

The synthesis and spectral properties determination of 3-substituted phenyl-1,5-diphenylformazans

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Abstract

In this study novel 3-substituted-phenyl-1,5-diphenylformazans were synthesised with $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{OH}$ and $-\text{Br}$ groups at *o*-, *m*- and *p*-positions. Their structures were elucidated with ^1H -NMR, ^{13}C -NMR and IR spectroscopy. Their UV–vis spectra indicated that their λ_{max} showed a shift amount of which was dependent upon the type and position of the substituent on the ring. There was a good correlation between these shifts and Hammett substituent coefficients. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

There have been numerous formazans synthesised up to now [1–5]. Tetrazolium salts were employed in test indicators using their change in colour with their enzymatic reduction to formazans [6]. This technique gave satisfactory results on animal tissues, curage of peanuts [7], tumorous tissue of sunflower [8] and brucella determination in milk [9] and as a vitality test indicator of chick heart [10], bull sperm and egg yolk embryo [11].

It has also been utilised for analytical purposes and used in trace element determination [12,13] and it was found that when complexed with metals they could act as dyes [14–16]. Due this wide spread use of formazan it is necessary to synthesise its derivatives and investigate their properties.

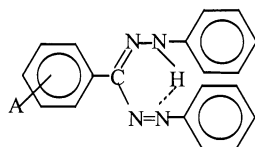
In this study, novel formazans with various substituents on 3-phenyl ring have been synthesised (Fig. 1) and their structures were elucidated with NMR and IR spectroscopy. The effect of substituents was also examined by the use of UV–vis spectra. The formazans we have synthesised have different tones of red depending upon the substituent attached to the 3-phenyl ring. Therefore, they have great potency for the dyestuff industry and the determination of λ_{max} values is of great importance in both the scientific and dye industry point of view

2. Experimental

2.1. General

The structures of the 3-substituted phenyl-1,5-diphenylformazans were determined with Gemini

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Compound	A	Compound	A
1 TPF	H	6 MTDPF	m-CH ₃
2 MBPDPF	m-Br	7 PTDPF	p-CH ₃
3 PBPDPF	p-Br	8 MMPDPF	m-OCH ₃
4 MHPDPF	m-OH	9 PMPDPF	p-OCH ₃
5 PHPDPF	p-OH		

Fig. 1. Structure of formazan derivatives.

Varian 200 MHz ¹H-NMR, ¹³C-NMR and MATTSON 1000FT-IR spectrophotometers. The substituent effect upon λ_{max} was evaluated by UV-160A Shimadzu spectrophotometer (with quartz cells 1 cm). The melting points of the compounds were determined using Buch 530 melting point apparatus. Substituted benzaldehydes, aniline, hydrazine and all the solvents employed were purchased from MERCK Germany in analar grade and used without further purification.

2.2. Synthesis

The synthesis of 1,3,5-triphenylformazan (TPF) was carried out following the route suggested by Busch and Pfeiffer [4] and Tezcan et al. [17] taking benzaldehyde (0.01 mol), aniline (0.01 mol) and phenylhydrazine (0.01 M) (m.p. 172–173 °C; lit: 170–173 °C, yield 78%). This compound was taken as the reference in the comparison of λ_{max} values. The other formazan derivatives were synthesised using the same route. Here we will only explain the synthesis of 3-(*m*-bromophenyl)-1,5-diphenylformazan (MBPDPF) as a reference and only mention the parts differing from this in the synthesis of the other derivatives.

2.2.1. Synthesis of 3-(*m*-Bromophenyl)-1,5-diphenylformazan (MBPDPF)

m-Bromobenzaldehyde (1.85 g, 0.01 mol) was placed in a round bottomed flask on magnetic stirrer and phenylhydrazine (1.08 g, 0.01 mol) was added to it in dropwise manner with constant stirring. Light yellow *m*-bromobenzaldehyde phenylhydrazone crystals precipitated out. It was kept stirring for 1 h and left on the bench for 1 day, then filtered out and recrystallised from methanol giving light yellow crystals. The precipitate washed with water and methanol and dried, yield: 96%. *m*-Bromobenzaldehyde phenylhydrazone (1.38 g, 0.05 mol) was dissolved in methanol (35 ml) by heating and stirring under reflux and kept at room temperature for coupling reaction.

