The Effect of Solvents on the Electronic Absorption Spectra of Mesoionic 1,3,4-Thiadiazolium-2-thiolate Derivatives

A. M. Kiwan and H. M. Marafie

Department of Chemistry, University of Kuwait, Kuwait

Received July 28, 1976

The electronic absorption spectra of 4,5-diphenyl-, 4-phenyl-5-(4-fluorophenyl)-, 4-phenyl-5-(4-chlorophenyl)-, and 4-phenyl-5-methyl-1,3,4-thiadiazolium-2-thiolates have been measured in twenty-one pure solvents, aqueous ethanol and acetone solutions and cyclohexane-chloroform mixtures. They were found to exhibit three characteristic absorption bands; the first in the range 330-440 nm, the second at 260-280 nm and the third near 200 nm. The first band was assigned to n → π^* transition whereas the other two bands were assigned to $\pi \rightarrow \pi^*$ transition. The n → π^* transition band was found to be very sensitive, and the polarity of solvents, and some correlations between well-known solvent polarity parameters and the transition energies of these compounds have been presented.

J. Heterocyclic Chem., **13**, 1273 (1976).

Introduction

The effect of solvents on the electronic absorption spectra of many substances were recognised a long time ago (1,2). This phenomenon which is known as solvatochromism, was attributed to the difference in stabilization of the ground and excited states of the solute molecules by intermolecular forces, which may increase or decrease their excitation energies (3).

A survey of the literature has shown a little information on the effect of solvents on the electronic absorption spectra of the mesoionic 1,3,4-thiadiazolium derivatives. Kiwan and Irving (4) have recently investigated the electronic absorption spectra of 4-phenyl-1,3,4-thiadiazolium-2-thiolate in fourteen pure solvents and aqueous ethanol, acetone and pyridine solutions. They reported that its characteristic long wavelength absorption band is very sensitive to the polarity of solvents and have demonstrated linear correlations between the Kosower Z (5) and the Winstein Y (6) polarity parameter on the one hand and its solvent-induced hypsochromic shifts on the other. Talukdar and Sengupta (7) have also investigated the effect of solvents on the corresponding long wavelength absorption band of 4,5-diphenyl-1,3,4-thiadiazolium-2-thiolate in five organic solvents and acetone-chloroform mixtures and have also reported linear correlation between the hypsochromic shifts and the Z polarity parameter.

This paper describes a further investigation on the effect of solvents on the electronic absorption spectra of 4,5-diphenyl-, 4-phenyl-5-(4-fluorophenyl)-, 4-phenyl-5-(4-chlorophenyl)-, and 4-phenyl-5-methyl-1,3,4-thiadiazolium-2-thiolates in twenty-one pure solvents, aqueous ethanol and acetone solutions and cyclohexane-chloroform mixtures. In an attempt to further our knowledge of these mesoionic compounds, we present some correlations between their solvatochromic shifts and some of the well-known polarity parameters. We have also made some tentative assignments for their characteristic absorption bands.

EXPERIMENTAL

Preparation of 4-Phenyl-5*R*-1,3,4-thiadiazolium-2-thiolates.

4,5-Diphenyl- Ia, 4-phenyl-5-(4-fluorophenyl)- Ib, 4-phenyl-5-(4-chlorophenyl)- Ic, and 4-phenyl-5-methyl-1,3,4-thiadiazolium-2-thiolates Id, were prepared according to Busch *et al.*, (8) *viz.*, by reacting the potassium salt of phenyl dithiocarbazinic acid with acyl or aroyl chloride. The crude products were purified by crystallization from ethanol-chloroform mixture and Table I summarizes their analytical data.

Solvents.

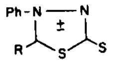
Spectroscopically pure, AnalaR or freshly distilled pure solvents were used throughout.

Uv. and Visible Absorption Spectra.

These were recorded on a Unicam SP 8000 spectrophotometer using 1 cm fused silica cells.

