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Triphenylmethane dyes containing the *N*-methyl-*N*-2,2,2-trifluoroethyl group

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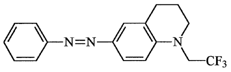
Dedicated, on the occasion of his 65th birthday, to Dr. Geoffrey Hallas: 'An inspiration and a good friend'

Abstract

Analogues of Malachite Green containing terminal *N*-methyl-*N*-2,2,2-trifluoroethyl groups have been prepared and their electronic absorption spectra and lightfastness properties determined. The reduced electron donating effect of the fluorinated moiety results in a hypsochromic shift of $\lambda_{\max}(x)$ in the unsubstituted analogue. *Meta*- and *para*-substituents in the phenyl ring modify the position of the *x*-band which can be correlated linearly with the appropriate Hammett σ constant. In contrast to the Malachite Green series, substitution by methyl groups *ortho* to the terminal amino moieties produces a small red shift of the first frequency band. The steric deconjugation of the more weakly donating *N*-methyl-*N*-2,2,2-trifluoroethyl group is dominated by the electron release of the methyl groups at the 'active' 3′- and 3″-positions. Some of the analogues exhibit enhanced photostability relative to the corresponding Malachite Green derivatives. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The nature of the terminal basic group plays an important part in the light stability of the triphenylmethane dyes [1]. Investigations [2] of azo dyes containing the *N*-2,2,2-trifluoroethyl group (**1**) have established the superior lightfastness properties of these compounds when applied to nylon and polyester fibres. With this in view, we have examined the effects of introduction of the *N*-methyl-*N*-2,2,2-trifluoroethylamino moiety at the terminal positions of Malachite Green (**2**) on the colour and the lightfastness properties of these dyes. In order to establish the colour–structure relationship for the system, a range of substituted analogues (**3**) and (**4**) has been prepared and their electronic absorption spectra determined. Photofading characteristics of the dye cations on basic dyeable polyacryonitrile have been ascertained.



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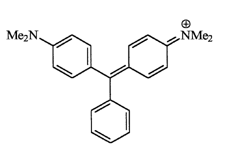

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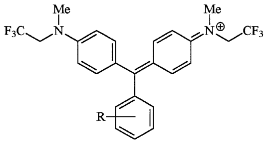

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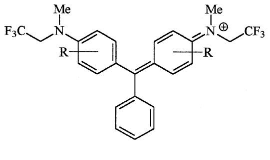

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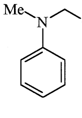
2. Results and discussion

The synthesis of the *N*-2,2,2-trifluoroethyl precursors is outlined in Scheme 1. *N*-Methyl-*N*-2,2,2-trifluoroethylaniline (**5**) was prepared from *N*-methylaniline by trifluoroacetylation of the amine followed by reduction of the resulting *N*-methyl-*N*-phenyltrifluoroethanamide using sodium borohydride and aluminium trichloride in ethoxyethane. Ring-substituted analogues (**6**) were prepared from the commercially available derivatives of aniline by conversion to the substituted *N*-methylaniline *via* methanoic acid and reduction ($LiAlH_4$), followed by trifluoroacetylation and reduction. The *para*-bromo derivatives of the substituted amines (**7**) were obtained by bromination of the appropriately substituted *N*-methyl-*N*-trifluoroethylaniline using bromine in dioxan [3] or, when a 3-substituent was present in the amine, with 2,4,4,6-tetrabromocyclohexa-2,5-dienone [4].



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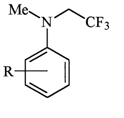

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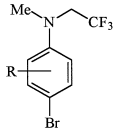

