Impact para position on rho value and rate constant and study of liquid crystalline behavior of azo compounds

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ARTICLE INFO

ABSTRACT

A series of new mesogenic ester compounds were successfully synthesized. Azo compounds were prepared by coupling diazonium salt (which prepared from phenyl diamine with 1:1HCl and $NaNO_2$) with phenol, and the prepared compounds were reacted with substituted benzoic acid to give esterification. FT-IR and ^1H NMR spectrometers were used to confirm the structures of the prepared compounds the optical microscope polarization and DSC have been studied in the liquid crystal phases. It was observed that the thermal stability of the nematic phase increased with an increase in the polarity of the substituted groups at the para and meta position, as following ($Cl > OCH_3 > NO_2 > CH_3$) also, the thermal stability of nematic phase was highest at meta substituted compared with para substituted. In addition to, the kinetic behavior of the prepared compounds showed the effect para position through p-CH_3 and p-OCH_3 due to the presence of resonance effect in addition inductive effect, so (σ +) was used instead of (σ p_x). The results of the kinetic study showed through a Rho (ρ) value a decrease in the electronic density and an increase in the growth of the positive charge in the reaction center, this means that the reaction is stabilized with the presence of donating groups.

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Second International Conference on Aspects of Materials Science and Engineering (ICAMSE 2021).

1. Introduction

A direct connection between kinetic data and thermodynamic parameters is provided by linear free-energy relationships (LFER), offering insights into mechanism of reactions [1]. LFERs establish a relation between many measurable quantities and well-known parameters, Hammett substituent constants (either σ, σ + or σ-) are possibly the most renowned example [2]. One of the best mathematical relationships concerning the effect of compensators on reaction velocity is the Hammett equation. This equation relates the chemical equilibrium constants of the dissociation or ionization of benzoic acid and the substituted benzoic acid in position (meta and para) against the reaction velocity constant or the equilibrium velocity constant of the compound under study [3]. In physical-organic chemistry, the Hammett equation has proven to be of considerable value and has even undergone application in numerous other areas of chemistry [4]. Several hundred papers have appeared in chemical literature in the last century on the impact of reactivity, structure and very few on thermodynamic stability and kinetic reactivity of intermediates [5]. Indeed, recent studies have shown the significance of the Hammett methodology of linear correlation in numerous fields of current interest [6–9]. The increase or decrease in the electronic density of the compound under study is considered a measure of the inductive and resonance effects of the substituent groups at the Meta and para position, accordingly [10–12]. Hammett correlation analyses have been performed to rationalize how geometric parameters, electronic structures, and the chemical reactivity of azo compounds were affected by the nature and type of attached substituents. Liquid crystals are an intermediate state (mesophase) described as a fourth state of matter, first named as flowing crystals. Fluid crystals appear between the solid phase and the isotropic phase which is the same. Random arrangement [13–15].

Liquid crystals are linear, rod like, or discotic shapes. Although liquid crystals show certain properties similar to the solid and liquid states, they have special features that are not present in both states (solid and liquid) [16].

