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Spectrophotometric Studies on Some 1,3,5-Triphenyl Formazans

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Some 1,3,5-triphenyl formazans were prepared. The spectra of these compounds were scanned in different organic solvents and water. The values of wavelength maxima (λ_{max}) of the bands and the corresponding molar absorptivities (ε_{max}) were calculated. The spectra in ethanol display mainly three sets of bands, each comprising four bands lying at wavelength ranges 222-265, 250–303, 337–388 and 417–505 nm respectively. The bands were assigned to the different electronic transitions. The effect of substituents on the position of λ_{max} was studied. The effect of different solvents on the position of the C.T. bands was studied, an attempt to correlate the position of these bands with different solvent parameters was tried. It was found that, there is no single parameter governing the band shift, but the shift in band position is the resultant of the effect of different parameters.

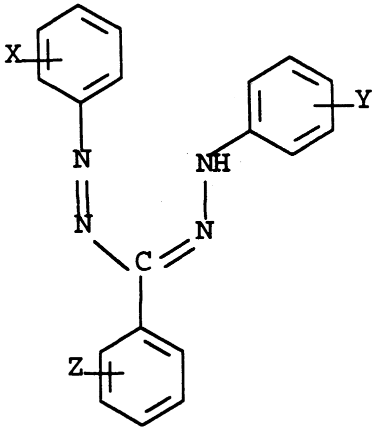
INTRODUCTION

Formazans are those compounds which contain the characteristic chain of atoms —N=N—C=N—NH—. Such compounds form a distinct class with characteristic properties. Their structure was first elucidated by Bamberger[1] and Pechmann.[2] Formazans serve as good analytical reagents, dyestuffs and play a vital role in many biological and industrial processes.[3] Spectrophotometric studies on formazans show that most formazans absorb fairly intensively at wavelengths in the red and violet regions[4] and this gives rise to their characteristic intense colours. They also absorb strongly in the ultraviolet region at about 250–350 nm.

Spectrophotometric studies on formazans including absorption spectra[5, 6] of the compounds, determination of the acid dissociation constants[7, 9], and their use as analytical reagents for spectrophotometric determination of various metal ions[10–12] were carried out.

Recently, some new triphenyl formazans were prepared[13] and their structure was studied by potentiometry, IR, NMR and TGA data.

The present investigation aims to study the absorption spectra of some triphenyl formazans in the UV and visible regions. Band assignment and solvent effect on the band position of these compounds have been discussed. The triphenyl formazans studied have the following structural formula:



where: X = Y = Z = H (I); X = Y= H, Z = o-NO_2 (II); X = Y = H, Z =p-NO_2 (III); X = Y = H, Z = o-OH (IV); X = Y = H, Z = p-CH_3 (V); X = Y = H, Z = p-Cl (VI); Y = Z = H, X = o-$AsO(OH)_2$ (VII); Y = Z = H, X = o-OH (VIII); X = o-$AsO(OH)_2$, Y = H, Z = p-NO_2 (XI).

EXPERIMENTAL

The chemicals used in this investigation were all of the highest purity available. The 1,3,5-triphenyl formazans were prepared by coupling the corresponding diazotized amine with the substituted phenyl hydrazone in NaOH medium as described before.[14] The resulting precipitates were twice recrystallized from the appropriate solvent. The purity of the prepared formazans were confirmed by elemental analysis and m.p. constancy.[13] Stock 10^{-3} M solutions of the formazans were prepared by dissolving an accurately weighed amount of the recrystallized product in the appropriate volume of the required solvent and the stock solutions were diluted to contain the amount required for spectrophotimetric measurements. The organic solvents used were either spectroscopic pure from BDH or purified according to recommended methods.[14] The absorption spectra were scanned within the UV and visible regions using Perkin-Elmer Lambda 4B spectrophotometer with 1 cm matched quartz cell.

