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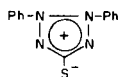
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The electronic absorption spectra of 2,3-di(2-fluorophenyl)-, 2,3-di(4-fluorophenyl)-, 2,3-di(2-chlorophenyl)-, 2,3-di(2-methylphenyl)-, 2,3-di(4-methylphenyl)- and 2,3-di(2-methoxyphenyl)-2H-tetrazolium-5-thiolates have been measured in pure and mixed solvents. They were found to exhibit three characteristic absorption bands at 480-380 nm, near 250 and near 210; the longest wavelength band of which was assigned to an  $n \rightarrow \pi^*$  transition.

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Although dehydrodithizone, I, (2,3-diphenyl-2H-tetrazolium-5-thiolate) was the first mesoionic compound to be synthesized in 1882 (2), its formulation as a mesoionic compound has been only confirmed by X-ray crystallography in 1969 (3). As may be anticipated from its structure (I), its long wavelength band [ $\lambda_{\text{max}}$  (chloroform) 460 nm] was found (4) to be very sensitive to the polarity of solvents; it underwent a regular hypsochromic shift as the polarity of solvents increased.



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We extend our investigation here to include six new analogues of dehydrodithizone and present their spectral data in thirteen pure solvents and three pairs of mixed solvents.

The electronic absorption spectra of the mesoionic tetrazolium compounds investigated here, were found to exhibit three absorption bands, the first of which appears in the range 380-480 nm, the second near 250 nm and the

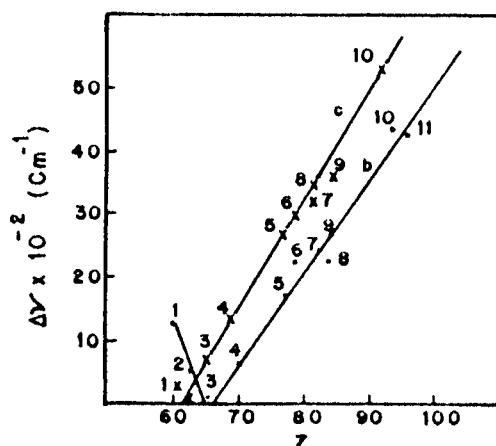


Figure 1. Correlation between the hypsochromic shifts,  $\Delta\nu$ , with  $z$  values for IIb and IIc in various solvents. Ethyl acetate 1, chloroform 2, acetone 3, acetonitrile 4, propanol 5, ethanol 6, formamide 7, methanol 8, ethanediol 9, water 10, 1 N hydrochloric acid 11.

third near 210 nm. The longest wavelength band was found to undergo a hypsochromic shift as the polarity of

Table 1

Analytical Data, Colours and Melting Points of Mesoionic Tetrazolium-5-thiolate Derivatives

Compound -2H-tetrazolium-5-thiolate	M.p. <sup>o</sup>	Colour		C	H	N	S	Halogen	MW
1) 2,3-di(2-fluorophenyl)-	154	Red	Calcd.	53.37	2.78	19.3	11.03	13.1	290
			Found	53.54	2.85	19.1	10.9	13.3	293
2) 2,3-di(4-fluorophenyl)-	189	Yellow	Calcd.	53.37	2.78	19.3	11.03	13.1	290
			Found	53.48	2.86	19.2	10.90	13.20	290
3) 2,3-di(2-chlorophenyl)	166	Orange	Calcd.	48.29	2.47	17.33	9.91	--	--
			Found	48.41	2.51	17.30	10.20	--	--
4) 2,3-di(2-methylphenyl)	168	Orange-red	Calcd.	63.80	4.95	19.85	11.34	--	282
			Found	64.00	5.00	18.80	11.00	--	290
5) 2,3-di(4-methylphenyl)	194	Yellow	Calcd.	63.80	4.95	19.85	11.34	--	--
			Found	63.60	4.90	19.30	10.90	--	--
6) 2,3-di(2-methoxyphenyl)	185	Red	Calcd.	57.30	4.16	17.83	--	--	--
			Found	57.15	4.23	18.00	--	--	--