Calamictic Liquid Crystals, This type of mesogene has an elongated shape that is responsible for the emergence of anisotropy, it is important in the molecular shape of thermotropic mesogens [17].
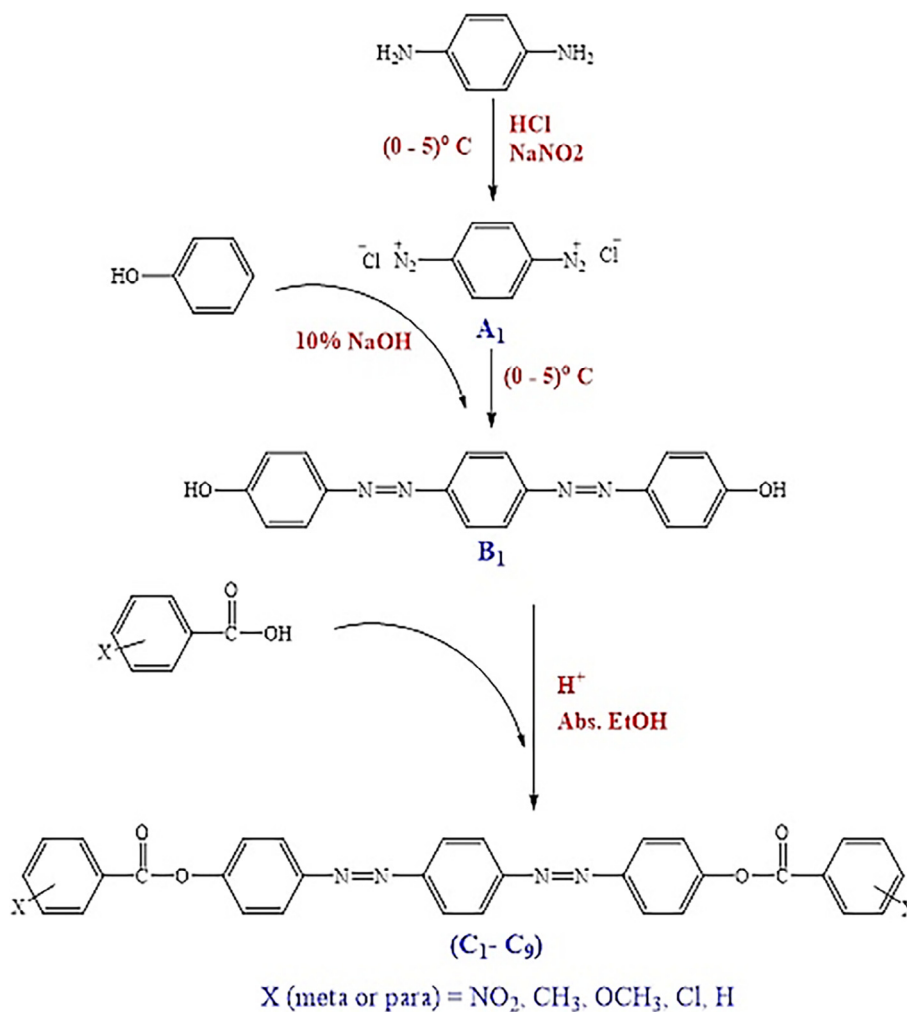
Fig. 1. Synthesis pathway of the prepared compounds.

Azo compounds are compounds carrying the diazenyl R-N = N–R' functional group, of which either may be aryl or alkyl. Azo compounds are described by IUPAC as: "Derivatives of diazene (diimide), HN = NH, in which all hydrogens, e.g. PhN = NPh azobenzene, are substituted by hydrocarbyl groups [18]. Two aryl groups are present in the more stable derivatives. The group N = N is alluded to as an azo group. The name azo derives from azote, a French term originating from the Greek for nitrogen. Aromatic azo compounds can be synthesized by azo coupling, which entails an electrophilic substitution reaction where an aryl diazonium cation is attacked by another aryl ring, especially those substituted with electron-donating groups [19]:

A homologous series of mesogenic azo compounds comprising three major core rings and replacing the central benzene nucleus with aromatic or hydroxyl groups has been identified [20,21].

This work aims to study the effect of the Para position on the rate of chemical reaction of some liquid crystalline compounds prepared by normal esterification method.

2. Experimental

2.1. Characterization

The melting point of the prepared compounds was measured using Griffin –Made in Britain-London – Serial NO. 90–01-154.

apparatus. Using the Shimadzu Fourier transform infrared spectrophotometer FTIR − 8400-S scale (4000–400) cm-1 with (KBr), the infrared spectra of the resulting compounds were reported.

^{1}H NMR was registered at the University of Isfahan (Iran) using the Ultra Shield 300 MHz Switzerl. Using the polarizing optical microscope form (BEAM ENGINEERS (INDIA)) and differential scanning calorimeter (DSC-60) Shimadzu, the study of liquid crystalline properties was carried out. The reaction was followed up for the purpose of the kinetic study using UV– Vis. Spectrophotometer / GASCO-V-530.