Table I

Analytical Data for 4-Phenyl-5*R*-1,3,4-thiadiazolium-2-thiolates



R	M.p.	Colour		C	H	N	S	Halogen
4-Fluorophenyl	208	orange	Required	55.33	3.13	9.72	22.22	6.60
			Found	58.4	3.2	9.9	22.3	6.2
4-Chlorophenyl	233	orange	Required	55.11	2.91	9.19	20.99	11.68
			Found	55.2	3.2	9.4	20.8	11.5
5-Phenyl	228	orange	Required	62.22	3.7	10.73	23.7	
			Found	62.1	3.8	10.5	23.7	
5-Methyl	215	yellow	Required	51.92	3.85	13.46	30.77	
			Found	52.1	3.9	13.3	30.6	

Elemental Analysis.

These were done at Alfred Bernhardt Mikroanalytisches laboratorium, West Germany.

Results and Discussion.

The electronic absorption spectra of Ia-d were recorded in twenty-one pure solvents, ethanol-water, acetone-water and chloroform-cyclohexane mixtures. They were found to exhibit three characteristic absorption bands as shown in the example Figure 1; the first at 330-440 nm, the second at 260-280 nm and the third around 200 nm.

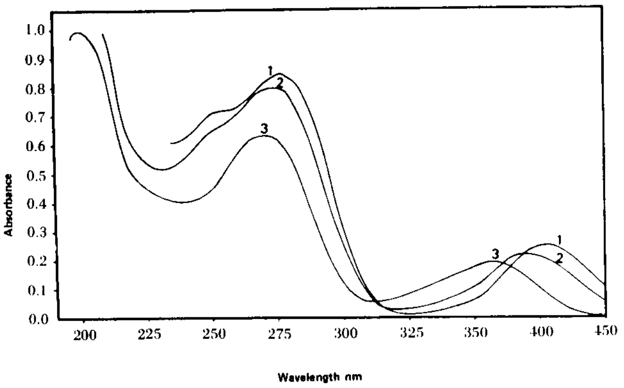


Figure 1: Absorption spectra of mesoionic 4,5-diphenyl-1,3,4-thiadiazolium-2-thiolate in 1, acetonitrile; 2, methanol and 3, water.

The longest wavelength band was very sensitive to the polarity of solvents and, as the polarity of solvents increased (Table II) the band was regularly blue-shifted, indicating that it is an n → π* transition band. Further hypsochromic shifts were observed in concentrated hydrochloric acid in every case which confirms our n → π* assignment.

The corresponding long wavelength band of 4-phenyl-1,3,4-thiadiazolium-2-thiolate has been previously ascribed (4) to π → π* transition owing to the finding that 1*N* hydrochloric acid has not shifted its position. Although this is actually true, 1*N* hydrochloric acid is now found to be too weak to differentiate between n → π* and π → π* transitions for such feebly basic (pK_a HB^+ -2.46 to -2.63) (9) compounds. Unfortunately, Talukdar *et al.*, (7) have also made a similar assignment for the corresponding long wavelength band of 4,5-diphenyl-1,3,4-thiadiazolium-2-thiolate presumably on the basis of its intensity. The molar absorptivity of this band seems actually to be rather high for a normal n → π* transition but we attributed that to some slight interaction between the n → π* and π → π* transition in the mesoionic system.

The positions of the second and third (shortest wavelength) bands as well as their molar absorptivities ($\epsilon \approx 2 \times 10^4$) are characteristic of π → π* transitions. However, the second band disappears on acidification which is rather unusual for π → π* transition and may be also indicative of some degree of interaction with the n → π* transition in these compounds.

Correlation of Transition Energies in Pure Solvents with Polarity Parameters.

Good linear correlations between the transition energies (E_T) of these mesoionic compounds and Kosower Z-values (5), Dimroth-Reichardt E_T values (10) and Brooker X_B values (11) were observed in every case (Figures are not included). There were some deviations, however, in chloroform which suggested that its Z value should lie between 66.5 and 69. A similar anomaly for the same solvent has been reported by Kosower (5) himself who stated that its value lies in the range 63.2-71.6.

