Steric Effects in Di- and Tri-arylmethane Dyes. Part XI.[1] Electronic Absorption Spectra of Derivatives of Michler's Hydrol Blue, Crystal Violet, and Malachite Green containing *o*-Trifluoromethyl Groups

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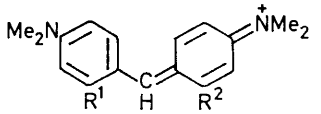
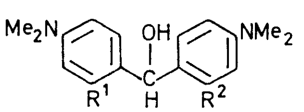
Spectral changes caused by the effects of *o*-trifluoromethyl groups in Michler's Hydrol Blue, Crystal Violet, and Malachite Green are described and discussed. Pronounced bathochromic shifts of the first bands are observed for the electronically symmetrical dyes. The introduction of a trifluoromethyl group into the 2′-position of Malachite Green brings about a marked conformational change resulting in a hypsochromic shift of the first band. In certain cases, the combined steric and electronic effects of the trifluoromethyl groups are sufficient to shift the equilibrium between dye base and univalent dye cation in acid solution in favour of the former species.

IN earlier papers of this series [2-5] extensive use was made of the effect of methyl substituents on the electronic absorption spectra of di- and tri-arylmethane dyes, since the steric and electronic effects are normally opposed and this fact assists analysis of the spectral shifts. The influence of the trifluoromethyl group in this field is of interest on several counts. From a practical viewpoint, the presence of trifluoromethyl groups often results in improved brightness and greater fastness to light in anthraquinonoid and azo dyes,[6] but the effects of this group in basic triarylmethane dyes have been little studied; Inukai *et al.* report [7] that the 2-trifluoromethyl derivative of Crystal Violet (III; $R^1 = CF_3$, $R^2 = R^3 =$ H) shows superior light fastness. The increased size of the trifluoromethyl group, when compared with the methyl group,[8] may be expected to lead to pronounced conformational changes and corresponding modifications in the electronic absorption spectra of the substituted dyes.



(I)



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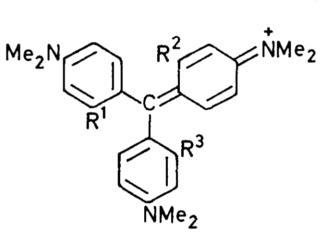

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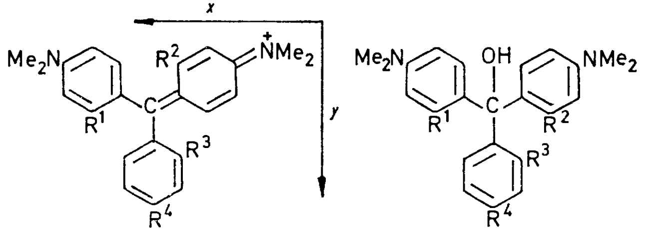

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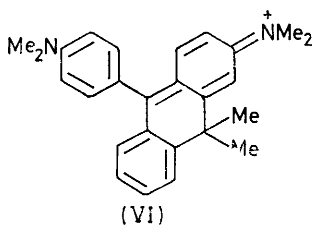

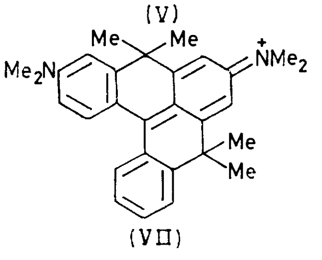

(VI) (VII)