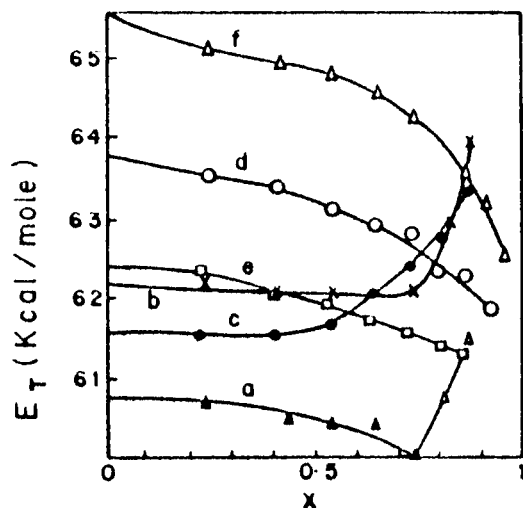


Figure 2. Correlation between the transition energies of IIa-IIf and the mole fraction X, of cyclohexane in admixture with chloroform.

solvents increased (Table 2). This phenomenon was similar to that observed previously with dehydrodithizone (4). However, the corresponding band of the latter compound was ascribed (4) to an  $\pi \rightarrow \pi^*$  transition owing to the observation that 1N hydrochloric acid has not changed its position. Although this is true, 1N hydrochloric acid is actually too weak to differentiate between  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions especially for such weak bases ( $pK_{BH^+} - 1.12$  to  $-2.05$ ) (5). As shown in Table 2, there was a remarkable hypsochromic shift on acidification with concentrated hydrochloric acid which suggest that the characteristic long wavelength band of dehydrodithizone and its present analogues should be assigned to an  $n \rightarrow \pi^*$  rather than  $\pi \rightarrow \pi^*$  transition.

Correlation of the Hypsochromic Shifts with Solvent Polarity Parameters:

a) Correlation with Kosower's  $Z(5)$  and Dimroth Reichardt's  $E_T(6)$  parameters.

Table 2

Electronic Absorption Data of Mesoionic Compounds IIa-IIf in Various Solvents  
[Values in Parentheses are Molar Absorptivities ( $1.\text{mole}^{-1} \text{cm}^{-1}$ )]

Solvent	IIa	IIb	IIc	II d	IIe	II f
Ethyl acetate	461	443	472	471 (1010)	466	464
Pyridine	462	456	471 (1210)	460 (1050)	462 (1350)	453 (1110)
Acetone	473 (940)	468 (870)	458 (1110)	445 (1040)	456 (1150)	448 (1020)
Chloroform	467 (950)	458 (900)	464 (1160)	456 (1020)	453 (1320)	437 (1030)
Acetonitrile	461 (1080)	456 (960)	446 (1180)	438 (920)	440 (1270)	434 (1120)
Nitromethane	458 (970)	453 (920)	449 (1110)	442 (1070)	440 (1020)	430 (1070)
Propanol	435 (1000)	435 (950)	418 (1200)	413 (990)	411 (1160)	410 (1010)
Ethanol	428 (1050)	424 (960)	412 (1170)	406 (1080)	405 (1320)	405 (1070)
Formamide	425 (1080)	423 (960)	409 (1190)	406 (1070)	405 (1470)	405 (1200)
Methanol	423 (970)	420 (930)	405 (1140)	402 (1030)	400 (1390)	399 (1000)
Ethanediol	420 (1050)	416 (940)	405 (1260)	400 (1150)	398 (1460)	398 (1200)
Water	393	390 (1040)	376	376	370	
1N HCl	393	390 (940)	375	370	370	
10N HCl	315	315	315	315	315	315

Table 3

Electronic Absorption Data of Mesoionic Compounds IIa-IIf in EThanol-Water Mixtures

% Ethanol v/v	IIa	IIb	IIc	II d	IIe	II f
99	427 (1060)	426 (970)	412 (1130)	406 (1040)	405 (1310)	405 (1130)
90	421 (1070)	420 (980)	(404 (1180)	402 (1060)	400 (1350)	400 (1140)
80	418 (1100)	417 (990)	400 (1220)	398 (1110)	395 (1340)	396 (1156)
70	414 (1110)	414 (1010)	398 (1240)	397 (1080)	392 (1400)	390 (1180)
60	412 (1130)	411 (1010)	395 (1250)	394 (1090)	390 (1460)	388 (1180)
50	409 (1140)	409 (1030)	392 (1230)	390 (1100)	387 (1510)	385 (1230)
40	406 (1180)	405 (1050)	388 (1310)	387 (1140)	384 (1520)	379 (1390)
30	403 (1210)	402 (1110)	385 (1340)	384 (1180)	382 (1670)	374 (1400)
20	400 (1260)	398 (1140)	384 (1400)	380 (1180)	380 (1700)	374 (1470)
10	398 (1250)	397 (1140)	380 (1400)	375 (1180)	378 (1710)	374 (1530)

