.3 ppm (t,6H,N(CH₃)₂; 2.5 ppm (s,3H,CH₃) ; 7.2 previously⁽¹²⁾. Probably, the mesomorphic properties of the series III is due to that ,the imine linkage gives rise to a more planer structure , allowing for stronger molecular interactions in the liquid crystalline phase which explain the mesomorphism of the Schiff's bases derivatives .

The transition temperatures and enthalpies for these compounds are given in Table 3.

All synthesized compounds showed nematic mesomorphic behaviour. Fig.(3) shows the thread -like texture characteristics of nematic phase .

The absence of liquid crystalline of the unsubstituted compound (R=H) reflects the importance of symmetry to crystalline lattice stability , because any deviation from linearity leads to diminish the liquid crystalline properties except no 1.

Methyl substituent , which represents the less polar group gives the lowest nematic-isotropic transition temperature ppm (d-d ,2H,C₆H₄) 7.3-8ppm(m,2H,C₆H₄); 8.7ppm(s,1H,CH=N), 11ppm may due to the solvent. (23)

Liquid crystalline properties were examined by D.S.C and hot- stage polarizing microscopy. The transition temperatures and enthalpies were determined by DSC measurements .

The transition temperatures were checked using polarizing microscope equipped with a hot stage. The transition temperatures ,enthalpies and entropies for these compounds [III] are given in Table 3, DSC thermogram of compound [IIIId] as a representative are plotted in Figure 8.

All compounds [IIIa-e] showed enantiotropic liquid crystalline properties , with broad mesomorphic range .

However ,we have synthesized new mesogenic Schiff's bases (series III) in which the double bond is in the central position similar to the derivatives described ($T_n - I$,Table 2), while more compact , polar groups ,NO₂, give the highest .

The high $T_n - I$ temperature of methoxy group ,could be explained by the increasing of symmetry induced by this group to crystalline lattice stability . The size and polarity of terminal substituted seems to be the principal factors that influence the $T_n - I$ temperatures .Data published by kelker ,et.al.,(24) in good agreement with our results .

The high $T_n - I$ temperature of N(CH₃)₂ substituent could be explained by the fact that this group causes the molecule to be

broad, so that decreasing its axial ratio (ratio of length to width of molecule), and which makes the molecule to be more compact and more stiffness (25).

The data of Table 2 reflect that the melting points (crystal-nematic transition temperatures) do not follow the same trend as nematic-isotropic transition temperature. Dewar and Goldberg (6) pointed out that the melting point is enhanced by symmetry and strong intermolecular attractive forces. The latter are provided by polar and easily polarizable segments of the molecule.

2-Characterization of 2-amino 5-(4-Toluene sulphonyl phenyl) 1,3,4-oxadiazole IV.

This compound was prepared from the reaction between semicarbazide and bromine with fused sodium acetate. The structure of this compound was characterized from IR and ^1H NMR spectra.

The IR spectrum Fig (4) for this compound exhibited the absorption band at 3300-3500 and 1600 cm^{-1} assignable to the (NH_2) and to $\text{C}=\text{N}$ groups respectively in addition to the aliphatic and aromatic C-H bands at about 3000 cm^{-1} .

^1H NMR spectrum for the prepared compound is in accordance with the formula for this compound. The ^1H NMR spectrum is shown in Fig (5). ^1H NMR (90 MHz, DMSO- d_6). $\delta = 7-7.5$ ppm (m, 4H, C_6H_4), 7.5-8 ppm (m, 4H, C_6H_4); 2 ppm (s, 3H, CH_3); 9.8 ppm (s, 2H, NH_2).

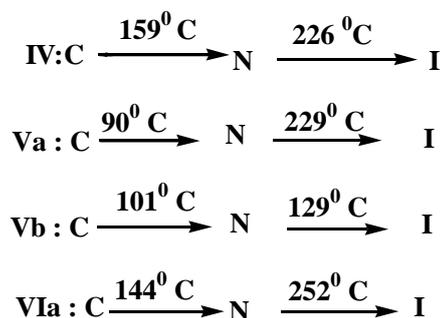
3-Characterization of the monomers : 2-[(acryloylamide, methacryloylamide) 5-(4,4'-methyl phenyl) sulphonyl] 1,3,4-oxadiazole Va,b .