A basic buffer solution was prepared dissolving NaOH (1.76 g) and sodium acetate (2.46 g) in methanol (35 ml) by heating–stirring under reflux and adding it to *m*-bromobenzaldehyde phenylhydrazone solution prepared as outlined above.

Diazonium solution was prepared taking aniline (0.47 g, 0.05 mol), concentrated hydrochloric acid (1.25 ml) and iced water (1.25 ml) and cooling them down to 0 °C. Then NaNO₂ solution (0.38 g) in water (1.5 ml) was added to it in dropwise

manner with constant stirring keeping the temperature between 0 and 5 °C.

The coupling reaction: the basic *m*-bromobenzaldehyde phenylhydrazone solution prepared as described above was placed into a ice-water bath and benzene diazonium chloride solution was added to it in dropwise manner with constant stirring. Ice cubes were added into the medium in order to keep the temperature at 0–5 °C. The mixture took a dark red color during this addition process. A bright red precipitate formed after the mixture was kept on the bench for two days. They were filtered out and recrystallised from methanol. The crystals were washed with water and methanol and dried in an oven at 60 °C.

2.2.2. Synthesis of 3-(*p*-bromophenyl)-1,5-diphenylformazan (PBPDPF)

The synthesis of this compound was carried out as outlined above.

2.2.3. Synthesis of 3-(*m*-hydroxyphenyl)-1,5-diphenylformazan (MHPDPF)

m-Hydroxybenzaldehyde (2.44 g, 0.02 mol) was dissolved in methanol (16.5 ml). It was reacted with phenylhydrazine (2.16 g, 0.02 mol) to give *m*-hydroxybenzaldehyde phenylhydrazone as mentioned above. *m*-Hydroxybenzaldehyde phenylhydrazone (2.12 g, 0.01 mol) was dissolved in methanol (16 ml) by heating and constant stirring. There were NaOH (7.5 ml, 10%) an equivalent amount of CH₃COONa added to it and it was then cooled to 0 °C. It was then coupled with an equivalent amount of benzene diazonium chloride solution. There appeared a crimson red colour after the reaction and an amorphous and resinous crimson red coloured formazan was formed. The best yield was obtained in acetic acid media in a pH range of 5–6. The product was kept under these conditions for 5 days and a brown-red coloured final product precipitated. The experiment was repeated several times.

2.2.4. Synthesis of 3-(*p*-hydroxyphenyl)-1,5-diphenylformazan (PHPDPF)

This compound was synthesised as outlined above for the synthesis of MHPDPF. Same

problems were also encountered here. The red-brown product was formed.

2.2.5. Synthesis of 3-(*m*-tolyl)-1,5-diphenylformazan (MTDPF)

m-Methylbenzaldehyde (2.40 g, 0.02 mol) was dissolved in methanol (20 ml) and reacted with phenylhydrazine (2.16 g, 0.02 mol) to give *m*-methylbenzaldehyde phenylhydrazone. It was then coupled with equivalent amount of benzene diazonium chloride at 0–5 °C giving a red coloured formazan.

2.2.6. Synthesis of 3-(*p*-tolyl)-1,5-diphenylformazan (PTDPF)

This was synthesised as outlined for MTDPF giving a bright red coloured product.

2.2.7. Synthesis of 3-(*m*-methoxyphenyl)-1,5-diphenylformazan (MMPDPF)

m-Methoxybenzaldehyde (2.72 g, 0.02 mol) was dissolved in methanol (16.5 ml). It was then treated with phenylhydrazine (2.16 g, 0.02 mol) and an equivalent amount of diazonium solution, which resulted in the formation of bright red coloured formazan.