The work of Brooker [9] led to the prediction [2] that the steric response of an electronically symmetrical dye such as Michler's Hydrol Blue (I; $R^1 = R^2 =$ H) or Crystal Violet (III; $R^1 = R^2 = R^3 =$ H) should be a bathochromic shift and a reduction in intensity of the first band. For these dyes, in which the first unoccupied molecular orbital is symmetric, theory also suggests that crowding substituents should produce bathochromic shifts of the first band.[10] Dewar has shown theoretically [11] that the effect of an electron-donating *ortho*-substituent is hypsochromic whereas that of an electron-withdrawing *ortho*-substituent is bathochromic. Thus, the steric and electronic effects are opposed when an *o*-methyl group is introduced into a dye of this type and it is found that the crowding effect predominates.[2] In the case of an *o*-trifluoromethyl group the bathochromic steric effect is enhanced by the electronic effect and, as anticipated, the progressive introduction of *o*-trifluoromethyl substituents into Michler's Hydrol Blue or Crystal Violet leads to large bathochromic shifts of the first band (Table 1).

The 2-trifluoromethyl derivative of Crystal Violet (III; $R^1 = CF_3$, $R^2 = R^3 =$ H) shows a bathochromic shift of 30 nm together with a small decrease in $\varepsilon_{max.}$ when compared with the parent dye; this result is at variance with the data of the Japanese workers [7] who claim unreasonably that Crystal Violet and its 2-trifluoromethyl derivative both absorb at 586 nm. Further batho-

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[1] Part X, C. Aaron and C. C. Barker, *J. Chem. Soc.* (*B*), 1971, 319.

[2] C. C. Barker, M. H. Bride, and A. Stamp, *J. Chem. Soc.*, 1959, 3957.

[3] C. C. Barker, G. Hallas, and A. Stamp, *J. Chem. Soc.*, 1960, 3790.

[4] C. C. Barker, M. H. Bride, G. Hallas, and A. Stamp, *J. Chem. Soc.*, 1961, 1285.

[5] C. C. Barker and G. Hallas, *J. Chem. Soc.*, 1961, 1529.

[6] A. E. Pavlath and A. J. Leffler, 'Aromatic Fluorine Compounds,' Reinhold, New York, 1962, p. 676.

[7] K. Inukai, T. Ueda, and Y. Maki, *Kogyo Kagaku Zasshi*, 1957, **60**, 1329.

[8] R. Filler, *Adv. Fluorine Chem.*, 1970, **6**, 1.

[9] L. G. S. Brooker, F. L. White, R. H. Sprague, S. G. Dent, and G. Van Zandt, *Chem. Rev.*, 1947, **41**, 325.

[10] M. J. S. Dewar, 'Steric Effects in Conjugated Systems,' ed. G. W. Gray, Butterworths, London, 1958, p. 46.

[11] M. J. S. Dewar, *J. Chem. Soc.*, 1950, 2329.

chromic shifts and decreases in ε are observed as additional *o*-trifluoromethyl groups are introduced into Crystal Violet (Table 1) but, unlike the corresponding methyl derivatives,[2] these shifts are not uniform and it may be concluded that irregular conformational changes take place to accommodate the bulky substituents. Thus, the unexpectedly small decrease in $\varepsilon_{\text{max.}}$ for the 2-trifluoromethyl dye (2000), compared with that shown by the 2-methyl derivative (7000), can be accounted for by assuming that the substituted ring undergoes all or most of the necessary rotational adjustment. Molecular models show that marked changes in molecular conformation are brought about by the introduction of more than one *o*-trifluoromethyl group, in agreement with the drop in ε from 115,000 to 70,000 and 55,000 (Table 1).

TABLE 1

Spectral data for 10^{-5}M solutions of derivatives of Michler's Hydrol Blue, Crystal Violet, and Malachite Green containing *o*-trifluoromethyl groups in 98% acetic acid

