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Dimeric Schiff Bases : Preparation, Characterization and Donor Properties

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Abstract:

The bis (*P*-substituted-2-methoxy aniline benzylidene-4-oxy) Octamethane was prepared and used as a donor to form 1:2 complexes with (2, 3-Dichloro-5, 6-dicyanobenzoquinone) (DDQ), respectively. The equilibrium constants (K), molar absorptive extinction coefficients (ε) and the dissociation energies of the charge transfer complexes excited states (w) have been calculated and discussed. The ionization potentials of Schiff bases have been determined and has been concluded that these complexes are predominantly of the (n → π) type.

الخلاصة:

حضر المركب بس (بارا-معوض-2 -ميثوكسي أنيلين بنزيليدين-4 -أوكسي) أوكتاميثان وأستخدم كمانح للإلكترونات ليعطي المعقد 2:1 مع (3,2 -ثنائي كلورو– 6,5 - داي سيانوبنزوكوينون) (DDQ) . وتم حساب ثوابت التوازن (K) ومعاملات الامتصاص المولاري (ε) وطاقات الحالة المثارة(w) . وأخيرا تم حساب جهد التأين لقاعدة شف وللمعقدات المحضرة لمعقدات انتقال الشحنة كما وأستنتج أن هذه المعقدات تظهر أنتقال من نوع (n←π).

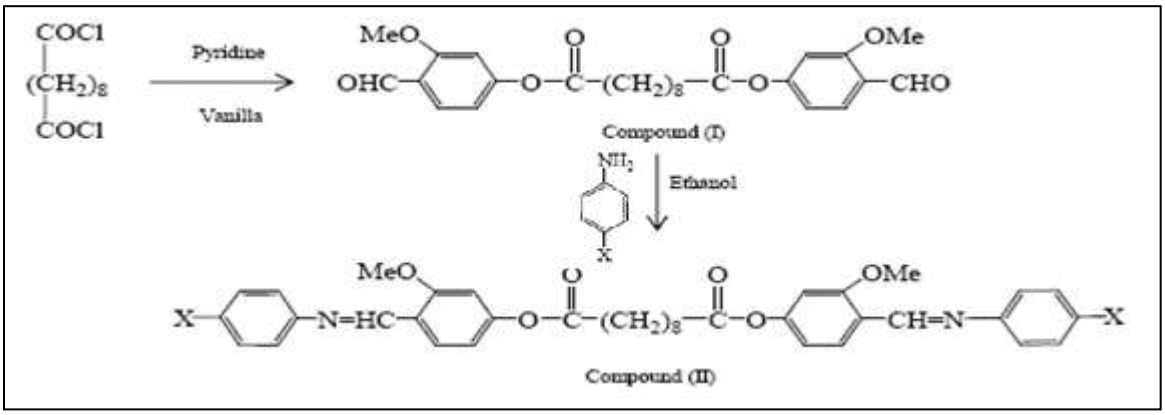
Introduction:

In the second half century there has been considerable interest in the studies on the charge-transfer complexes of Schiff bases compounds with DDQ, TCNQ[1-9].Their formation can influence reaction pathways may be detected spectroscopically [10-17].

The DDQ form CT complex with some aliphatic and aromatic amines[11,12] and some Schiff bases donors to form stable (n → σ*) CT complex with iodine in chloroform[13].On the other hand, very little information is available in the literature concerning CT complexes of dimeric Schiff bases compounds. The aim of the present work is to synthesize new charge transfer complexes with bis (*P*-substituted-2-methoxy aniline benzilidine-4-oxy) octamethane, and to clarify the ability of the Schiff bases to act as an electron donor in the reaction with DDQ. The study involves estimation of ionization potential (IP) of Schiff bases ca1culation of the CT complexes parameters, equilibrium constant KCT, extinction coefficient ε CT, and dissociation energies of CT complex excited state W.