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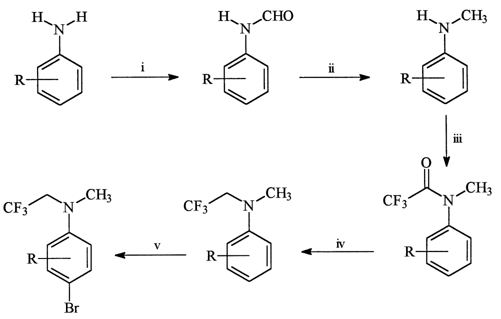
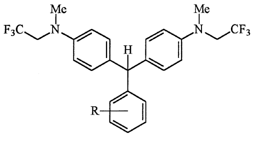
Acid catalysed condensation [5] of *N*-methyl-*N*-2,2,2-trifluoroethylaniline (**5**) with substituted aromatic aldehydes yielded the leuco-bases (**8**) which, on oxidation using 2,3-dichloro-5,6-dicyano-1,4-benzoquinone [6,7] and treatment with methanolic sodium methoxide, gave the triphenylmethyl methyl ethers (**9**), details of which are given in Tables 1 and 2. Dye bases (**10**) were prepared by the reaction of 2- or 3-substituted *N*-methyl-*N*-2,2,2-trifluoroethylaminophenyllithium with either methyl benzoate or 4-(*N*-methyl-*N*-2,2,2-trifluoroethyl)benzophenone (**11**) and are detailed in Table 3 Ketone (**11**) was prepared from *N*-methyl-*N*-2,2,2-trifluoroethylaniline and benzanilide *via* Vilsmeier methodology [8] The dye cations (**3**) were obtained from the corresponding methyl ethers (**9**) and the cations (**4**) from the dye bases (**10**) by dissolution in 98% ethanoic acid [9]. The spectral data for the dye cations are collated in Table 4.



Scheme 1. Reagents: (i), HCOOH; (ii), $LiAlH_4$; (iii), TFAA; (iv), $NaBH_4$, $AlCl_3$, Et_2O; (v), Br_2/diaoxan or dienone.

Metallation of 4-bromo-*N*-methyl-*N*-2,2,2-trifluoroethylaniline and its analogues was achieved using butyllithium in ethoxyethane at 25°C. A two-fold excess of butyllithium was found to give optimal conversion, since lithiation at carbon-1 of the 2,2,2-trifluoroethyl group occurs competitively with the lithium–bromine exchange process.



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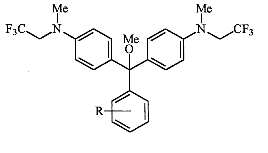

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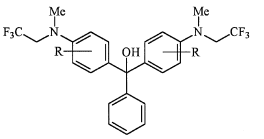

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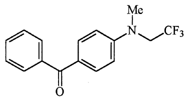

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The 4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)-triphenylmethyl cation [(**3**) R=H] exhibits an electronic absorption spectrum similar to that of Malachite Green (**2**), with two distinct bands in the visible region. The longer wavelength x-band is associated with a transition polarised along the axis containing the terminal nitrogen atoms [10]. The introduction of the electron withdrawing 2,2,2-trifluoroethyl group at this 'active' position produces the predicted [11] hypsochromic shift of the *x*-band (594 nm) compared to that of Malachite Green (621 nm), such that the dye exhibits a blue rather than a green coloration. The substitution has little effect (428 *cf.* 427.5 nm) on the *y*-band [11].

The molar absorbtivities of the *x*- and *y*-bands show a slight increase (11,750 and 2680) compared

Table 1
Preparative and analytical data for phenyl substituted derivatives of 4′,4″-di-(*N*-methyl-N-2,2,2-trifluoroethylamino)triphenylmethane (**8**)

R	m.p. (°C)	Yield (%)	Found (%)					Required (%)				
			C	H	N	F	Br	C	H	N	F	Br
H	80–83	86	64.3	4.90	5.65	24.3	–	64.4	5.20	6.00	24.4	–
2-CH$_3$	116–117	69	65.0	5.30	5.75	23.6	–	65.0	5.40	5.80	23.8	–
3-CH$_3$	109–111	66	64.7	5.30	5.70	23.9	–	65.0	5.40	5.80	23.8	–
4-CH$_3$	84–86	69	65.1	5.45	5.85	24.1	–	65.0	5.40	5.80	23.8	–
2-Br	131–133	67	54.8	4.15	5.00	20.8	15.0	55.1	4.20	5.10	20.9	14.7
3-Br	104–106	86	54.9	4.00	5.30	20.60	15.0	55.1	4.20	5.10	20.9	14.7
4-Br	99–102	73	54.8	4.10	5.00	20.7	14.5	55.1	4.20	5.10	20.9	14.7
2-OCH$_3$	140–142	72	62.7	5.25	5.55	23.1	–	62.9	5.20	5.65	23.0	–
3-OCH$_3$	140–141	69	62.7	5.10	5.40	22.9	–	62.9	5.20	5.65	23.0	–
4-OCH$_3$	103–104	68	62.7	4.95	5.70	23.3	–	62.9	5.20	5.65	23.0	–
3-NO$_2$	78–80	39	58.9	4.55	8.25	22.2	–	58.7	4.50	8.20	22.3	–
4–NO$_2$	121–124	60	58.7	4.45	8.10	22.0	–	58.7	4.50	8.20	22.3	–