Dye	Absorption maxima/nm ($10^{-4}\varepsilon$/l mol^{-1} cm^{-1})
Michler's Hydrol Blue	607·5 (14·75)
(I; $R^1 = CF_3$, $R^2 = H$)	624 (4·4)*
(I; $R^1 = R^2 = CF_3$)	650 (0·34)*
Crystal Violet	589 (11·7)
(III; $R^1 = CF_3$, $R^2 = R^3 = H$)	619 (11·5)
(III; $R^1 = R^2 = CF_3$, $R^3 = H$)	627 (7·0)
(III; $R^1 = R^2 = R^3 = CF_3$)	653 (5·5)
Malachite Green	621 (10·4); 427·5 (2·0)
(IV; $R^1 = CF_3$, $R^2 = R^3 = R^4 = H$)	604 (3·0); 431 (2·3)
(IV; $R^1 = R^2 = CF_3$, $R^3 = R^4 = H$)	678 (4·8); 478 (1·6) *
(IV; $R^1 = R^3 = CF_3$, $R^2 = R^4 = H$)	632 (3·6); 412 (1·4)
(IV; $R^1 = R^4 = CF_3$, $R^2 = R^3 = H$)	613 (2·6); 416 (1·9)
(IV; $R^1 = R^2 = R^3 = CF_3$, $R^4 = H$)	677 (0·36); 440 (0·085) *
(IV; $R^1 = R^2 = R^4 = CF_3$, $R^3 = H$)	690 (1·0); 466 (0·34) *

* Low, due to presence of dye base.

The two derivatives of Michler's Hydrol Blue examined similarly show substantial bathochromic shifts of the first band (Table 1) together with large decreases in $\varepsilon_{\text{max.}}$. In these examples, however, the values of ε are of doubtful significance in that the equilibrium between dye base and univalent dye cation is shifted in favour of the former species (II); the presence of un-ionised dye base is demonstrated by spectral measurements in ethanolic hydrogen chloride.[12] This behaviour is not unexpected since the bases of Crystal Violet and Malachite Green form univalent ions which are stable over a wider range of pH than is Michler's Hydrol Blue (pK_b 9·36, 6·90, and 5·61, respectively),[13] and Olah has shown [14] that trifluoromethyl groups destabilise diphenylmethyl carbonium ions.

In the case of Malachite Green (IV; $R^1 = R^2 = R^3 = R^4 = H$), the two absorption bands in the visible region respond differently to the effects of crowding substituents. Thus, the introduction of a substituent into the 2-position of the phenyl ring generally leads to a hypsochromic shift of the second band (*y* band) and to a decrease in its maximum intensity [4] in accord with the anticipated steric response of an electronically unsymmetrical dye.[9] The first band (*x* band) normally responds to a crowding substituent in the 2-position by a bathochromic shift, relative to the 4-substituted isomer, and an increase in intensity; [4] this increase varies with the van der Waals radius of the substituent and is associated with the progressive deconjugation of the phenyl group.[1] A 2′-methyl group in Malachite Green (IV; $R^1 = Me$, $R^2 = R^3 = R^4 = H$) produces a bathochromic shift and reduction in intensity of the *x* band, and this effect is consistent with rotation of one or both of the dimethylaminophenyl groups about the central bonds.[5] However, such rotation should result in increased departure from uniplanarity along the unsymmetrical *y* axis of the molecule and thus lead to a hypsochromic shift and reduction in intensity of the *y* band, whereas the observed shift is bathochromic (10 nm) and the intensity remains constant. The introduction of a second methyl group into the 2″-position (IV; $R^1 = R^2 = Me$, $R^3 = R^4 = H$) increases these spectral changes and causes a slight reduction in $\varepsilon_{\text{max.}(y)}$. These bathochromic shifts were tentatively attributed to the greater electronic symmetry along the *y* axis resulting from displacement of charge onto the phenyl group by rotation of the dimethylaminophenyl groups about the central bonds; [5] similar bathochromic shifts of the *y* band are brought about by methyl groups adjacent to the dimethylamino-groups in Malachite Green [3] and also by introducing an isopropylidene bridge into the parent dye.[1] The increase in $\varepsilon_{\text{max.}(x)}$ shown by the 2-methyl derivative (IV; $R^3 = Me$, $R^1 = R^2 = R^4 = H$) is repeated in the 2,2′-dimethyl and 2,2′,2″-trimethyl derivatives.[5] The small bathochromic shift of the *x* band shown by the first of these dyes contrasts with the small hypsochromic shifts shown by the *x* bands of the other two, but the most relevant comparison is between the corresponding 2-methyl and 4-methyl derivatives, in which case the spectral shifts are uniformly bathochromic; [5] it has been shown recently, however, that *ortho* and *para* electrical effects are not necessarily the same.[15]