These linear correlations may be expressed by equation 1

$$E_{T(M)} = ay + b \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

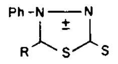
Table II

Ultraviolet and Visible Absorption Spectra of Mesoionic 4-Phenyl-5*R*-1,3,4-thiadiazolium-2-thiolates in Pure Solvents

Solvent	λ nm (ε)							
	4,5-Diphenyl		4-Phenyl-5-(4-fluorophenyl)		4-Phenyl-5-(4-chlorophenyl)		4-Phenyl-5-methyl	
Cyclohexane	440		440		448		393	
Ethyl acetate	435 (5270)	280 (18900)	434 (4920)	280 (19700)	440 (5670)	261 (22620)	383 (3770)	275 (12890)
Chloroform	421 (5720)	282 (20650)	421 (5180)	283 (20950)	432 (5360)	263 (25560)	380 (3390)	268 (12780)
Pyridine	427 (5870)		425 (4780)		433 (4810)		379 (2690)	
Acetone	421 (5700)		422 (5760)		427 (5790)		377 (4220)	
Acetonitrile	410 (5910)	278 (19780)	411 (5150)	278 (19840)	415 (6370)	280 (23070)	367 (3570)	268 (11790)
Nitromethane	406 (5490)		405 (4330)		413 (5060)			
Formamide	395 (5610)	278 (21730)	394 (6030)	279 (22650)	400 (5920)	282 (20300)	351 (3820)	269 (13030)
Isoamyl alcohol	405 (5080)	278 (19590)	404 (4520)	278 (19300)	411 (5580)	282 (20210)	364 (3100)	
n-Butanol	409 (5420)	277 (21000)	409 (5700)	277 (21000)	414 (5780)	280 (22180)	363 (3330)	264 (13570)
n-Propanol	408 (5490)	277 (21170)	406 (5740)	277 (19100)	414 (5710)	281 (21400)	362 (3530)	264 (13460)
Benzyl alcohol	390 (5150)		388 (4040)		394 (4840)		346 (3020)	
Ethanol	400 (4480)	275 (18180)	404 (6000)	278 (20750)	405 (5420)	280 (21270)	355 (3190)	260 (13120)
Methanol	395 (5520)	273 (19300)	397 (5500)	276 (20310)	400 (6220)	279 (21900)	354 (3740)	261 (13240)
Ethylene glycol	390 (4930)	276 (19250)	387 (5970)	276 (20120)	397 (5920)	279 (21150)	346 (3390)	263 (13130)
s-Butyl alcohol	411 (4700)	278 (18990)	409 (5010)	279 (20300)	414 (5630)	282 (20980)	263 (3010)	262 (13100)
Isobutyl alcohol	415 (4390)	278 (19130)	413 (5390)	279 (19890)	419 (4760)	280 (20880)	369 (2880)	270 (13250)
t-Amyl alcohol	400 (4940)	276 (19570)	404 (4960)	277 (19730)	410 (5430)	279 (21010)	360 (3210)	262 (12980)
Water	362 (6000)	271 (19260)	363 (6090)	275 (19050)	366 (5950)	275 (19900)	325 (3950)	260 (12750)
1*N* Hydrochloric acid	362 (6020)	270 (19250)	363 (6190)	275 (18080)	366 (6000)	272 (20110)	325 (3900)	260 (12520)
Isopropyl alcohol	406 (4730)	277 (15040)	405 (5370)	277 (16370)	408 (4610)	279 (15860)	362 (3280)	263 (13190)
10*N* Hydrochloric acid	318		320		323		278	

Table III

Correlations Between the Transition Energies of the Mesoionic 4-Phenyl-5*R*-1,3,4-thiadiazolium-2-thiolates with Various Polarity Parameters