Table 4

Electronic Absorption Data of Mesoionic Compounds IIa-IIf in Acetone-Water Mixtures  
[Values in Parentheses are the Molar Absorptivities ( $1.\text{mole}^{-1} \text{ cm}^{-1}$ )]

% Acetone (v/v)	IIa	IIb	IIc	II d	IIe	II f
100	474 (1010)	471 (950)	458 (1050)	456 (990)	453 (1220)	450 (1020)
90	451 (1010)	448 (930)	432 (1050)	430 (1020)	427 (1210)	429 (1070)
80	440 (1010)	439 (940)	421 (1090)	420 (1040)	416 (1270)	420 (1050)
70	434 (1040)	433 (950)	414 (1130)	415 (1060)	409 (1350)	413 (1090)
60	428 (1060)	425 (940)	408 (1190)	406 (1090)	403 (1430)	407 (1100)
50	422 (1070)	420 (960)	402 (1210)	401 (1080)	400 (1440)	400 (1130)
40	416 (1100)	411 (970)	397 (1250)	394 (1140)	390 (1460)	392 (1100)
30	410 (1120)	410 (1020)	391 (1280)	388 (1140)	388 (1570)	384 (1190)
20	405 (1170)	405 (1000)	386 (1320)	380 (1140)	382 (1660)	insoluble
10	402 (1190)	403 (950)	383 (1300)	378 (1100)	380 (1660)	insoluble

Good linear correlations were found between the hypsochromic shifts and some of the well-known polarity parameters *e.g.*,  $Z$  (Fig. 1) and  $E_T$ . However, IIa and IIb were found to behave rather anomalously in acetone, pyridine and ethyl acetate. This may be attributed to the tendency of these mesoionic compounds to undergo molecular association in weakly polar solvents. They are the weakest bases of the series, (-1.85 and -2.05 (5) respectively) and such association may arise from the interaction of the partially negative sulphur atom of one molecule with the partially positive tetrazolium ring of another. This molecular association in non-polar solvents will decrease the energy of the ground state, and hence leads to hypsochromic shifts.

#### b) Spectral Shifts in Ethanol-Water and Acetone-Water Mixtures.

Regular hypsochromic shifts of the absorption bands of the mesoionic compounds were also observed on increasing the concentration of water in its mixtures with ethanol or acetone as shown in Tables 3 and 4, respectively. Our extrapolated values of 3.64-4.0 for pure water and  $S$  value (0.025) for 80% acetone-water are close to the corresponding values reported in the literature (8,9).

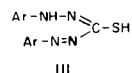
#### c) Spectral Shifts in Cyclohexane-Chloroform Mixtures.

The mesoionic derivatives investigated here may be classified into two categories according to the effect of composition of cyclohexane-chloroform mixtures on their transition energies. In the first category (Fig. 2) which comprises II d, IIe, and II f the transition energies of the longest wavelength decrease (red-shifted  $\lambda$  max) in an apparently irregular manner as the mole fraction of cyclohexane increased. In the second category, the transition energies of IIa, IIb, and IIc were found to decrease at first on the addition of cyclohexane until its mole fraction was about 0.5. As the concentration of cyclohexane increased further, the transition energy

started to increase (blue-shifted  $\lambda$  max). This behaviour may be also attributed to the tendency of these three mesoionic derivatives, which are weaker bases (4) than the other derivatives, to undergo molecular association in such non polar media where the concentration of cyclohexane becomes predominant.

#### EXPERIMENTAL

The dehydrodithizone analogues investigated here are: 2,3-di-(2-fluorophenyl)-, IIa; 2,3-di(2-chlorophenyl)-, IIb; 2,3-di(2-methylphenyl)-, II d; 2,3-di(4-methylphenyl)-, IIe; and 2,3-di(2-methoxyphenyl)-2*H*-tetrazolium-5-thiolate, II f, have been prepared by oxidising the parent 1,5-diaryl-3-mercaptoformazans, III, with potassium hexacyanoferrate (III) according to the method used by Corwin (10) for the preparation of dehydrodithizone. The only modification here was the use of carbon tetrachloride instead of chloroform which was found to improve the yield and enhance its purity. Table I summarises the analytical data of the mesoionic compounds.



#### Solvents.

Freshly distilled solvents were used throughout and deionized water was also used.

#### Ultraviolet and Visible absorption spectra.

These were measured on a unicam sp 8000 recording spectrophotometer using 10 mm fused silica cells.

#### Elemental Analyses.

These were done at Alfred Bernhardt-Mikroanalytisches Laboratorium, West Germany.

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