Experimental:

The general synthetic procedure to obtain bis (substituted (x)-2-methoxy aniline benzylidene-4-oxy) octamethane; (X = H, CH3, OMe, Cl, CN, NO2)is shown in scheme(1). IR spectra were recorded using a Pye Unicam model SP3-300S spectrophotometer. UV and visible absorption spectra were taken for methylene chloride solution using Pye Unicam SP8-100 ultraviolet spectrophotometer and 1cm path way quartz cells.



(X = H, Cl,CH_3, OCH_3, $COCH_3$, NO_2, CN)

Scheme (1): Preparation of compounds that use in manuscript.

Preparation of compound (I) :
Vanilla (0.1 mole) in (5 mL)of dry pyridine was added with the sebacoyl chloride (0.05 mol) in (5 mL) of dry pyridine was stirred at room temperature under nitrogen atmosphere overnight. The solid product was filtered off and wash with distilled water then dried. The crude product was recrystallized from ethanol.

Preparation of compound (II) :
4-substituted aniline (0.084 mole) was added to a hot solution of compound (I) (0.04 mole) in absolute ethanol (30 mL) in a (50 mL) conical flask fitted with calcium chloride guard tube - while cooling to room temperature the mixture was stirred for 1h. Acreamy yellow precipitate formed which was filtered off and recrystallized from ethanol to give crystals which were dried in vacuum at 30°C.

Preparation of the solid Charge Transfer (CT) complexes :
A saturated solution of the compound (II) (0.02 mole) in dichloromethane was mixed with saturated solution of DDQ (0.04 mole) in dichloromethane and refluxed for (2-2.5h.). Then the solution was evaporated to a small volume where on cooling the solid CT complexes were separated as fine crystals. The precipitate was washed with a small amount of dichloromethane and recrystallized from ethanol. The analytical data of the prepared complexes with some of their physical properties and melting points are given in Table (2).
Due to low solubility character of the donors (I-VII) in methylene chloride, all spectral measurement were carried out in methylene chloride. Stock solution of the donors or acceptors were prepared in methylene chloride where they were freshly prepared prior use.
The CT complex was followed by measuring the absorbance of the new absorption band of complexes in the range 300-600 nm at 25°C. The concentration of DDQ being kept constant ($2x10^{-4}$M) and that of Shiff base

was variable in every set of solutions (1-20x10^{-3}M).
The plots of the initial concentration of DDQ divided by the absorbance of complexes at λmax against the reciprocal of the initial concentration of Schiff bases gave according to Benesi-Hilder brand equation (eq. 1) a very good straight lines of which the intercepts equal to (1/ε CT) and the slopes equal to (1/KCT . ε CT) in every case. From these values ε CT and KCT can be evaluated.

$$\frac{[DDQ]\ .\ 1}{A_{CT}} = \frac{1}{K_{CT}\ .\ \varepsilon_{CT}} + \frac{1}{[\text{Schiff base}]} + \frac{1}{\varepsilon_{CT}} \qquad \ldots\ (1)$$

[DDQ] and [Schiff base] are the initial concentration of the acceptor and donor, respectively. The number 1 is the path length = 1 cm; *A*CT is the absorbance at λmax due only to the complex.

Characterization of compounds:

` The structures of the dimeric series and the solid CT complexes were verified by elemental analysis and IR spectra. The elemental analyses are in good agreement with the calculated values as shown in Table (1) and (2). The most important vibrational bands in IR spectra of the series of these compounds are listed in Table (3) and (4).