RESULTS AND DISCUSSION

The electronic absorption spectra of all the formazans (I–IX) were scanned in some organic solvents of different polarities as ethanol, methanol, 1-propanol, iso-propanol, *n*-butanol, iso-butanol, dioxane, ethyl acetate, methylene chloride, DMF, DMSO, benzene, toluene, carbon tetrachloride, cyclohexanol, water, glacial acetic acid, 1-pentanol, acetone, cyclohexane, chloroform and *n*-hexane. The values of the wavelength maxima (λ_{max}) of the bands and the corresponding molar absorptivities (ε_{max}) are given in Table-1

TABLE-1 WAVELENGTH MAXIMA (λ_{max}) AND MOLAR ABSORPTIVITIES (ε_{max}) OF THE MAIN SPECTRAL BANDS

Solvent	Band A		Band B		Band C		Band D		Band A		Band B		Band C		Band D	
	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$
					I								II			
Iso-propanol	233	1.60	269	2.59	292	2.70	485	1.41	249	2.82	280 s	2.12	345	1.94	408	1.33
1-Propanol	233	1.22	268	1.70	297	2.30	485	1.45	248	2.16	288	1.26	346	1.83	407	1.28
Dioxane	—	—	270	1.64	298	2.12	486	1.26	—	—	288	1.39	342	1.76	404	1.31
n-Butanol	246	0.52	—	—	297	1.99	486	1.44	246	0.64	290	1.05	346	1.76	411	1.20
Ethyl acetate	—	—	266	1.57	297	2.16	484	1.40	—	—	287	1.19	342	1.66	399	1.17
CH_2Cl_2	—	—	271	1.63	299	2.24	486	1.41	246	2.04	288	1.38	338	1.64	402	1.15
Benzene	—	—	—	—	299	2.07	489	1.27	—	—	288	1.33	344	1.60	406	1.16
DMF	—	—	—	—	292	2.72	484	1.32	—	—	283	2.14	346	1.88	410 s	1.16
DMSO	—	—	—	—	303	1.74	487	1.29	—	—	297	0.92	349	1.66	405 s	0.98
Methanol	230	1.51	266	1.62	296	2.18	482	1.37	244	2.21	287	1.32	343	1.84	400 s	1.24
CCl_4	—	—	—	—	300	2.23	491	1.45	—	—	286	1.29	349	1.60	410	1.20
Cyclohexanol	—	—	—	—	330	0.88	488	1.42	—	—	—	—	347	1.71	413	1.18
Water	238 s	1.28	—	—	338	1.40	525 s	0.90	—	—	—	—	—	—	—	—
Glacial CH_3COOH	—	—	267	1.67	297	2.25	484	1.41	—	—	287	1.31	340	1.78	395	1.24
1-Pentanol	231	1.50	269	1.80	297	2.31	487	1.41	248	2.23	287	1.30	347	1.79	413	1.24
Acetone	—	—	—	—	334	0.95	479	1.19	—	—	—	—	342	1.92	393 s	1.34
Cyclohexane	231	1.05	—	—	296	2.21	490	1.54	250 s	1.52	285	1.16	348	1.43	406	1.11
Ethanol	227	1.96	263	1.78	296	2.30	484	1.42	250 s	2.50	286	1.38	345	1.91	417 s	1.34
Toluene	—	—	—	—	299	1.89	489	1.13	—	—	291	1.17	343	1.39	407	1.01
Chloroform	—	—	268	1.40	296	1.56	476 s	1.00	254	1.78	292 s	1.26	339	1.30	405	0.90
n-Hexane	230	1.58	269	1.92	296	2.45	488	1.55	246	2.29	284	1.27	347	1.72	406	1.26
Iso-butanol	231	1.52	267	1.76	297	2.30	485	1.47	247	2.22	288	1.26	346	1.83	411	1.24