Table 2
Preparative and analytical data for phenyl substituted derivatives of 4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)triphenylmethyl methyl ether (**9**)

R	m.p. (°C)	Yield (%)	Found (%)					Required (%)				
			C	H	N	F	Br	C	H	N	F	Br
H	137–140	49	62.9	5.52	5.80	22.8	–	62.9	5.25	5.6	22.9	–
2-CH$_3$	141–144	33	63.5	5.50	5.35	22.3	–	63.5	5.50	5.50	22.3	–
3-CH$_3$	92–95	16	63.3	5.40	5.70	22.3	–	63.5	5.50	5.50	22.3	–
4-CH$_3$	60–62	13	63.1	5.35	5.39	22.3	–	63.5	5.50	5.50	22.3	–
2-Br	132–135	54	54.4	4.40	4.65	19.9	13.7	54.2	4.35	4.8	19.8	13.9
3-Br	97–99	17	54.5	4.30	4.55	19.7	13.8	54.2	4.35	4.8	19.8	13.9
4-Br	87–88	91	54.0	4.65	4.55	19.4	13.9	54.2	4.35	4.8	19.8	13.9
2-OCH$_3$	163–165	33	61.5	5.15	5.35	21.4	–	61.6	5.3	5.3	22.9	–
3-OCH$_3$	106–109	3	61.4	5.20	5.10	21.3	–	61.6	5.3	5.3	22.9	–
4-OCH$_3$	120–121	14	61.2	5.15	5.45	21.9	–	61.6	5.3	5.3	22.9	–
3-NO$_2$	50–52	13	57.4	4.50	7.80	21.2	–	57.7	4.6	7.8	21.0	–
4-NO$_2$	114–117	40	57.9	4.70	7.55	21.0	–	57.7	4.6	7.8	21.0	–

with Malachite Green (11,200 and 2000). As in the case of the parent Malachite Green system [12] there is a linear relationship between $\lambda_{\max}(x)$ and the appropriate Hammett substituent constant (σ) for a range of 3- and 4-substituted derivatives of the 4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)-triphenylmethyl cation (**3**). Substitution in the 2-position results in bathochromic shifts of $\lambda_{\max}(x)$ and, with the exception of the 2-methoxy derivative, hypsochromic shifts of the y-bands concomitant with a reduction in $\varepsilon_{\max}(y)$. These responses are consistent with steric crowding and rotation of the phenyl ring about an essential single bond [13].

The effects of substitution at the non-terminal positions on the x-axis on the spectrum of Malachite Green and its analogues are well documented [14–18]. Thus, the introduction of the electronically contrasting methyl and trifluoromethyl groups at the 'inactive' 2′-position of the 4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoro-ethylamino)triphenylmethyl cation produces the expected bathochromic

Table 3
Preparative and analytical data for aminophenyl substituted derivatives of 4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)triphenylmethanol (**10**)

R	m.p. (°C)	Yield (%)	Found (%)				Required (%)			
			C	H	N	F	C	H	N	F
2′-CH_3	Gum	60	62.4	5.30	6.00	22.9	62.9	5.24	5.64	23.0
3′-CH_3	Gum	77	62.7	5.42	5.81	22.7	62.9	5.24	5.64	23.0
2′2″-di-CH_3	Gum	31	63.4	5.40	5.24	22.4	63.5	5.49	5.20	22.4
3′,3″-di-CH_3	Gum	10	63.2	5.25	5.15	22.5	63.5	5.49	5.20	22.4
2′,2″,5′,5″-tetra-CH_3	131–133	21	64.0	5.90	4.95	22.1	64.6	5.95	5.20	21.2
3′-CF_3	Gum	31	56.8	4.20	4.95	30.9	56.7	4.20	5.10	31.1
3′,3″-di-CF_3	125–126	39	52.2	3.80	4.60	36.4	52.4	3.60	4.50	36.9