Table (1) : The melting points, yields and elemental analysis for all compounds of dimeric series

Substituent	Melting Point °C	%Yield	Calculated			Found		
			%C	%H	%N	%C	%H	%N
H	83	80	73.55	6.45	4.45	73.12	6.34	4.62
Cl	101	86	66.18	5.52	4.07	65.98	5.44	4.12
CH_3	92	90	74.07	6.79	4.32	73.95	6.48	4.41
OCH_3	94	90	70.59	6.47	4.12	70.20	6.42	4.22
$COCH_3$	132	75	71.59	6.25	3.98	70.93	6.06	4.21
NO_2	162	88	64.22	5.35	7.88	64.21	5.22	7.91
CN	170	82	74.30	5.88	8.67	74.14	5.69	8.85

Table (2) : The melting points, yields and elemental analysis for all compounds of the solid CT complexes

Substituent	Melting Point °C	%Yield	Calculated			Found		
			%C	%H	%N	%C	%H	%N
H	102	75	64.60	3.98	8.37	64.71	3.82	8.41
Cl	111	85	60.44	3.53	7.83	60.52	3.47	7.87
CH_3	115	80	65.17	4.26	8.14	65.21	4.18	8.28
OCH_3	130	82	63.21	4.13	7.90	63.30	4.11	7.94
$COCH_3$	151	85	64.03	4.04	7.72	64.25	4.01	7.79
NO_2	200	87	59.28	3.47	10.24	59.29	3.41	10.51
CN	207	86	63.81	3.60	10.63	63.62	3.59	10.71

Table (3) : IR Data (cm^{-1}) for Dimeric Series

Sub.	C-H (str.) Armoatic (w)	C-H (str.) Armoatic (w)	C=O ester (s)	C=N azomethane (s)	C=C Armoatic (w)	C-O-C ether (s)	Other peaks
H	3050-3040	2960-2840	1745	1610	1595	1165,1260	-
Cl	3050-3045	2965-2840	1750	1625	1590	1160,1270	C-Cl st. 675 (m)
CH_3	3055-3040	2955-2835	1750	1620	1590	1165,1260	-
OCH_3	3050-3040	2965-2840	1750	1620	1590	1160,1270	-
$COCH_3$	3050-3035	2960-2840	1740	1615	1595	1160,1270	C=O keton 1645 (s)
NO_2	3055-3040	2955-2830	1750	1625	1590	1160,1255	NO_2 1515(s) , 1310(s)
CN	3050-3045	2950-2835	1750	1620	1590	1165,1250	C=N st. 2220 (m)

s=strong , m=medium , w=weak

Table (4) : IR Data(cm^{-1}) for solid CT complexes

Sub.	C=N azomethan (s)	C=N (str.) Cyano (m)	C-l (str.) (m)	C=C Armoatic (s)	C=O keton (s)	C=O ester(s)	C-H (str.) armoatic (w)	C-H (str.) aliphatic (w)
H	1600	2224	675	1585	1660	1750	3055-3054	2970-2850
Cl	1610	2220	680	1585	1665	1752	3055-3045	2970-2855
CH_3	1605	2225	680	1592	1660	1755	3060-3050	2970-2830
OCH_3	1600	2228	685	1580	1665	1750	3055-3050	2975-2860
$COCH_3$	1610	2228	690	1575	1660	1750	3056-3045	2970-2865
NO_2	1615	2227	685	1575	1665	1755	3058-3046	2975-2870
CN	1610	2224	685	1580	1665	1755	3050-3050	2980-2875

s=strong , m=medium , w=weak

Results and Discussion:

The reaction of bis (*P*-X-2-methoxyanilinebenzylidene-4-oxy) octamethane with DDQ in dichloromethane gave complexes of 1:2 stoichiometry (Table 2). The change in their color from pale yellow to black-brown as the number of benzene rings increased may be attributed to the distribution of the free electron over the benzene rings [18].