Solvent	Band A		Band B		Band C		Band D		Band A		Band B		Band C		Band D	
	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}
					III								IV			
Iso-propanol	—	—	264	1.25	389	0.32	475	0.39	—	—	280 s	1.36	342	1.06	-	—
1-Propanol	222	0.51	254	0.82	388	0.58	475	0..72	245	1.40	295 s	1.12	344	1.07	—	—
Dioxane	—	—	259	0.42	393	0.31	476	0.28	—	—	298	1.10	336 s	1.08	—	—
n-Butanol	246	0.11	254	0.13	392	0.23	475	0.29	246	0.42	295	0.91	340	1.05	—	—
Ethyl acetate	320 s	0.22	—	—	387	0.27	475	0.31	—	—	—	—	335	1.01	—	—
CH_2Cl_2	—	—	257	1.38	401	1.06	476	1.27	245	1.32	—	—	330	1.18	—	—
Benzene	—	—	—	—	394	0.24	481	0.24	—	—	304	1.06	329 s	1.06	—	—
DMF	—	—	—	—	400 s	0.40	473	0.50	—	—	—	—	349	0.85	446 s	0.40
DMSO	—	—	—	—	405 s	0.40	475	0.49	—	—	306	0.74	354	0.80	447 s	0.30
Methanol	—	—	251	0.48	394	0.33	471	0.41	—	—	295 s	1.10	339	1.08	—	—
CCl_4	—	—	—	—	381	1.02	482	1.18	—	—	—	—	336	1.07	—	—
Cyclohexanol	—	—	—	—	307	0.14	478	0.29	—	—	—	—	342	1.19	—	—
Water	—	—	263	0.37	427	0.26	—	—	—	—	—	—	343 s	0.98	—	—
Glacial CH_3COOH	—	—	—	—	389	0.86	474	1.06	—	—	—	—	331	1.18	—	—
1-Pentanol	—	—	256	0.46	391	0.27	477	0.33	—	—	276 s	1.12	345	1.07	—	—
Acetone	—	—	—	—	399	0.43	471 s	0.36	—	—	—	—	340	1.15	—	—
Cyclohexane	—	—	285	—	378	—	485	—	241 s	0.34	286	0.54	338	0.53	—	—
Ethanol	—	—	247 s	0.86	389	0.41	473	0.50	—	—	—	—	338	1.10	—	—
Toluene	—	—	—	—	390	0.33	489	0.38	—	—	299	1.03	339	1.03	—	—
Chloroform	—	—	266	0.23	404	0.29	—	—	254	1.11	—	—	338	1.04	—	—
n-Hexane	—	—	258	0.72	371	0.32	480	0.37	—	—	—	—	334	0.70	—	—
Iso-butanol	—	—	253	0.38	393	0.24	474	0.29	—	—	295 s	1.08	341	1.04	—	—

Solvent	Band A		Band B		Band C		Band D		Band A		Band B		Band C		Band D	
	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$
				V								VI				
Iso-propanol	231	1.40	269	2.32	296	2.63	491	1.46	237	1.83	263	2.06	300	2.27	485	1.08
1-Propanol	231	1.17	269	1.86	298	2.44	491	1.46	241	1.49	261	1.58	303	2.11	485	1.07
Dioxane	—	—	271	1.78	299	2.25	492	1.28	—	—	263	1.50	303	1.94	486	0.94
n-Butanol	—	—	—	—	297	2.11	491	1.43	246	0.47	—	—	303	1.81	487	1.06
Ethyl acetate	—	—	268	1.68	298	2.28	490	1.39	—	—	261	1.46	304	2.01	484	1.05
CH_2Cl_2	—	—	272	1.84	300	2.47	491	1.47	243	1.50	264	1.55	305	2.15	487	1.08
Benzene	—	—	—	—	301	2.18	495	1.29	—	—	—	—	305	1.83	490	0.91
DMF	—	—	—	—	292 s	3.00	489	1.28	—	—	—	—	—	—	484	0.95
DMSO	—	—	—	—	302	2.01	492	1.29	—	—	—	—	308	1.67	486	0.93
Methanol	229	1.38	268	1.79	297	2.34	487	1.41	234	1.71	260	1.54	302	2.04	482	1.05
CCl_4	—	—	—	—	301	2.30	497	1.41	—	—	—	—	306	2.03	492	1.04
Cyclohexanol	—	—	—	—	328	0.87	494	1.42	—	—	—	—	329	1.06	488	1.10
Water	—	—	—	—	300 s	0.56	—	—	238	1.15	—	—	340	0.99	—	—
Glacial CH_3COOH	—	—	269	1.77	297	2.34	489	1.38	—	—	—	—	302	2.00	484	1.01
1-Pentanol	231	1.31	270	1.86	299	2.43	492	1.45	236	1.69	263	1.62	—	—	487	1.06
Acetone	—	—	—	—	—	—	486	1.24	—	—	—	—	333	0.97	481	0.93
Cyclohexane	231	0.82	—	—	297	2.25	496	1.43	234	1.16	—	—	302	1.98	491	1.11
Ethanol	227	1.76	269	1.91	297	2.41	489	1.44	235	1.65	261	1.52	303	2.05	484	1.05
Toluene	—	—	—	—	299	2.01	494	1.14	—	—	—	—	304	1.85	490	0.92
Chloroform	—	—	273	1.53	297	1.68	485	1.05	—	—	260	1.47	299	1.41	484 s	0.74
n-Hexane	231	1.44	270	2.22	296	2.65	493	1.47	236	1.84	263	1.80	300	2.27	488	1.08
Iso-butanol	231	1.35	269	1.89	298	2.45	491	1.46	235	1.70	262	1.61	303	2.08	486	1.06