Table 4
Spectral data of derivatives of the 4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)triphenylmethyl cation in 98% acetic acid

Substituent in (**3**) or (**4**)	*x*-Band		*y*-Band	
	λ_{max}(nm)	$10^{-4}\varepsilon_{max}$	λ_{max}(nm)	$10^{-4}\varepsilon_{max}$
None	594	11.75	428	2.68
2-CH_3	598	12.27	424	2.42
3-CH_3	587	10.00	429	2.52
4-CH_3	586	12.29	439	3.76
2-Br	614	11.03	414	1.17
3-Br	606	8.34	426	1.94
4-Br	599	6.62	434	1.82
2-OCH_3	600	8.49	464	0.86
3-OCH_3	596	4.66	436	0.98
4-OCH_3	577	9.28	471	4.08
3-NO_2	610	12.2	416	2.50
4-NO_2	611	7.88	417	2.03
2′-CH_3	608	8.13	433	2.80
3′-CH_3	596	5.35	436	1.66
2′,2″-di-CH_3	620	9.37	446	2.47
3′,3″-di-CH_3	600	3.04	446	1.09
2′,2″,5′,5″-tetra-CH_3	630	2.28	470	1.03
2′-CF_3	586	4.09	442	2.78
2′,2″-di-CF_3	644	2.73	480	1.07

(608 nm) and hypsochromic (586 nm) shifts of $\lambda_{max}(x)$, respectively. At the 3′-position in the dialkylaminophenyl ring, the methyl group gives rise to a small bathochromic shift (2 nm) of the *x*-band together with a reduction in intensity as anticipated.

The spectral changes resulting from symmetrical di-substitution by methyl and trifluoromethyl groups at the 2′- and 2″-positions are in accord with theoretical predictions, but the 3′,3″-dimethyl derivative exhibits a bathochromic shift (6 nm) of $\lambda_{max}(x)$ when compared with the unsubstituted parent system, whilst the 3′,3″-dimethyl derivative of Malachite Green shows a comparative hypsochromic shift (−4 nm). This hypsochromic shift of the first frequency band in Malachite Green derivatives has been rationalised in terms of deconjugation of the terminal dimethylamino groups by electron releasing methyl moieties at ‘active’ positions in an electronically symmetrical system [14–18]. Molecular models demonstrate that the the steric interaction between the *ortho* methyl group and the terminal dialkylamino group can produce the same departure from coplanarity with the aromatic ring for both the *NN*-dimethylamino group and the *N*-methyl-*N*-2,2,2-trifluoroethyl group. Hence both terminal moieties can be considered to be deconjugated to the same extent. In the case of the Malachite Green derivatives, the bathochromic effect of the methyl groups at the 3′- and 3″-positions is overwhelmed by the hypsochromic effect of deconjugation of the *NN*-dimethylamino group, which increases the energy difference between the NBMO and the LUMO, resulting in the small overall hypsochromic shift of $\lambda_{max}(x)$. Since the electron donating characteristics of the *N*-methyl-*N*-2,2,2-trifluoroethyl group are reduced compared with the *NN*-dimethylamino group, steric deconjugation does not increase the separation between the NBMO and the LUMO to the same extent and thus the bathochromic effect of the *meta*-methyl groups predominates to give an overall red shift of $\lambda_{max}(x)$.