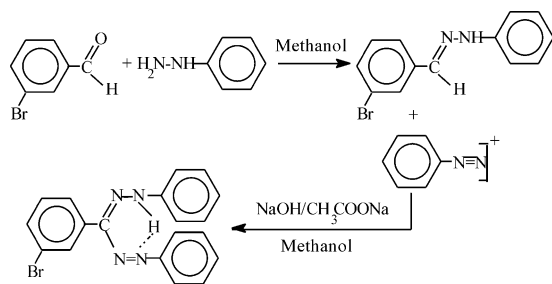
2.2.8. Synthesis of 3-(*p*-methoxyphenyl)-1,5-diphenylformazan (PMPDPF)

The synthesis of this compound was the same as outlined for MMPDPF above. However, the pH of the medium was adjusted to 4–6 by the addition of acetic acid (0.6 ml) and water (4 ml). A bright red coloured formazan was obtained.

3. Results and discussion

3.1. Structural determination

The formation of the substituted formazans by coupling of substituted benzaldehydephenylhydrazones and phenyl diazonium salts follows the route depicted in Scheme 1 [17,18]. The structure of the compounds was determined by the comparative investigation of the formazan structures given in Fig. 1, ¹H-NMR data in Table 1, ¹³C-NMR data Table 2 and IR data in Table 3.



Scheme 1. The route followed in the synthesis of formazans.

The fact that there occurred 15 aromatic H (*m*) and one NH hydrogen signal (*s*) in ^1H -NMR spectrum of TPF (Table 1) verifies the structure proposed in Fig. 1.

Table 2 shows that there are 9 C signals contrary to the expected 13 C signals. This can be

explained by the fact that the proton attached to hydrazone nitrogen in TPF molecule making hydrogen bond with azo nitrogen and causing chealation in the molecule and the presence of a symmetry plane as illustrated Scheme 2. This is in good accordance with literature [17,19].

When one investigates Table 1 to see the structure of newly synthesised formazans one can see that the compounds 2 and 3 corresponding to *m*-Br and *p*-Br give one N–H hydrogen signal in addition to 14 aromatic hydrogens while compounds 4 and 5 (*m*-OH and *p*-OH) display an additional OH hydrogen (probably coincides with NH signal) and compounds 6 and 7 (*m*-CH₃ and *p*-CH₃) contain signals belonging to three CH₃ hydrogens. Compound 8 and 9 (*m*-OCH₃ and *p*-OCH₃) also have three signals corresponding to

Table 1
Experimental and ^1H -NMR data of 3-substituted phenyl-1,5-diphenylformazans

Compound	Substituent (A)	m.p (°C)	Yield (%)	^1H -NMR data ^b		
				Aromatic H δ (ppm) ^a	Azo H δ (ppm) ^a	Other H δ (ppm)
1	H	172–173	63	8.20–7.26(15H) <i>m</i>	3.4(1H) <i>s, broad</i>	
2	<i>m</i> -Br	165–166	70	8.28–7.26(14H) <i>m</i>	1.6(1H) <i>s, broad</i>	
3	<i>p</i> -Br	194–195	75	8.03–7.26(14H) <i>m</i>	1.5(1H) <i>s, broad</i>	
4	<i>m</i> -OH	195–199	62	7.64–7.48(14H) <i>m</i>	4.79–4.72 <i>m</i>	Broad coincides with (OH)
5	<i>p</i> -OH	200–203	61	8.18–7.25(14H) <i>m</i>	1.8(1H) <i>s, broad</i>	2.2OH(1H) <i>m</i>
6	<i>m</i> -CH ₃	159–160	60	7.96–7.21(14H) <i>m</i>	1.6(1H) <i>s, broad</i>	2.47CH ₃ (3H) <i>s</i>
7	<i>p</i> -CH ₃	154–157	58	7.60–6.87(14H) <i>m</i>	1.6(1H) <i>s, broad</i>	2.41CH ₃ (3H) <i>s</i>
8	<i>m</i> -OCH ₃	160–162	71	7.79–6.90(14H) <i>m</i>	4.70–4.59(1H) <i>m</i>	3.92OCH ₃ (3H) <i>s</i>
9	<i>p</i> -OCH ₃	170–171	43	8.09–7.01(14H) <i>m</i>	1.62(1H) <i>s</i>	3.88OCH ₃ (3H) <i>s</i>

^a *m*: Multiplet, *s*: singlet.