Solvent	Band A		Band B		Band C		Band D		Band A		Band B		Band C		Band c	
	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}	λ nm	ε × 10^{-4}
	VII								VIII							
Iso-propanol	233	2.16	292 s	1.40	—	—	494	0.45	237	2.02	264	1.75	300	1.88	503	1.08
1-Propanol	243	1.83	293	1.31	333 s	0.82	497	0.45	241	1.66	263	1.52	302	1.78	503	1.06
Dioxane	—	—	293	1.29	336 s	0.84	509	0.41	—	—	269	1.61	301	1.71	527	1.06
n-Butanol	246	0.42	292	1.10	332 s	0.80	493	0.42	246	0.44	—	—	300	1.33	503	0.86
Ethyl acetate	—	—	292	1.18	339 s	0.72	503	0.40	—	—	—	—	301	1.49	520	0.86
CH_2Cl_2	—	—	291	1.31	331 s	0.86	503	0.40	243	1.78	269	1.68	301	1.47	535	0.99
Benzene	—	—	291	1.24	339 s	0.70	508	0.39	—	—	—	—	301	1.54	536	0.99
DMF	—	—	301	1.73	—	—	506	0.92	—	—	—	—	305	1.60	506	0.92
DMSO	—	—	300	0.89	336 s	0.60	507	0.40	—	—	—	—	308	1.29	510	0.87
Methanol	232	2.17	289 s	1.34	—	—	491	0.45	235	1.84	263	1.55	300	1.82	500	1.14
CCl_4	—	—	294	1.22	—	—	505	0.39	—	—	—	—	299	1.51	534	0.91
Cyclohexanol	—	—	—	—	335	0.69	507	0.42	—	—	—	—	329	0.54	511	0.75
Water	241 s	2.00	300 s	1.04	417	0.52	—	—	236	1.31	—	—	—	—	—	—
Glacial CH_3COOH	—	—	292 s	1.20	324 s	0.70	497	0.38	—	—	—	—	—	—	—	—
1-Pentanol	234	2.09	292	1.32	—	—	493	0.43	237	1.95	265	1.54	302	1.77	506	1.04
Acetone	—	—	—	—	335	0.77	504	0.45	—	—	—	—	—	—	495	1.01
Cyclohexane	229	—	285	—	334	—	521	—	232 s	0.42	289 s	0.86	301	0.92	533	0.93
Ethanol	—	—	289 s	1.44	—	—	500	0.45	—	—	266	1.71	301	2.02	502	1.30
Toluene	—	—	295	1.20	—	—	505	0.39	—	—	—	—	300	1.38	536	0.84
Chloroform	251	0.16	288 s	1.08	329	0.75	505	0.37	250	1.54	269	1.42	298	1.21	536	0.90
n-Hexane	227	1.42	289	1.00	332 s	0.66	505	0.26	237	2.33	271	1.79	294	1.63	527	0.82
Iso-butanol	234	1.92	292	1.10	336 s	0.68	493	0.34	237	2.37	—	—	300	1.51	503	0.76

Solvent	Band A		Band B		Band C		Band D	
	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$	λ nm	$\varepsilon \times 10^{-4}$
				IX				
Iso-propanol	266	2.11	286	2.01	356	1.09	503	2.04
1-Propanol	263	1.43	294	1.53	355	1.08	504	1.97
Dioxane	270 s	1.36	294	1.54	361	1.24	516	1.75
n-Butanol	—	—	293	1.41	357 s	1.04	503	2.11
Ethyl acetate	264	1.39	294	1.56	361	1.28	506	1.95
CH_2Cl_2	266	140	294	1.55	363	1.70	513	1.92
Benzene	—	—	293	1.56	355	1.23	515	1.82
DMF	—	—	295 s	1.36	—	—	494	0.45
DMSO	—	—	299	1.22	377	1.02	512	2.03
Methanol	262	1.42	292	1.47	354	1.17	504	1.88
CCl_4	—	—	298	1.66	350	1.28	511	1.95
Cyclohexanol	—	—	—	—	360	1.14	509	1.92
Water	260 s	0.96	300 s	0.90	428	0.91	—	—
Glacial CH_3COOH.	—	—	292	1.49	349	1.27	507	1.71
1-Pentanol	264	1.59	294	1.64	258 s	1.02	503	2.09
Acetone	—	—	—	—	366	1.31	508	1.91
Cyclohexane	—	—	286	—	351	—	512	—
Ethanol	261	1.58	290	1.58	355	1.18	505	1.92
Toluene	—	—	296	1.55	353	1.26	513	1.85
Chloroform	269	1.35	292	1.42	362	1.16	514	1.97
n-Hexane	270 s	1.14	286	1.16	342 s	0.74	509	0.90
Iso-butanol	263	1.53	294	1.60	355 s	1.08	504	2.11