Analogous derivatives of Malachite Green have now been prepared in which the methyl groups are replaced by trifluoromethyl groups (Table 1). As in the case of the electronically symmetrical dyes, the electron-withdrawing effect of the trifluoromethyl group should result in a bathochromic shift at an inactive position.[11] Thus, on both steric and electronic grounds it might be expected that a 2′-trifluoromethyl group in Malachite Green (IV; $R^1 = CF_3$, $R^2 = R^3 = R^4 = H$) would produce a large bathochromic shift of the *x* band, relative to that of the parent dye, whereas a considerable hypsochromic shift (17 nm) is observed (Table 1) together with a large reduction in $\varepsilon_{\text{max.}(x)}$. At the same time, the *y* band responds by showing a bathochromic shift (3·5 nm) and a small increase in intensity. It seems likely that this result can be associated with a marked change in the electronic

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[12] A. S. Ferguson and G. Hallas, *J. Soc. Dyers and Colourists*, 1973, **89**, 22.

[13] R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1949, 1724.

[14] G. A. Olah and C. U. Pittman, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 3310.

[15] M. Charton, *J. Amer. Chem. Soc.*, 1969, **91**, 6649.

symmetry of the dye. Thus, if the substituted dimethylaminophenyl group undergoes all or most of the enforced rotational adjustment, the x axis will become electronically unsymmetrical with a resultant hypsochromic shift and reduction in intensity of the x band. This process will also increase the electronic symmetry along the y axis, by transfer of charge, with a resultant bathochromic shift and increase in intensity of the y band, as is observed. These conclusions are supported by recent work on bridged analogues of Malachite Green.[1] Thus, the dye (VI), in which the unsubstituted dimethylaminophenyl group is twisted out of the molecular plane, shows a pronounced hypsochromic shift and reduction in intensity of the x band and a bathochromic shift of the y band when compared with the corresponding bands of the doubly-bridged dye (VII).

Electronic symmetry is largely restored to the x axis when a trifluoromethyl group is introduced into the 2-position of the phenyl ring of the 2′-trifluoromethyl derivative of Malachite Green (Table 1). In this dye (IV; $R^1 = R^3 = CF_3$, $R^2 = R^4 = H$), the x band shows a bathochromic shift of 28 nm compared with that of the 2′-trifluoromethyl derivative (+11 nm compared with Malachite Green itself) together with an increase in intensity. Crowding along the unsymmetrical y axis is clearly shown by the hypsochromic shift and reduction in intensity of the y band compared with that of Malachite Green or its 2′-trifluoromethyl derivative (Table 1). The isomeric 4,2′-bistrifluoromethyl derivative of Malachite Green (IV; $R^1 = R^4 = CF_3$, $R^2 = R^3 = H$) is, as anticipated, electronically unsymmetrical along the x axis. Although, compared with Malachite Green itself, the dye shows a hypsochromic shift of the x band (Table 1) in accord with the overall change in symmetry, a bathochromic shift is observed relative to that of the parent dye (the 2′-trifluoromethyl derivative) as in the case of the 4-trifluoromethyl derivative of Malachite Green.[16] In view of the relatively low values of $\varepsilon_{max.}$ for the 2′-trifluoromethyl derivatives, it is necessary to establish whether the dye bases are completely ionised in the 98% acetic acid used for the spectral measurements; each of the three derivatives of Malachite Green considered so far exhibits virtually identical spectra in acetic acid and in ethanol containing 10 equivalents of hydrogen chloride, with no evidence of residual dye base.