^b The ^1H -NMR spectra were recorded with 200 MHz (in CDCl₃).

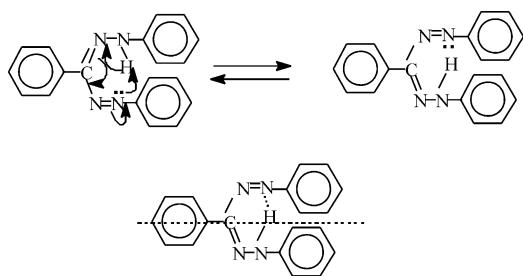
Table 2
 ^{13}C -NMR data (50 MHz in CDCl₃)

Compound	δ (ppm)	
	Imino-C (C=N)	Other carbons
1	148.41	141.63, 137.87, 129.87, 128.85, 128.03, 127.93, 126.35, 119.30 (total nine)
2	149.66	11.73, 141.58, 12.28, 131.85, 131.45, 130.63, 129.75, 126.26, 124.71, 120.88 (total 11)
3	149.72	138.44, 133.73, 133.45, 131.44, 19.68, 128.12, 123.75, 120.82 (total nine)
4	149.82	144.11, 142.05, 131.54, 131.39, 130.83, 120.85, 120.74, 119.88, 116.75, 114.67 (total 11)
5	149.91	143.15, 139.88, 131.44, 130.40, 129.64, 127.85, 120.95, 120.81 (total nine)
6	149.94	139.64, 139.33, 131.40, 130.47, 130.31, 129.42, 128.42, 125.12, 120.79, 120.63, 23.72 (CH ₃) (total 12)
7	146.90	140.48, 139.68, 134.66, 131.38, 131.32, 128.22, 121.96, 114.80, 23.41(CH ₃) (total ten)
8	161.86	149.87, 143.15, 141.20, 131.42, 129.52, 120.81, 120.53, 118.03, 115.11, 113.53, 57.33 (OCH ₃) (total 12)
9	161.50	150.01, 143.30, 132.21, 131.38, 129.28, 120.64, 115.98, 115.83, 57.35 (OCH ₃) (total 10)

Table 3
IR data of selected compound (in cm^{-1} , with KBr pellets)^a

Compound	IR data
1	3060 <i>s</i> (aromatic C–H), 3290 (N–H), 1610 (ar C=C), 1505 (C=N), 1455 (N=N), 1365 (C–N), 1250, 1200, 1090, 1060, 1035, 930, 905, 775, 705, 650 (fingerprint region) (CNNC lattice vibrations and aromatic inner plane bending)
2	3100 (aromatic C–H), 2570 (H–H), 1610 (aromatic C=C), 1520 (C=N), 1544 (N=N), 1370 (C–N), 1240, 1195, 1170, 1090, 1060, 1030, 900, 860, 840, 770, 705, 650 (fingerprint region)
3	3100 (aromatic C–H), 2570 (N–H), 1605 (aromatic C=C), 1450–1410 (N=N), 1310 (C–N), 1250–650 (fingerprint region)

^a The IR data for the other compounds are similar.



Scheme 2. Chelation.

methyl hydrogens in addition to aromatic hydrogens. These data show us that the structures comply with our expectance and the compounds contain the substituents mentioned above.

When Table 2 is examined it is seen that there are 11 C signals in compound 2 while it decreases down to 9 due to the symmetrical reasons i.e. the attachment of Br at *para* position in compound 3. The same phenomena was also observed in other formazan derivatives and the number of carbons observed was two less in *p*-substituted ones compared with *meta* substituted ones due to symmetrical considerations. According to these results one make out the following conclusions: first the expected structures were formed and second the fact there observed two less carbons in the case of *para* substitution proves the formation of symmetry.

Table 3 which gives the IR spectral data shows that all the vibrational bands expected from the proposed structures are present which further verifies these structures.