Polarity (a) parameter	R			
	p-FC$_6$H$_4$-	p-ClC$_6$H$_4$	C$_6$H$_5$-	CH$_3$-
Z (5)	$E_T = (0.3 + 0.04) Z + 48 \pm 2$	$E_T = (0.31 \pm 0.02) Z + 46.1 \pm 1.7$	$E_T = (0.29 \pm 0.02) Z + 48.5 \pm 2$	$E_T = (0.34 \pm 0.02) Z + 53.4 \pm 2$
E_T (10)	$E_T (M) = (0.39 \pm 0.04) E_T + 51.6 \pm 2$	$E_T (M) = (0.43 \pm 0.04) E_T + 48.8 \pm 2$	$E_T (M) = (0.39 \pm 0.04) E_T + 51.8 \pm 1.8$	$E_T (M) = (0.44 \pm 0.04) E_T + 58.1 \pm 2.1$
X_B (11)	$E_T = (0.4 \pm 0.11) X_B + 48 \pm 6.0$	$E_T = (0.45 \pm 0.1) X_B + 44.7 + 5.8$	$E_T = (0.41 \pm 0.09) X_B + 47.7 + 5.4$	$E_T = (0.44 \pm 0.11) X_B + 54.8 \pm 6.2$

(a) References.

Table IV

Application of the Complementary Lewis Acid-Base Description to the Transition Energy of Mesoionic 4-Phenyl-5*R*-thiadiazolium-2-thiolates

R	Q_0	$\bar{\alpha}$	$\bar{\beta}$
CH_3	57.0 ± 4	80.4	19.5
C_6H_5	49.3 ± 5	85.7	14.3
p-FC_6H_4	50.3 ± 5	87.6	12.4
p-ClC_6H_4	47.0 ± 5	95.7	4.3

Table V

Sensitivities of Mesoionic Compounds to Changes in Solvent Polarity

Mesoionic Compound	R-value
4,5-Diphenyl-1,3,4-thiadiazolium-2-thiolate	0.366
4-Phenyl-5-(4-fluorophenyl)-1,3,4-thiadiazolium-2-thiolate	0.322
4-Phenyl-5-(4-chlorophenyl)-1,3,4-thiadiazolium-2-thiolate	0.353
4-Phenyl-5-methyl-1,3,4-thiadiazolium-2-thiolate	0.288
4-Phenyl-1,3,4-thiadiazolium-2-thiolate (4)	0.230
2,3-Diphenyl-2*H*-tetrazolium-5-thiolate (4)	0.800
1,4-Diphenyl-1,2,4-thiazole-2-one (18)	0.386
3-(5-tolyl)-*pseudo*-1,2,3-thiadiazoline (18)	0.224
4,5-Diphenyl-1,3,4-oxadiazolium-2-thiolate (18)	0.759
1,4,5-Triphenyl-*pseudo*-1,3,4-thiazole-2-thione (18)	0.493
4,5-Diphenylisosydnone (18)	0.277
3-Phenylsydnone	0.080

where $E_T(M)$ is the transition energy of the mesoionic compound, y is the polarity parameter Z, E_T or X_B, a and b were determined by the method of least squares and have the values given in Table III.

Correlation with the Acid-Base Character of Solvents.

In a recent study, Krygowski and Fawcett (12) described solvent effects in such a way that all solute-solvent interactions influencing the various physical and chemical properties can be defined in terms of the general concept of Lewis acidity and basicity of the solvent. They postulated that the solvent effect on a physicochemical quantity Q may be expressed as the linear function of two independent but complementary parameters describing the Lewis acidity A and Lewis basicity B of a given solvent. Thus

$$Q = Q_0 + \alpha A + \beta B \quad \dots\dots\dots\dots\dots\dots \quad (2)$$

where α and β are constants describing the sensitivity of the property Q to the acidic and basic properties of the solvent and Q_0 is the physicochemical quantity in absence of solvent interaction. The Dimroth-Reichardt parameter (10) E_T, and Gutmann (13) donor number DN were chosen as measures for the acidity and basicity of the solvent respectively. Hence equation 2 may be rewritten as

$$Q = Q_0 + \alpha E_T + \beta DN \quad \dots\dots\dots\dots\dots \quad (3)$$

Table VI

Ultraviolet and Visible Spectra of 4-Phenyl-5*R*-1,3,4-thiadiazolium-2-thiolates in Ethanol-Water Mixtures