2.2. General procedure

2.2.1. Preparation of diazonium salt (A1) and azo compound (B1)

In a conical flask, a 1: 1 ratio of concentrated hydrochloric acid was mixed with water, this solution was cooled and then 0.25 mmoles of p-Phenylenediamine were added to it, after that, 0.027 mmoles of NaNO2 dissolved in 10 ml of water were added, and the addition was slowly, Keeping the temperature of the solution below 10C. then, the solution was stirred in an ice-bath for 20 min. Then, phenol (2.5 g, 27 mmol) was dissolved separately in a 25 ml solution of 10 percent NaOH. To the diazonium salt containing solution under stirring, this prepared solution was slowly added, the temperature was maintained below 5○ c with 45 min of stirring continued. The yellow-orange solid formed has been

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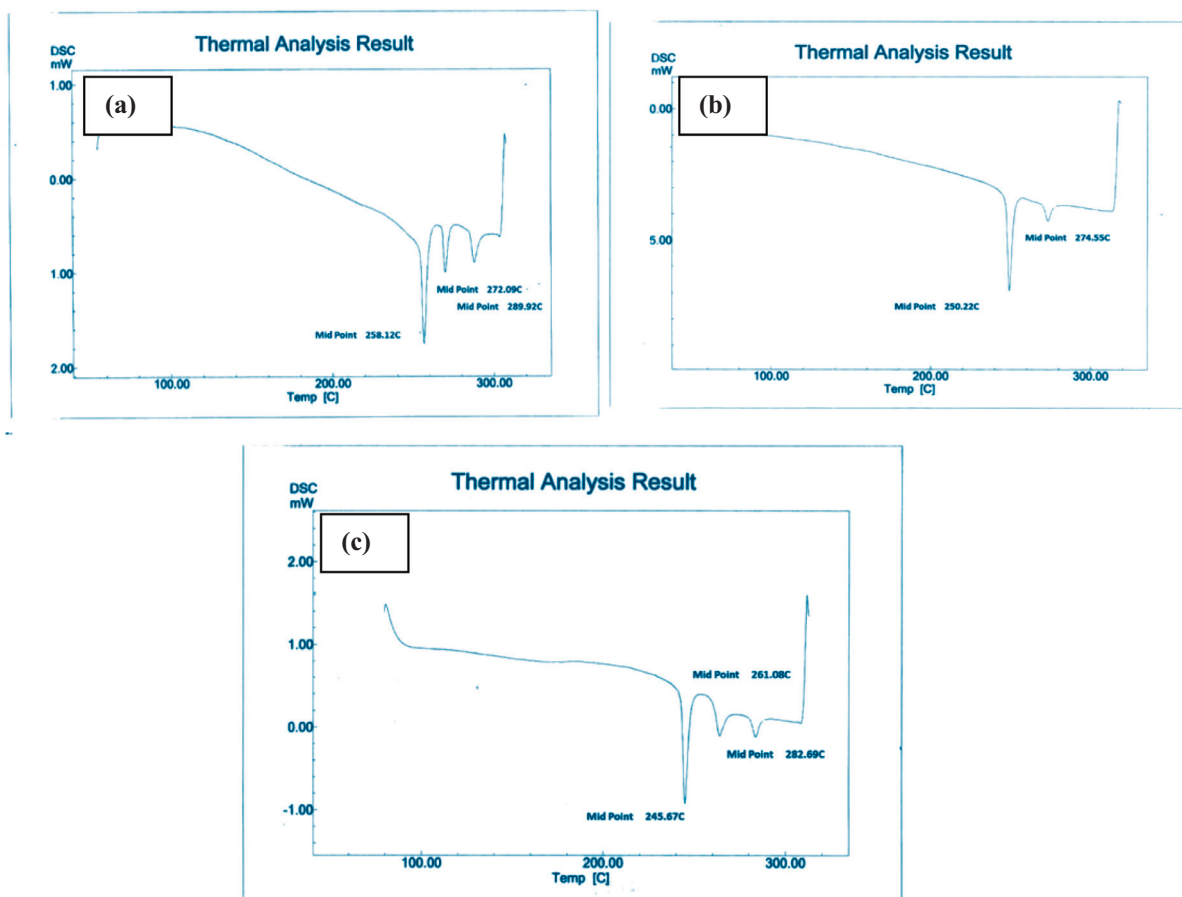
Fig. 2. DSC of the compounds (a) C6, (b) C3 and (c) C8.
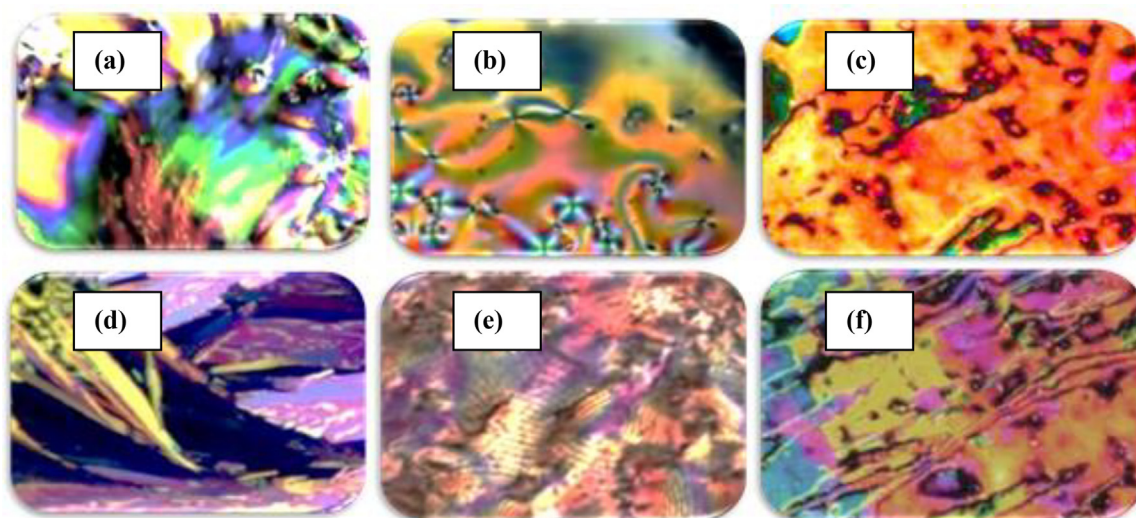
Fig. 3. (a) N of C7, (b) N of C9, (c) Sc of C8, (d) SA of C7, (e) SA of C7 and (f) Sc of C7.