3.2. Substituent effect upon λ_{max} values

Table 4 gives the UV–vis data of formazans obtained by coupling substituted benzaldehyde-

Table 4
UV–visible absorption maxima of 3-substituted phenyl-1,5-diphenylformazans

Compound	$\lambda_{\text{max}1}$ (nm)	$\lambda_{\text{max}2}$ (nm)	$\lambda_{\text{max}3}$ (nm)	$\Delta\lambda_{\text{max}1}$ (nm)	σ (20)
1	487	301	272	–	–
2	488	304	274	+1	0.37
3	488	306	275	+1	0.26
4	480	301	258	–7	0.13
5	503	305	277	+16	–0.38
6	489	301	274	+2	–0.06
7	488	302	275	+1	–0.14
8	488	302	274	+1	0.10
9	508	300	–	+21	–0.12

phenylhydrazones with phenyl diazonium salts. Fig. 2 shows the spectra of TPF and its *m*-substituted phenylformazans displaying the shift in λ_{max} values as an example. The UV spectral $\lambda_{\text{max}1}$ data of *p*-substituted derivatives are very similar to these.

The broad peak observed between 480 and 490 nm in Fig. 2 is characteristic of formazan [17,18]. The peaks observed at 301 and 272 nm in the case of TPF are due to $n\text{--}\pi^*$ transitions of --N=N-- and --C=N-- groups. The other data relating to substituted formazans are given in Table 4.

When Table 4 is examined it is observed that there is a 1 nm shift in $\lambda_{\text{max}1}$ value towards higher wavelengths (bathochromic effect) with respect to TPF (487 nm) when 3 phenyl ring is substituted at *meta* and *para* position (488 nm). The fact that bromide behaves as result of two opposite effects as electron withdrawing inductively and electron donating as regards to resonance, it behaves as a weak electron donator in this case.

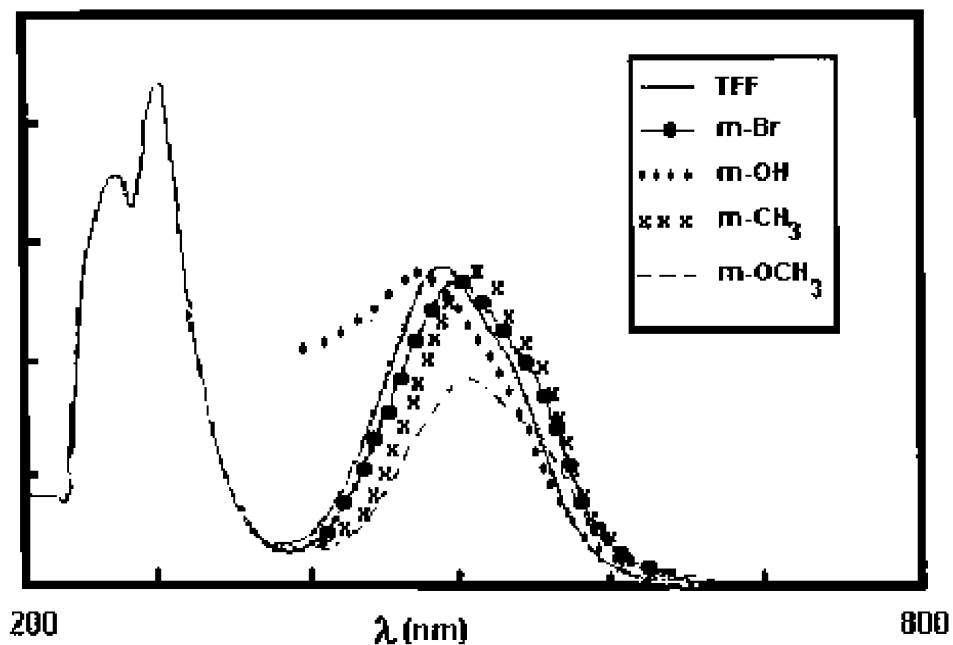


Fig. 2. Uv-vis spectra of formazan derivatives (CHCl_3 , 10^{-4} mol/l).