In UV-Visible region a new band in the visible spectrum 300-600 nm Has been observed on mixing solution of Schiff base and π-acceptor DDQ in dichloromethane at 25 °C. This absorption is ascribed to charge-transfer complexes formed, since neither the Schiff bases nor the *P*-acceptor DDQ alone absorbs in this region. The stiochiometeric ratio of the different complexes studies 1:2 as indicated by linear plots of the Benesi-Hiledbrand equation [19-20]. From equation (1) and the plots between [DDQ]o / ACT at their λmax against 1/[Schiff base] will give a straight line. Then KCT will be calculated. On the other hand, the λmax, hυCT, KCT, and ΔGo for CT complexes of DDQ with Schiff bases. Gibbs free energy has been calculated from the equation :

$\Delta Go = - RT \ln KCT$ ... (2)

The ionization potential of donors (Schiff bases) and the dissociation energies of CT complex excited state W were estimated from energies of the charge transfer band by applying the empirical equation (3) and (4).

$H\upsilon\ CT = a\ I.P + b$ …(3)

$W = I.P - E\alpha - h\upsilon CT$ …(4)

reported by Aloisi abd Pignataro [21,22].

Ea refer to electron affinity of DDQ which is equal to 1.42 ev. The close values of I.P of Schiff bases and W of their CT complexes with DDQ which reflects the similarity of chemical nature due to the higher value of KCT for *para* substituted Schiff base for donating groups than the corresponding withdrawing group (Fig. 1) fair correlation with σP substituent as (Fig. 2) was observed. It was found that a stronger complex was formed with

donating groups and weak complexes with drawing groups, so we can conclude that the CT complex is of (n →n^*) nature in which the nitrogen atom of the imine group [-CH=N-] in the Schiff base molecules donates n-electrons to (n^*) orbital of DDQ [23,24].

A comparison of the important I.R spectral bands of the free donors and acceptors with those of the complexes give some information about the nature of the CT complexes formed.

There are slight shift in frequency and some alterations in the intensity, which reflect the molecular association [9].

Table (5) : Spectral Characteristics, Ionization Potential, Equilibrium Constants Energies of Transition, Free Energies, and the Dissociation Energies of the CT Complex Excited States (W).

X.	λ_{max} (nm) Schiff base	λ_{max} (nm) CT	I.P (ev)	K_{CT} ($mol.dm^{-3}$)	hυ (ev)	ΔG $KJ.mol^{-1}$	W (ev)
H	380	490	10.00	11400	2.525	23.80	5.40
Cl	367	450	9.71	10000	2.76	22.73	5.50
CH_3	390	510	9.48	24150	2.43	25.63	5.30
OCH_3	365	450	9.69	11020	2.64	24.77	5.14
$COCH_3$	350	425	8.99	7400	2.92	21.92	5.10
NO_2	353	430	9.84	7200	2.12	21.93	5.09
CN	351	470	9.53	9910	2.82	23.00	5.16