Ia, R = C_6H_5; Ib, R = p-FC_6H_4; Ic, R = p-ClC_6H_4; Id, R = CH_3

Solvent v/v% Ethanol-water	Compound	λ_3 max, nm	E_T Kcal. mole^{-1}
98	Ia	400	71.48
	Ib	404	70.77
	Ic	410	69.73
	Id	355	80.54
90	Ia	398	71.85
	Ib	398	71.85
	Ic	403	70.94
	Id	354	80.76
80	Ia	394	72.56
	Ib	392	72.93
	Ic	397	72.02
	Id	351	81.45
70	Ia	389	73.51
	Ib	389	73.51
	Ic	393	72.76
	Id	347	82.39
60	Ia	386	74.08
	Ib	385	74.25
	Ic	391	73.13
	Id	343	83.34
50	Ia	384	74.45
	Ib	383	74.65
	Ic	389	73.51
	Id	341	83.86
40	Ia	381	75.05
	Ib	379	75.45
	Ic	386	74.08
	Id	338	84.60
30	Ia	375	76.24
	Ib	374	76.45
	Ic	380	75.25
	Id	335	85.34
20	Ia	371	77.05
	Ib	372	76.85
	Ic	--	--
	Id	333	85.86
10	Ia	369	77.48
	Ib	369	77.48
	Ic	--	--
	Id	330	86.64
0	Ia	362	78.98
	Ib	363	78.76
	Ic	366	78.11
	Id	325	87.97

Table IV summarizes the results of applying Krygowski and Fawcett's equations for the determination of the percentage contribution of solvent acidity ($\bar{\alpha}$) and basicity ($\bar{\beta}$) to the transition energies of the mesoionic 1,3,4-thiadiazolium derivatives. They were calculated for ethyl acetate, pyridine, acetone, acetonitrile, nitromethane, ethanol and water which gave the best linear plot of the transition energies against Dimroth-Reichardt E_T (10). The results (Table IV) indicated that these solvents behaved mainly as Lewis acids as their $\bar{\alpha}$ values ranged from 80-96. The presence of the electron donating methyl group at C (5) of the mesoionic compound has obviously enhanced the relative acidic character of the solvents whereas the electron withdrawing fluorine or chlorine atom in the *para* positions of the phenyl groups attached to the same C (5) have produced opposite effects presumably by increasing and decreasing the basicities (12) of the mesoionic compounds, respectively.

Correlation of the Transition Energies with Brownstein - S Values (14).

The hypsochromic shifts of Ia-d in various solvents have been also correlated with Brownstein S values, and the corresponding R parameter (14) which describes the sensitivity of compounds towards solvent polarity was determined and compared with the corresponding values of other mesoionic compounds (Table V).

The results indicate that the introduction of electron donating group like CH_3 at C (5) has decreased its R value whereas the presence of phenyl, *p*-chlorophenyl-, or *p*-fluorophenyl- has enhanced it. It is also obvious that 1,3,4-thiadiazolium-2-thiolates are relatively less sensitive to the polarity of solvents than 2,3-diphenyl-2*H*-tetrazolium-5-thiolate and its analogues, although they are apparently more sensitive than a few other mesoionic compounds (Table V).

Correlation Between the Transition Energies and Y (6) Values of Ethanol-Water and Acetone-Water Mixtures.

Excellent linear relationships between the transition energies of mesoionic 1,3,4-thiadiazolium-2-thiolates and Winstein Y (6) values in ethanol-water mixtures (Table VI) or acetone-water (Table VII) mixtures are observed in every case. The straight lines (plots not included) were found to converge with increasing water content to a Y value in the range 3.5-3.6 for pure water which is in good agreement with its reported value (3.493) by Grunwald and Winstein (6).