In contrast to the effect of the 2′-trifluoromethyl group, the presence of two o-trifluoromethyl groups in the 2′,2″-bistrifluoromethyl derivative of Malachite Green (IV; $R^1 = R^2 = CF_3$, $R^3 = R^4 = H$) results in a large bathochromic shift of the x band (57 nm) and a marked reduction in $\varepsilon_{max.(x)}$ (Table 1). The y band also shows a pronounced bathochromic shift (50·5 nm) and a reduction in intensity compared with that of Malachite Green. The response of the x band is consistent with a substantial crowding effect in an electronically symmetrical system and the additional bathochromic shift, compared with that of the 2′,2″-dimethyl derivative (27 nm), can be attributed to the greater steric effect of the trifluoromethyl substituents[8] together with the electron-withdrawing nature of the groups. The bathochromic response of the y band can also be associated with the crowding effect of the o-trifluoromethyl groups which brings about an extensive rotation of the substituted dimethylaminophenyl groups about the central bonds with a consequent displacement of charge onto the phenyl ring and an increase in electronic symmetry along the y axis. Although the intensity of the x band is less than that of the analogous dimethyl derivative, as expected, in this case the dye base is not entirely converted into the univalent cation in 98% acetic acid. Thus, the spectrum of the 2′,2″-bistrifluoromethyl derivative in ethanol shows a maximum value for $\varepsilon_{max.(x)}$, with 100 equivalents of hydrogen chloride, which is rather higher (52,000) than that obtained in acetic acid (48,000) and the band associated with the dye base (V; $R^1 = R^2 = CF_3$, $R^3 = R^4 = H$) at 269 nm has not completely disappeared; similar behaviour has recently been observed with derivatives of Malachite Green containing more than one electron-withdrawing group in the phenyl ring.[12]

A change in electronic symmetry is brought about by the presence of a third crowding substituent in the 2,2′,2″-tristrifluoromethyl derivative of Malachite Green (IV; $R^1 = R^2 = R^3 = CF_3$, $R^4 = H$). The hypsochromic shift (38 nm) of the y band (Table 1), compared with that of the 2′,2″-bistrifluoromethyl derivative, could be associated with a rotation of the 2-trifluoromethylphenyl group, but the response of the x band is slightly hypsochromic (1 nm). The most relevant comparison, however, is that between the x bands of the 2,2′,2″-tristrifluoromethyl derivative and its 4,2′,2″-isomer (Table 1). Thus, the x band of the 2-trifluoromethyl compound shows a significant hypsochromic shift (13 nm) compared with that of the 4-substituted isomer, whereas a bathochromic shift is anticipated, and it appears likely that the rotation of the components of the x axis in the 2,2′,2″-tristrifluoromethyl dye is not uniform. Both the trisubstituted dyes exhibit low absorption intensities and the absorption spectra in ethanolic hydrogen chloride clearly indicate the presence of un-ionised dye base (V; $R^1 = R^2 = R^3 = CF_3$, $R^4 = H$ and $R^1 = R^2 = R^4 = CF_3$, $R^3 = H$), respectively.

Preparations.—The dye bases were obtained by a variety of methods involving several new intermediates. Interaction of 4-dimethylaminobenzoyl chloride[17] with *NN*-dimethyl-3-trifluoromethylaniline,[18] prepared in 65% yield by methylation of the amino-compound using trimethyl phosphate,[19] gave the 2-trifluoromethyl derivative of Michler's ketone. The corresponding derivative of Michler's hydrol (II; $R^1 = CF_3$, $R^2 = H$) was obtained by reduction of this ketone with lithium aluminium hydride and the 2′-trifluoromethyl derivative of

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[16] G. Hallas, D. E. Grocock, and J. D. Hepworth, *J. Soc. Dyers and Colourists*, 1970, **86**, 200.

[17] J. Décombe, *Bull. Soc. chim. France*, 1951, 416.

[18] J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Amer. Chem. Soc.*, 1950, **72**, 408.