Band Assignments

The spectra of the studied formazans in ethanol display mainly three sets of bands. The first set comprises two bands (bands A and B) lying within the wavelength range 222–265 and 250–303 nm. These may be assigned to the medium energy level π–π^* electronic transition within the benzene ring (1La–1a) and the transition (1Lb–1A) of the aromatic system, respectively.[15] These bands are characterized by their high molar absorptivities ($\varepsilon \approx 10^4$), which may be taken as evidence for these assignments.

The second set comprises mainly one band (band C) appearing within the range 337–388 nm. This band is believed to be due to an intramolecular charge transfer (C.T.) from the hydrazo group (C═N—NH—) to the aryl moiety joint to the carbon atom. This assignment may be assisted by the presence of this band in the spectra of the substituted formazans which contain electron withdrawing group, *e.g.*, NO_2 group.

The third set comprises one band (band D) lying within the range 417–505 nm assigned to $\pi - \pi^*$ transition within the azo group, influenced by intramolecular C.T. through the whole molecule. This band is shifted to lower wavelength (338 nm) in case of compound (IV). This may be explained by the presence of

OH group in the *o*-position to N=N group, which form intramolecular hydrogen bonding, and band was ascribed to the formation of the cyclic structure through hydrogen bonding.[16]

Effect of Substituent

There is a more or less linear realtionship between the variation of λ_{max} of the C.T. band and σ_x (Hammett's constant) of the substituent. Thus, Hammett's equation is valid in the form:

$$\lambda_X = \lambda_H - 19.5\sigma_X$$

This relation between variation of λ_{max} and σ_X is also linear for most of the other solvents used in this investigation.

Solvent Effect

It is well known that the bands due to local transitions are solvent insensitive, while the C.T. bands are sensitive to environmental changes. The shift in band position by changing solvent can be discussed in terms of dielectric constant of the solvent and the possibility of a specific solute-solvent interaction through formation of an intermolecular hydrogen bond between the solute and solvent molecules.[16] The forces participating in the solvent shift of the C.T. interaction bands are: (i) Polarization or dispersion forces resulting from the change in the refractive index of the medium, which leads to small shifts and is important in the caseswhere either the solute or solvent is of low polarity, and (ii) Red shift due to increased dielectric constant of the medium, which is important with solute or solvent molecules of moderate polarity.

One of the most important solvent parameters which shows a reasonable degree of correlation with transition energy is the static dielectric constant (D), or more precisely a function $\frac{D-1}{D+1}$, f(D) Φ(D),[17] where

$$f(D) = \frac{2(D-1)}{2D+1}, \quad \Phi(D) = \frac{D-1}{D+2}$$

Other solvent parameters which affect the transition energy are π^*[18], β[19] and Z[20]. All these parameters lead to a linear relation with transition energy if one of these parameters is the only one governing solvent shift.

The first set of bands (bands A and B) lying at shorter wavelengths is unaffected or slightly shifted to red with increasing solvent polarity. This small shift is in harmony with the fact that these bands are due to local transitions.

On the other hand, the positions of the C.T. bands (bands C and D) show a variation between wide limits. Generally, there is a red shift with increasing solvent polarity. This shift can be explained by the increased solvation stabilization of the excited state with increasing solvent polarity. However, the plots of $\frac{D-1}{D+1}$, f(D) and Φ(D) against λ_{max} are not strictly linear relations, except for moderately polar solvents (*e.g.*, ethanol, 1-propanol, iso-propanol, *n*-butanol, iso-butanol, acetone, DMF and DMSO), which give more or less linear relations with some compounds. Also, the plots of the other parameters (π^*, β and Z) are not strictly linear. This may be taken as an evidence that the spectral shifts are not governed solely by any of these parameters. Based on these results, it can be concluded that the shift in band position would be attributed to combined effects of the dielectric constant, refractive index, change in the solvation energies of the ground and excited states as well as the probable formation of the solute-solvent molecular complexes. Another possible factor is the changes in the strength of intermolecular hydrogen bonding between solute and solvent molecules. These effects contribute to the band shift, whether to higher or lower energy, and the observed shift is the resultant of the effect of different factors.

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