These monomers were prepared from the reaction between 2-amino 5-(4,4'-tosyl phenyl) 1,3,4-oxadiazole with acryloyl, methylmethacryloyl chlorides in presence of pyridine as a base.

The structures of these monomers (Va,b) were deduced from IR spectra.

The IR spectra Fig (5) for compound (Va) showed the absorption bands at 2900, 1650, 1620, 1050 and 1100 cm^{-1} characteristic to the ν C-H, ν (C=O amide), (C=C aliphatic), asymm.C-O-C, and symm.

C-O-C functions and disappearance of absorption band at 3500 cm^{-1} , which attributed to ν (N-H) group of amino oxadiazole.



4-Characterization of the polymers : poly {2-acryloyl, methylmethacryloyl amide} 5-(4,4'-Tosyl phenyl) 1,3,4-oxadiazole VIa,b .

These polymers were prepared according to Kapzuk's method. The polymerization of the monomers (Va,b) was carried out in toluene with benzoyl peroxide as initiator. The structures of the obtained polymers were confirmed from their melting points and IR spectra.

Both polymers were soluble in all common organic solvents, such as DMF and DMSO. The IR spectra showed the disappearance of the absorption band of 1600-1620 cm^{-1} assigned to the acrylic double bond in the monomers Fig (7).

5-Liquid crystalline properties of the monomers and its polymers [IV, Va and VI].

Individual thermal microscopic observations of compounds [IV, Va,b, VIa,b] by mean of hot-stage polarized microscopy were investigated to study their liquid crystalline behavior. The compounds [IV], [Va,b] and [VIa,b] showed nematic liquid crystal texture when examined by hot-stage polarizing microscopy with typical thread-like texture Fig (8). The transition temperatures of those compounds are as follows

Gray (5), has explained the rarity of mesomorphism in such compounds by taking into consideration, the intermolecular hydrogen bonding, which raise the melting points above the mesomorphic isotropic

liquid transition temperatures and may encourage a nonlinear structural arrangement that is incompatible with mesophase formation .

It is known that intermolecular hydrogen bonding will increase the rigidity, in such a situation presence of a flexible central linkage would help to overcome strong attractive forces. Moreover in the molecule of compound IV , the heterocyclic ring due to the presence of lone pair of electrons on two nitrogen atoms will enhance lateral cohesive forces due to high polarizability of the molecules .this will raise the melting point of the system.

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حضرت مجموعة جديدة من المركبات المشتقة من السيميكاربازايد والاكسادايازول المحتوية على اصرة الازوميثان وقد وجد انها ذات خواص بلورية سائلة . ان قواعد شف هذه اشتقت من التفاعل بين السيميكاربازايد ومشتقات مختلفة للبنزالديهايد بوجود قطرات من حامض الخليك الثلجي كعامل مساعد والكحول الايثيلي المطلق كمذيب.

وتم تحويل السيميكاربازايد الى 2-امينو اوكسادايازول من خلال حولته بواسطة البروم وخالات الصوديوم المنصهرة ومن ثم مفاعله مع كلوريد الاكربيلول و المثيل مثيركليلول . كما تمت بعد ذلك بلمرة هذه المونمرات عن طريق البلمرة بالجذور الحرة لتكوين بوليمرات جانبية السلسلة وباستخدام بنزوايل بيروكساييد أو AIBN كباديء .

تم تشخيص التراكيب الكيميائية لهذه المركبات باستخدام أطياف ال IR و UV وكذلك H^1NMR للبعض منها وتحليل العناصر الدقيق, كما شخصت الخواص البلورية السائلة لهذه المركبات باستخدام مجهر الضوء المستقطب المزود بمسخن كهربائي ومسعر المسح التفاضلي كما سجلت درجات الانتقال الحرارية .