[19] J. H. Billman, A. Radicke, and B. W. Mundy, *J. Amer. Chem. Soc.*, 1942, **64**, 2977; W. A. Sheppard, *Org. Synth.*, 1969, **49**, 111.

Malachite Green base (V; $R^1 = CF_3$, $R^2 = R^3 = R^4 =$ H) was obtained from the ketone and phenyl-lithium. Phenyl-substituted derivatives of the latter dye base, including the 2-trifluoromethyl derivative of Crystal Violet base, were analogously prepared from the ketone and the appropriate aryl-lithium compound.

Bromination of 3-trifluoromethylaniline [20] followed by methylation gave 4-bromo-*NN*-dimethyl-3-trifluoromethylaniline which was converted into the nitrile on heating with copper(I) cyanide in dimethylformamide; [21] the required bromo-amine was also obtained by the direct bromination of *NN*-dimethyl-3-trifluoromethylaniline using 2,4,4,6-tetrabromocyclohexa-2,5-dienone.[22] Treatment of the bromo-compound with the n-butyl-lithium–1,2-bisdimethylaminoethane complex [23] afforded 4-dimethylamino-2-trifluoromethylphenyl-lithium which yielded the 2,2′-bistrifluoromethyl derivative of Michler's ketone *via* reaction with 4-dimethylamino-2-trifluoromethylbenzonitrile. Reduction of the ketone gave the corresponding hydrol (II; $R^1 = R^2 = CF_3$) while reaction with 2-trifluoromethylphenyl-lithium afforded the 2,2′,2″-tristrifluoromethyl derivative of Malachite Green base (V; $R^1 = R^2 = R^3 = CF_3$, $R^4 =$ H). 4-Dimethylamino-2-trifluoromethylphenyl-lithium was used to obtain the four remaining dye bases by reaction with ethyl 4-dimethylaminobenzoate, dimethyl carbonate, methyl benzoate, and methyl 4-trifluoromethylbenzoate, respectively. Typical reaction conditions have been described previously.[16, 24]

The dye bases were purified by crystallisation; details are given in Table 2.

TABLE 2

Derivatives of Michler's hydrol, Crystal Violet base, and Malachite Green base

Compound	Solvent	M.p. (°C)	Found (%)				Formula	Required (%)			
			C	H	F	N		C	H	F	N
(II; $R^1 = CF_3$, $R^2 =$ H)	*a*	89—90	63·9	6·1	16·8	8·2	$C_{18}H_{21}F_3N_2O$	63·9	6·2	16·9	8·3
(II; $R^1 = R^2 = CF_3$)	*b*	149—150	56·2	4·9	28·5	6·8	$C_{19}H_{20}F_6N_2O$	56·2	4·9	28·1	6·9
(V; $R^1 = CF_3$, $R^4 = NMe_2$, $R^2 = R^3 =$ H)	*c*	191—192	68·2	6·7	12·1	8·9	$C_{26}H_{30}F_3N_3O$	68·3	6·6	12·5	9·2
(V; $R^1 = R^2 = CF_3$, $R^4 =$ NMe, $R^3 =$ H)	*b*	223—224	61·8	5·7	21·3	8·1	$C_{27}H_{29}F_6N_3O$	61·7	5·5	21·7	8·0
(V; $R^1 = R^2 = R^3 = CF_3$, $R^4 = NMe_2$)	*d*	296 (decomp.)	56·5	4·9	28·5	6·9	$C_{28}H_{28}F_9N_3O$	56·7	4·8	28·8	7·1
(V; $R^1 = CF_3$, $R^2 = R^3 = R^4 =$ H)	*b*	172·5—173	69·7	6·3	13·7	6·7	$C_{24}H_{25}F_3N_2O$	69·6	6·0	13·8	6·8
(V; $R^1 = R^2 = CF_3$, $R^3 = R^4 =$ H)	*e*	169—170	62·2	5·0	23·7	5·8	$C_{25}H_{24}F_6N_2O$	62·2	5·0	23·7	5·8
(V; $R^1 = R^3 = CF_3$, $R^2 = R^4 =$ H)	*d*	194—195	62·4	5·2	23·4	5·7	$C_{25}H_{24}F_6N_2O$	62·2	5·0	23·7	5·8
(V; $R^1 = R^4 = CF_3$, $R^2 = R^3 =$ H)	*a*	138—140	62·3	5·1	23·8	5·8	$C_{25}H_{21}F_6N_2O$	62·2	5·0	23·7	5·8
(V; $R^1 = R^2 = R^3 = CF_3$. $R^4 =$ H)	*d*	237—238	57·1	4·3	31·4	5·3	$C_{26}H_{23}F_9N_2O$	56·7	4·2	31·1	5·1
(V; $R^1 = R^2 = R^4 = CF_3$, $R^3 =$ H)	*b*	180—182	56·5	4·4	31·5	5·1	$C_{26}H_{23}F_9N_2O$	56·7	4·2	31·1	5·1