The corresponding plots (not included) with Brownstein S parameter were found to deviate from linearity as the water increased beyond 50% implying that the ionising power of acetone-water mixtures as expressed by the S values changes rather irregularly.

Table VII

Ultraviolet and Visible Spectra of 4-Phenyl-5*R*-1,3,4-thiadiazolium-2-thiolates in Acetone-Water Mixtures

Ia, R = C_6H_5; Ib, R = *p*-FC_6H_4; Ic, R = *p*-ClC_6H_4; Id, R = CH_3

Solvent v/v% Acetone-water	Compound	λ_3 max, nm	E_T Kcal. mole^{-1}
100	Ia	421	67.91
	Ib	422	67.75
	Ic	427	66.96
	Id	377	75.85
90	Ia	410	69.73
	Ib	410	69.73
	Ic	417	68.56
	Id	369	77.48
80	Ia	401	71.31
	Ib	401	71.31
	Ic	409	69.90
	Id	361	79.19
70	Ia	396	72.19
	Ib	397	72.02
	Ic	403	70.93
	Id	356	80.31
60	Ia	391	73.12
	Ib	391	73.12
	Ic	399	71.65
	Id	351	81.45
50	Ia	383	73.51
	Ib	388	73.71
	Ic	393	72.76
	Id	344	83.11
40	Ia	383	74.65
	Ib	383	74.65
	Ic	388	73.68
	Id	339	84.34
30	Ia	377	75.83
	Ib	378	75.63
	Ic	384	74.45
	Id	--	---
20	Ia	373	76.65
	Ib	373	76.65
	Ic	379	75.45
	Id	--	---
10	Ia	369	77.48
	Ib	369	77.48
	Ic	--	---
	Id	--	---
0	Ia	362	78.93
	Ib	363	78.76
	Ic	366	78.11
	Id	325	87.97

Correlation Between the Transition Energies and the Mole Fraction of Cyclohexane in Cyclohexane-Chloroform Mixtures.

The characteristic long wavelength absorption band of

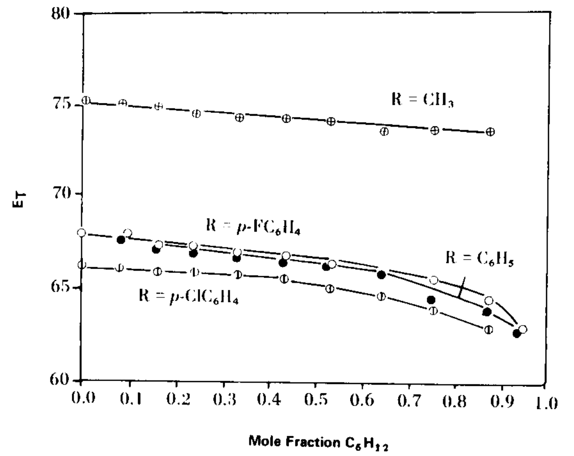


Figure 2: Plots of E_T-values of 4-phenyl-5*R*-1,3,4-thiadiazolium-2-thiolates against mole fraction of cyclohexane in chloroform.

the mesoionic 1,3,4-thiadiazolium-2-thiolates was found to undergo a red shift as the mole fraction of cyclohexane increased. The plots of transition energies of 4-phenyl-5-methyl-1,3,4-thiadiazolium-2-thiolate *vs.* the mole fraction of cyclohexane (Figure 2) gave a linear plot implying a regular change of polarity with the change of solvent composition. The corresponding plots (Figure 2) of the other mesoionic compounds were found to deviate from linearity as the mole fraction of cyclohexane increased beyond 50%.