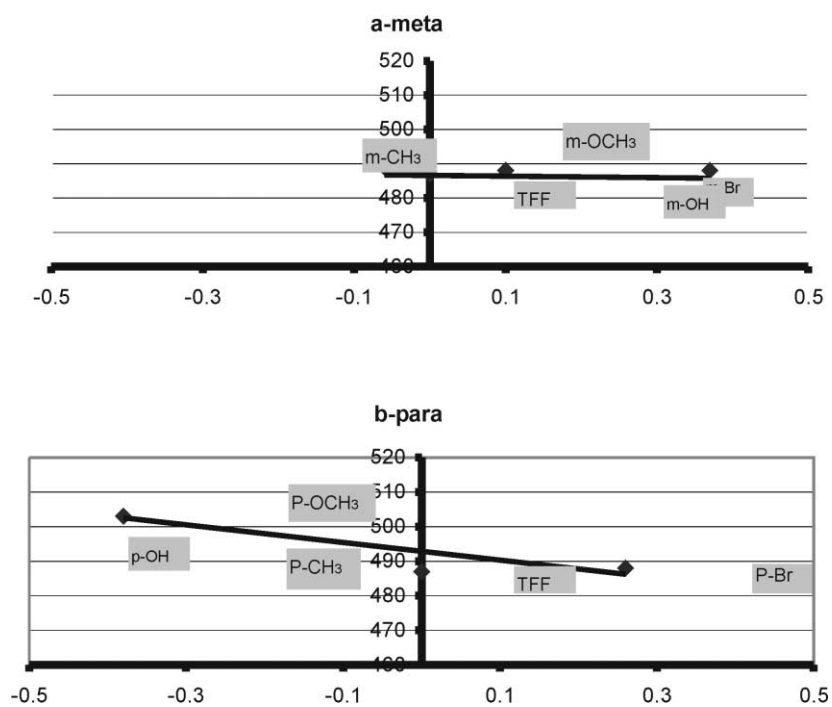


Fig. 3. The plot of Hammett substituent constants against λ_{max1} for a: *meta* and b: *para* derivatives.

The λ_{\max} values were observed to be 480 and 503 nm in the case of *m*-OH and *p*-OH. The shift toward lower wavelength in *m*-OH ($\Delta\lambda_{\max} = -7$ nm) compared with TPF (hypsochromic effect) can be explained by the fact that the inductive effect of OH group dominates. The significant shift in the case of *p*-OH ($\Delta\lambda_{\max} = 16$ nm) (bathochromic effect) is due to the dominance of resonance effect.

There is a small bathochromic shift in the case of TPF is substituted by *m*-CH₃, *p*-CH₃ and *m*-OCH₃ ranging 1–2 nm. However, there is a significant bathochromic shift in the case of *p*-OCH₃. This can be interpreted as the resonance effect of oxygen dominates in the case of *p*-OCH₃.

It was observed that there was the shift in *p*-substituted derivatives was bigger than of *m*-substituted ones. This can be explained by the fact the resonance effect is much more dominant in para position compared with *m*-position.

In conclusion it can be said that the electron donating substituents shift the λ_{\max} value towards the red wave length (bathochromic effect) while the electron withdrawing ones cause a shift towards the blue wave lengths (hypsochromic effect). Although the results are small enough to make any generalisation the experiments were repeated so many times in order to avoid the experimental discrepancy. The results were found to be parallel with our former study where 18 formazans substituted on 1-phenyl ring giving the similar shifts (but more significant), in λ_{\max} values. This can be attributed to the position of 1 and 3 rings in the molecule.

4. Conclusions

4.1. The relation between the $\Delta\lambda_{\max}$ and Hammett substituent coefficients σ_m and σ_p :

Fig. 3 shows the λ_{\max} values plotted against Hammett substituent constant values for both meta and para substituted derivatives. There is an almost linear relationship between these values

apart from a small deviation in the case of *p*-OCH₃. This shows that Hammett substituent coefficients can be employed for the evaluation of absorption parameters [20].

The synthesis of *o*-substituted formazans were not successful in spite of all efforts. The yield was either very small or there obtained a resinous compound, which was impossible to crystallise. This was thought to be due to the steric hindrance of *o*-substituted benzaldehydephenylhydrazone at the coupling step.

Acknowledgements

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