3. Lightfastness studies

The dye precursors (**9**) and (**10**) (0.13 mmole) were dissolved in ethanoic acid (10 cm^3) and diluted with warm (70°C) distilled water (30 cm^3). The solution was warmed (80°C), a sample of Orlon 42 (0.34 g) was added with stirring, the temperature of the dye bath was raised to 100°C over 20 min and maintained at that temperature for 30 min. The cloth sample was removed, washed with warm water and dried. Specimens of the dyed fabric (4 × 1 cm) were mounted on cards and half the fabric area was covered. Eight standard dyeings of a range of blue dyes on woollen cloth were prepared similarly. The samples and standards were exposed to the light from a Xenon Lamp and the fastness assessed by reference to the first perceptible change of the first appropriate standard. The lightfastness ratings thus derived are given in Table 5.

4. Experimental

Absorption spectra were measured with a Hewlett–Packard HP 8451A for solutions of the dye bases and methyl ethers in 98% acetic acid. ^{1}H-nmr spectra were determined in $CDCl_3$ solution using a Jeol FX-90Q spectrometer; J values are given in Hz.

All synthetic intermediates were shown to be $>99\%$ pure by gas-liquid or thin-layer chromatography and structures confirmed by ^{1}H NMR spectroscopy.

Table 5
Lightfastness ratings of 4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)triphenylmethyl cation derivatives on Orlon 42

R in (**3**) or (**4**)	Fastness	R in (**3**) or (**4**)	Fastness
H	1–2	4-OCH_3	5
2-CH_3	3–4	3-NO_2	<1
3-CH_3	3	4-NO_2	<1
4-CH_3	5	3′-CH_3	1–2
2-Br	1–2	2′,2″-di-CH_3	<1
3-Br	1–2	2′,2″,5′,5″-tetra-CH_3	<1
4-Br	5	2′-CF_3	5
2-OCH_3	3	2′,2″-di-CF_3	2–3
3-OCH_3	<1		

4.1. N-*Methyl*-N-*2,2,2-trifluoroethylaniline (5)*

Trifluoroethanoic anhydride (57.6 g; 0.27 mol) was added dropwise (0.5 h) to a stirred solution of *N*-methylaniline (20.0 g; 0.27 mol) in dry ether (250 cm^3), the mixture was held at ambient temperature for 24 h and hydrochloric acid (50 cm^3; 4 M) then added. The separated organic phase was washed with water (200 cm^3), sodium carbonate (2 × 100 cm^3; 1 M), water (2 × 200 cm^3), dried ($MgSO_4$) and the solvent was removed to yield *N*-methyl-*N*-phenyltrifluoroethanamide (47.9 g: 86%).

N-Methyl-*N*-phenyltrifluoroethanamide (50.87 g; 0.25 mol) was added in small portions to a stirred solution of aluminium trichloride (35.6 g; 0.26 mol) in dry ether (800 cm^3). The mixture was heated at reflux for 1 h, sodium borohydride (21.4 g; 0.563 mol) was added in portions and the mixture stirred at reflux for a further 37 h. Water (600 cm^3) was added dropwise, the organic phase was separated, washed with water (300 cm^3), dried ($MgSO_4$) and the solvent removed to leave a pale yellow oil (46 g), which was distilled to yield *N*-methyl-N-2,2,2-trifluoroethylaniline (32.4 g; 69%), b.p. 64-67 °C/5 mm Hg. δ_H 2.95 (3 H, s, NMe), 3.47 (2 H, q, J 5.9, NCH_2CF_3), 6.06–7.44 (5 H, m, Ar–H).

4.2. 4-Bromo-N-*Methyl*-N-*2,2,2-trifluoroethylaniline (7) (R=H)*

A solution of potassium hydroxide (11.2 g; 0.2 mol) in water (100 cm^3) was added to a stirred solution of *N*-methyl-N-2,2,2-trifluoroethylaniline (24.33 g; 0.129 mol) in 1,4-dioxan (150 cm^3). The mixture cooled (0°C) and a solution of bromine (33.3 g; 0.2 mol) in 1,4-dioxan (200 cm^3) was added dropwise over 2 h maintaining the solution at 0°C. The resultant dark red solution was poured into water (40 cm^3), extracted with ether (2 × 200 cm^3) and the organic phase dried ($MgSO_4$). Removal of the solvent gave a brown oil (33.1 g), which was distilled to yield 4-bromo-*N*-methyl-*N*-2,2,2-trifluoroethylaniline (32.7 g; 95%), b.p. 90–92°C/1.0 mm Hg, as a pale yellow oil. δ_H 2.95 (3 H, s, NMe), 3.78 (2 H, q, J 5.8, NCH_2CF_3), 6.76 (2 H, d, J 8.5, 2-H, 6-H), 7.31 (2 H, d, J 8.5, 3-H, 5-H).