This anomaly may be attributed to the relatively higher tendency of these mesoionic compounds to associate in non-polar solvents. Since 4-phenyl-5-methyl-1,3,4-thiadiazolium-2-thiolate is more polar (μ = 8.5 D) (16) than 4-phenyl-5-(4-chlorophenyl)-analogue (μ = 6.93) (16), its interaction with the solvent molecules is expected to be greater and hence results in a less red shift in non-polar solvents. By following similar reasoning, and since 4-phenyl-5-(4-fluorophenyl)- and 4,5-diphenyl derivatives also undergo red shifts as 4-phenyl-5-(4-chlorophenyl)-derivative, it may be implied that their dipole moments are quite close. However, the reported dipole moment (9.25 D) (16) of 4,5-diphenyl derivative is unexpectedly high compared with other mesoionic 1,3,4-thiadiazolium-2-thiolate derivatives.

The deviation from linearity in the cases of 4-chloro-, 4-fluoro- and 4,5-diphenyl- derivative may be due to intermolecular association and possibly the formation of the chain S . . . thiadiazolium ring . . . S . . . *etc.* Analogous chain formation has been established (17) by X-ray crystallography in the mesoionic 2,3-diphenyl-2*H*-tetrazolium-3-thiolate involving the interaction between the negatively exocyclic sulphur atom and the positively charged tetrazole ring.

REFERENCES AND NOTES

(1) A. Kundt, *Poggendrofs*, *Ann. Phys. Chem.*, N.F. **4**, 34 (1878).

(2) S. E. Shepard, *Rev. Mod. Phys.*, **14**, 303 (1940); and references cited therein.

(3) G. Sheibe, E. Felger and Rosseler, *Ber.*, **60**, 1046 (1927).

(4) A. M. Kiwan and H. M. N. H. Irving, *J. Chem. Soc. B*, 898 (1971).

(5) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958); E. M. Kosower, *J. Chim. Phys.*, **61**, 230 (1964).

(6) S. Winstein, E. Grunwald and H. W. Jones, *J. Am. Chem. Soc.*, **73**, 2700 (1951).

(7) P. B. Talukdar and S. K. Sengupta, *J. Indian Chem. Soc.*, **47**, 51 (1970).

(8) M. Busch and H. Munker, *J. Prakt. Chem.*, **60**, 217 (1899); M. Busch, *ibid.*, **67**, 201 (1903).

(9) H. M. R. Marafie, M. Sc. Thesis, Kuwait University, 1975.

(10) K. Dimroth, C. Reichardt, T. Siepmann and F. Bohlmann, *Ann. Chem.*, **661**, 1 (1963); C. Reichardt, *Angew. Chem. Int. Ed. Engl.*, **4**, 29 (1965).

(11) L. G. S. Brooker, A. C. Craig, D. W. Heseltine, P. W. Jenkin and L. L. Lincoln, *J. Am. Chem. Soc.*, **87**, 2443 (1965).

(12) T. M. Krygowski and W. R. Fawcett, *ibid.*, **97**, 8, 2143 (1975).

(13) V. Gutmann and Wychera, *Inorg. Nucl. Chem. Letters*, **2**, 257 (1966); V. Gutmann and R. Schmied, *Coord. Chem. Rev.*, **12**, 263 (1974).

(14) S. Brownstein, *Can. J. Chem.*, **38**, 1590 (1960).

(15) A. Y. Kassim, Ph.D. (Kuwait University), 1975.

(16) C. W. Atkins, A. N. M. Bornes, P. G. Edgerly and L. E. Sutton, *J. Chem. Soc.*, 1194 (1949).

(17) Y. Kushi and Q. Fernando, *J. Am. Chem. Soc.*, **7**, 1965 (1970).

(18) P. B. Taluktar and S. K. Sengupta, *J. Indian Chem. Soc.*, **46**, 2, 182 (1969); P. B. Talukdar, S. K. Sengupta and Datta, *Indian J. Chem.*, **9**, 1018 (1971); *ibid.*, **48**, 6, 582 (1971); *ibid.*, **9**, 179 (1971).