filtered and washed with water, the substance has been recrystallized with a combination of ethanol / water [22]. See Fig. 1.

3. Results & discussion

3.1. Diagnosis of organic compounds

3.1.1. Diagnosis of 4,4′-(1,4-phenylenebis(diazene-2,1-diyl))diphenol
Properties: Yield = 83%, brown color m.p=(231–233)°C

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Table 1
The physical properties of the prepared compounds(C₁-C₉).

| Yield%	Colour	mp.°C	X	Comp. NO.
81	Deep Brown	263–265	Para-OCH₃	C₁
76	Brown	241–243	Para-CH₃	C₂
73	Brown	248–250	Para-Cl	C₃
66	Deep yellow	261–262	Para-NO₂	C₄
73	Brown	289–292	H	C₅
75	Brown	259–261	Meta-OCH₃	C₆
72	Brown	238–241	Meta-CH₃	C₇
70	Brown	244–245	Meta-Cl	C₈
68	Orange	257–259	Meta-NO₂	C₉

IR (KBr): 3327 cm^{-1} (OH), 3042 cm^{-1} (C–H Aromatic); 1508/1579 cm^{-1} (C = C Aromatic); 1541 cm^{-1} (N = N).

3.1.2. Diagnosis of ester compounds

Table 1.Table 2.

Table 2
Results of the FT-IR (cm^{-1}) for the prepared compounds.

Comp.NO.	X	N = N	Ar.	C–HAlf.	C–HAr.
C₁	Para-OCH₃	1643.08	1498.18 1566.74	2817.56	3059.18
C₂	Para-CH₃	1621.88	1508.33 1586.64	2867.08	3083.46
C₃	Para-Cl	1653.44	1457.26 1588.82	2901.15	3028.52
C₄	Para-NO₂	1637.12	1502.23 1576.98	2856.23	3067.15
C₅	H	1667.26	1479.80 1559.23	2885.42	3039.08
C₆	Meta-OCH₃	1618.25	1512.52 1587.56	2905.23	3061.54
C₇	Meta-CH₃	1648.56	1446.86 1568.35	2877.82	3055.27
C₈	Meta-Cl	1629.37	1507.59 1576.54	2866.35	3081.19
C₉	Meta-NO₂	1651.22	1497.63 1581.87	2859.64	3043.71

^{1}H NMR (300 MHz, DMSO-d) δ/ppm to the (C₂) Compound: 2.64 (s, 6H, 2CH₃); (8.28–7.37) (m,20H, Aromatic benzene(. ^{1}H NMR (300 MHz, DMSO-d) δ/ppm to the (C₄) Compound (8.64–7.51) (m, 20H, Aromatic benzene (.^{1}H NMR (300 MHz, DMSO-d) δ/ppm to the (C₆) Compound: 3.56 (s, 6H, 2CH₃); (8.01–7.29) (m, 20H, Aromatic benzene (.

3.2. Discussion of liquid crystal phases

3.2.1. Overall concepts

The thermal transition rates of the liquid crystals and isotropic phases of most of the compounds prepared using DSC were measured by taking around (2–3) mg of dry matter and heating it in an inert atmosphere of N₂. A polarized heating microscope was used to diagnose the liquid crystals.

Compound (B₁) did not exhibit liquid crystalline properties, and this is likely due to the presence of hydrogen interconnection, which makes the molecular medium have a high hardness and a large decrease in elasticity and thus the molecules are arranged randomly and irregularly.

By observing the differential scanning calorimeter (DSC) of the compounds (C₁-C₉) and the results of the polarized microscope, shown in Table 3. The above compounds exhibit Smectic and nematic phases with a high temperature range, the reason for this is due to the presence of five aromatic rings in the molecular struc-

Table 3
Liquid crystal phase transitions in Differential scanning calorimeter and Mic.sc. for prepared compounds.

App.	No.	C	S$_A$	S$_C$	N	ΔT$_{SA}$	ΔT$_{SC}$	ΔT$_N$
DSC	B₁							
Mic.sc		231						
DSC	C₁							
Mic.sc		263	277	283	298	14	6	15
DSC	C₂							
Mic.sc		241		258	267		17	9
DSC	C₃	250			274			24
Mic.sc		248			273			25
DSC	C₄							
Mic.sc		261	273		285	12		12
DSC	C₅							
Mic.sc		289						
DSC	C₆	258	272		289	14		17
Mic.sc		259	274		294	15		20
DSC	C₇							
Mic.sc		238	251		268	13		17
DSC	C₈	245		261	282		16	21
Mic.sc		244		258	281		14	23
DSC	C₉							
Mic.sc		257			276			19