4.3. 4-(N-Methyl-N-2,2,2-trifluoroethylamino)benzophenone (**11**)

N-Methyl-*N*-2,2,2-trifluoroethylaniline (3.68 g; 0.0193 mol) was added to a warm solution of benzanilide (3.61 g; 0.0183 mol) in phosphoryl chloride (18 cm^3), the mixture heated under reflux for 5 h and poured into water (350 cm^3). The resulting suspension was neutralised with sodium carbonate solution and steam distilled to remove excess amine. Removal of solvent from the dried ($MgSO_4$) distillation residue afforded a pale yellow solid (4.15 g) which was recrystallised from ethanol to yield pale yellow crystals of 4-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)benzophenone (2.87 g; 51%), m.p. 75-79°C. δ_H 3.07 (3 H, s, NMe), 4.81 (2 H, q, *J* 5.8, NCH_2CF_3), 6.8 (2 H, d, *J* 8.5, 3-H, 5-H), 7.24–7.9 (5 H, m, 2′-H, 3′-H, 4′-H, 5′-H, 6′-H), 7.84 (2 H, d, *J* 8.5, 2-H, 6-H). (Found: C, 65.3; H, 4.90; F, 19.1; N, 5.0. $C_{16}H_{14}F_3NO$ requires C, 65.5; H, 4.80; F, 19.4; N, 4.80%).

4.4. General method of preparation of dye methyl ethers

A solution of *N*-methyl-*N*-2,2,2-trifluoroethylaniline (5.1 g; 0.027 mol), benzaldehyde (1.94 g; 0.0088 mol) and hydrochloric acid (3 cm^3; d. 1.18) in ethanol (15 cm^3) was heated under reflux (24 h), cooled, basified with ammonia (20 cm^3, d. 0.88) in ethanol (20 cm^3) and steam distilled. The residue was extracted into ether (3 × 10 cm^3), washed with water (50 cm^3), dried ($MgSO_4$), the solvent removed and the resulting yellow-brown oil (4.04 g) recrystallised from ethanol to give white plates of 4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)-triphenylmethane (3.55 g; 86%), m.p. 80–83°C.

A solution of 4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)triphenylmethane (1.0 g; 0.0021 mol), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.5 g; 0.0022 mol) in anhydrous methanol (30 cm^3) was heated under reflux (4 h), filtered into a solution of sodium methoxide (30 cm^3; 4 M) and the resulting solution added to water (200 cm^3). The organic phase was extracted into ether (4 × 20 cm^3), dried ($MgSO_4$) and removal of the solvent from the dried ($MgSO_4$) extracts gave a colourless oil (0.77 g), which was crystallised from ethanol to yield white crystals of 4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)triphenylmethyl methyl ether (0.51 g; 49%), m.p. 137–140°C.

4.5. General method of preparation of dye bases

A solution of butyllithium (7.3 cm^3; 1.6 M in hexane) in dry ether (20 cm^3) was added dropwise (0.1 hr) to a solution of 4-bromo-*N*,2-dimethyl-*N*-2,2,2-trifluoroethylaniline (1.64 g; 0.0058 mol) in dry ether (20 cm^3) at ambient temperature. After 0.5 h, a solution of methyl benzoate (1.58 g; 0.0116 mol) in dry ether (20 cm^3) was added (0.2 h), the mixture was stirred (0.5 h) and then quenched with water (50 cm^3). Removal of solvent from the dried ($MgSO_4$) organic phase afforded a yellow oil (2.82 g), which was eluted from silica (Merck keiselgel 60H) with trichloromethane to yield 2′,2″-dimethyl-4′,4″-di-(*N*-methyl-*N*-2,2,2-trifluoroethylamino)triphenylmethanol (0.92 g; 31%) an orange gum.

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