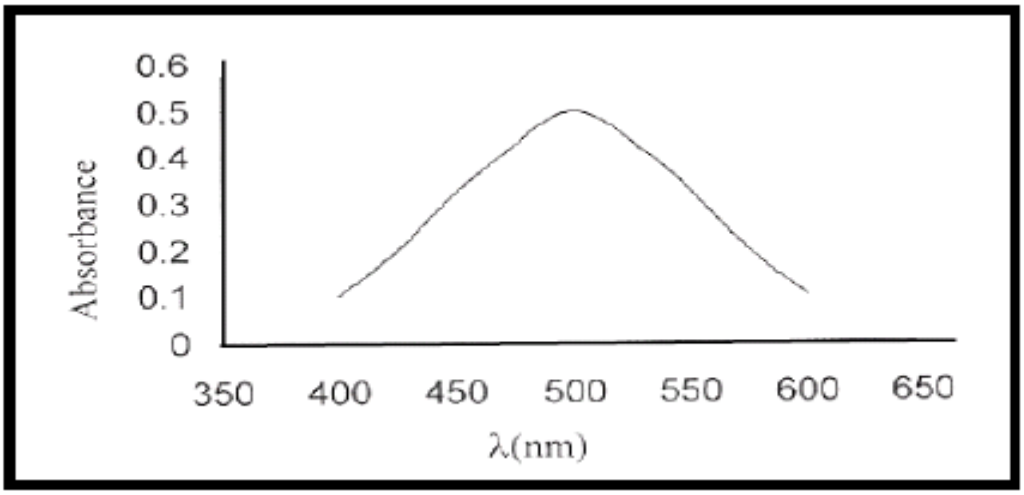


Fig. (1)
Electronic Spectra of CT complex between compound 7 and DDQ

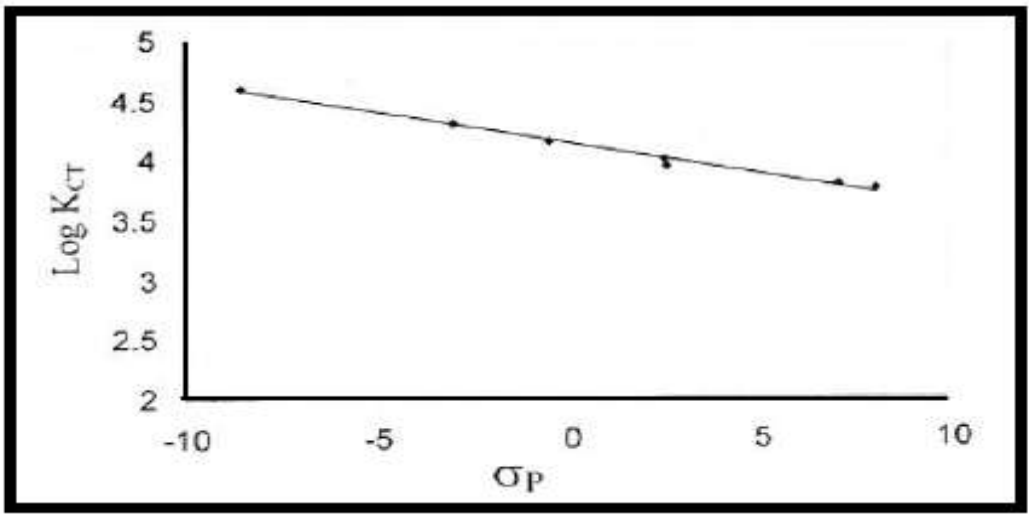
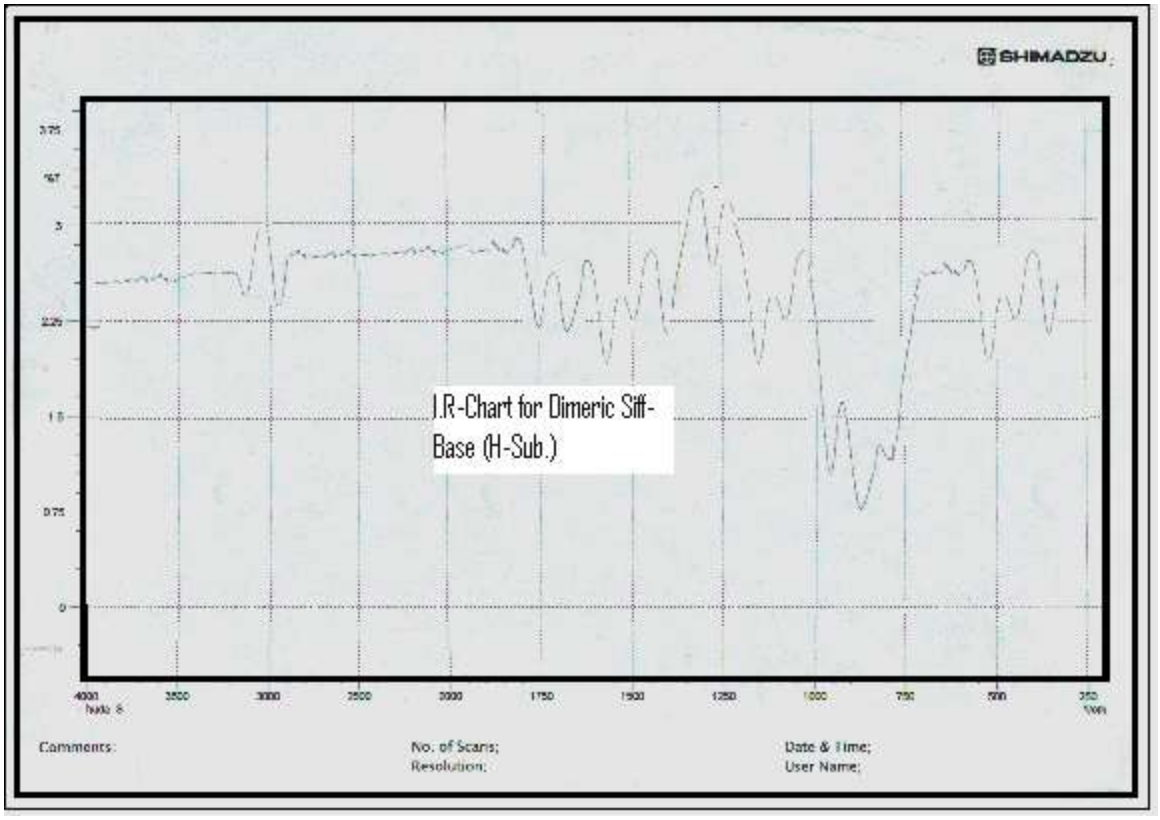