By observing DSC charts Fig. 2 (a-c), the nature of the transmission can be inferred to a large extent the transition from the crystalline phase to the liquid crystal (melting point) includes the highest change in enthalpy (ΔH) and the nematic liquid crystalline transition to isotropic includes the lowest enthalpy transport (ΔH) relative to the remaining liquid crystalline phases. See Fig. 3 (a-f).
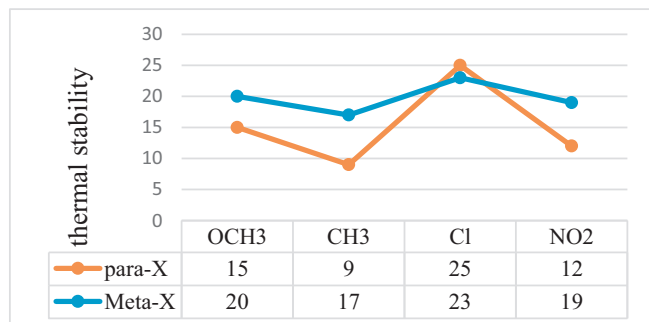
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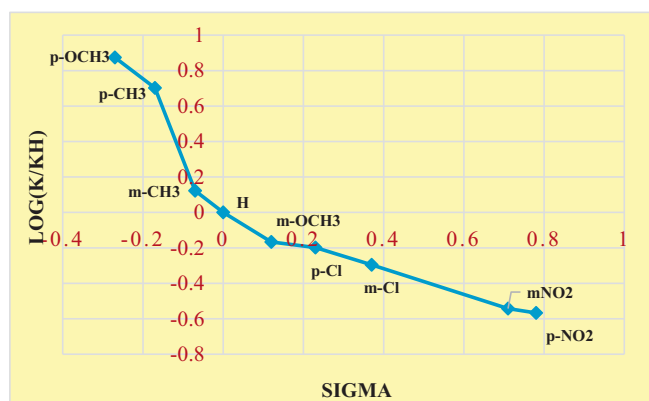**Fig. 4.** Thermal stability of nematic phase.

Fig. 5. Plot of log (k/k_H) values for meta- and *para*-substituted vs. Hammett (σ) constants.

Table 4
Plot of log (k/k_H) values vs. Hammett (σ) constants and slope value.

Comp. NO.	X	Sigma(σ)	Log(k/k_H)	P = slope
C1	Para-OCH$_3$	−0.27	0.8738	−1.22728
C2	Para-CH$_3$	−0.17	0.7026	
C3	Para-Cl	+0.23	−0.1985	
C4	Para-NO$_2$	+0.78	−0.4529	
C5	H	0	0	
C6	Meta-OCH$_3$	+0.12	−0.1188	
C7	Meta-CH$_3$	−0.07	0.1375	
C8	Meta-Cl	+0.37	−0.2498	
C9	Meta-NO$_2$	+0.71	−0.4174	

Table 5
Plot of log (k/k_H) values vs. Hammett (σmeta$_{-X}$) constants and slope value.

Comp. NO.	X	Sigma(σ)	Log(k/k_H)	P = slope
C6	Meta-OCH$_3$	+0.12	−0.1188	−0.80227
C7	Meta-CH$_3$	−0.07	0.1375	
C8	Meta-Cl	+0.37	−0.2498	
C9	Meta-NO$_2$	+0.71	−0.4174	

ture, which give the molecule the appropriate elongation, in addition to the expansion of the electronic sequence along the axis of the molecule.

This corresponds to the literature [23,24] which confirmed that the presence of more than three aromatic rings in the molecule increases its polarity and thus the emergence of liquid crystalline phases.

Table 6
Plot of log (k/k_H) values vs. Hammett (σ +) constants.