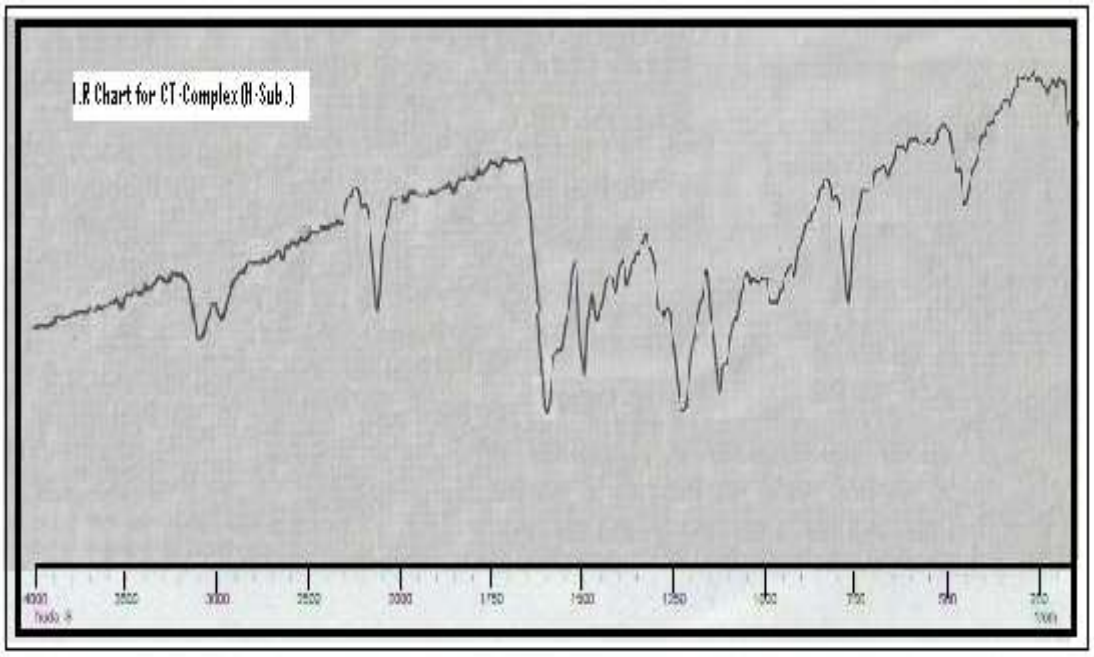


Fig. (2)
The Relation between logKCT complexes of compounds (1-7) and Hammett σ-para Substituents





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