Comp. NO.	X	Log (k/kH)	Sigma(σ)	Sigma(σ +)
C1	Para-OCH$_3$	0.8738	−0.27	−1.08916
C2	Para-CH$_3$	0.7026	−0.17	−0.87577
C3	Para-Cl	−0.1985	+0.23	0.24742
C4	Para-NO$_2$	−0.4529	+0.78	0.56453
C5	H	0	0	0
C6	Meta-OCH$_3$	−0.1188	+0.12	0.14808
C7	Meta- CH$_3$	0.1375	−0.07	−0.17139
C8	Meta-Cl	−0.2498	+0.37	0.31137
C9	Meta-NO$_2$	−0.4174	+0.71	0.52028
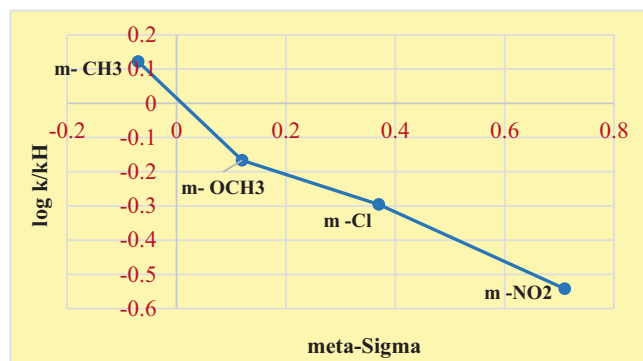
Fig. 6. Plot of log (k/k_H) values for *meta*-substituted vs. Hammett (σmeta$_{-X}$) constants.
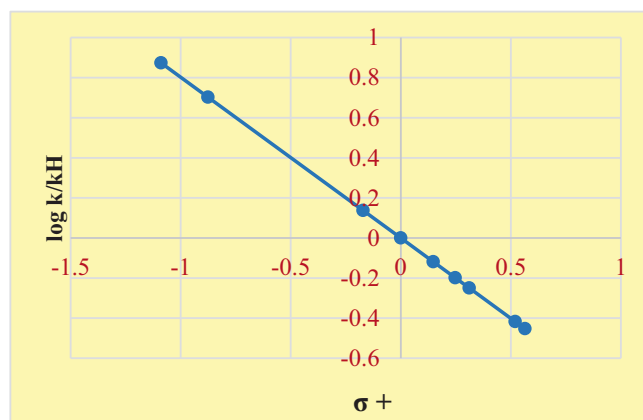
Fig. 7. Plot of log (k/k_H) values for meta and para substituted vs. Hammett (σ +) constants.

The compounds exhibited the nematic phase with a high temperature range due to the presence of (Cl, NO$_2$, OCH$_3$ and CH$_3$) as terminal groups, which are characterized by strong dipole moment that increases the ratio of the peripheral to side attraction forces. See Fig. 4.

3.3. Discussion of kinetic behavior

The standard kinetic measurements of the esterification were carried out in ethanol absolute solution by using UV–Vis. Spectrophotometer. The results shown in Table 4 and Fig. 5 were obtained.

By observing the results of the kinetic behavior of the prepared compounds shown in Table 4 and Fig. 4, the rate of reaction deviate from the linearity of Hammett's equation when the substituted are para(OCH$_3$, CH$_3$), the reason for this is effect para position decrease

in electron density at the transition state and buildup of positive charge at reaction center which are stabilized by electron donating groups. Also, the reactions that showed the effect of para position had a high rate of reaction compared with the rest of the reactions and the reason was due to the stability of intermediate

Therefore, the values of (σ +) can be substituted instead of the values of (σ_p), as show in Table 5, Table 6, Fig. 6 and Fig. 7.

4. Conclusion

The organic compounds were prepared by coupling diazonium salts with phenol, then reacting the product with substituted benzoic acid. Liquid crystalline compounds were obtained with high thermal stability as a result of the presence of high polarized groups at the Para position with the presence of five aromatic rings that increase the electron succession along the molecule. It was observed that the prepared compounds exhibit effect para position when the substitutes are (OCH_3, CH_3), so it deviated from the linearity of Hammtt's equation.

CRediT authorship contribution statement

Mohammed Mezher Aftan: Conceptualization, Investigation, Validation, Writing - review & editing. **Abdualwahid Abdualsatar Talloh:** Visualization, Investigation, Writing - review & editing, Formal analysis. **Adil Hussein Dalaf:** Data curation, Methodology, Investigation, Writing - review & editing, Formal analysis. **Hanaa Kaain Salih:** Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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