[a] Light petroleum (b.p. 60—80 °C). [b] Light petroleum (b.p. 80—100 °C). [c] Cyclohexane. [d] Methanol. [e] Ethanol.

EXPERIMENTAL

Absorption spectra were measured with a Unicam SP 800 recording spectrophotometer for solutions of the dye bases in 98% acetic acid and in ethanolic hydrogen chloride. ^{1}H N.m.r. spectra were obtained with a Varian HA 100 spectrometer for solutions in deuteriochloroform at the Physico-Chemical Measurements Unit, Harwell.

4,4′-Bisdimethylamino-2-trifluoromethylbenzophenone.—Freshly prepared 4-dimethylaminobenzoyl chloride (10·3 g), *NN*-dimethyl-3-trifluoromethylaniline (24·3 g), and anhydrous zinc chloride (2·4 g) were stirred at room temperature for 3 h, then at 55 °C for 20 h, and finally at 80 °C for 2 h. The brown gum which remained after basification of the cold reaction mixture and subsequent distillation in steam was eluted from alumina with benzene to give a yellow gum which crystallised on standing. Recrystallisation of the product from benzene gave pale yellow prisms of the *ketone* (8·0 g), m.p. 191—191·5 °C (Found: C, 64·3; H, 5·5; F, 17·1; N, 8·5. $C_{18}H_{19}F_3N_2O$ requires C, 64·3; H, 5·7; F, 17·0; N, 8·3%), τ 2·31 (2H, d, J_o 9·0 Hz, 2′- and 6′-H), 2·75 (1H, d, J_o 8·5 Hz, 6-H), 3·02 (1H, d, J_m 2·5 Hz, 3-H), 3·23 (1H, dd, J_o 8·5, J_m 2·5 Hz, 5-H), 3·39 (2H, d, J_o 9·0 Hz, 3′- and 5′-H), and 6·96 (12H, s, NMe_2).

4,4′-Bisdimethylamino-2,2′-bistrifluoromethylbenzophenone.—Trimethyl phosphate (11 ml) was added during 20 min to 4-bromo-3-trifluoromethylaniline (9·8 g) kept at 170—180 °C. The temperature was raised to 190—200 °C for 2 h after which the cooled mixture was boiled with an excess of aqueous sodium hydroxide for 2 h and then poured into water. The crude amine was extracted with ether, boiled with acetic anhydride, and distilled at reduced pressure to give *4-bromo-*NN*-dimethyl-3-trifluoromethylaniline* (10·0 g) as an oil, b.p. 136—138 °C at 15 mmHg, which solidified on refrigeration yielding crystals, m.p. 28—29 °C (Found: C, 40·7; H, 3·6; Br, 29·5; F, 20·7; N, 5·6. $C_9H_9BrF_3N$ requires C, 40·3; H, 3·4; Br, 29·9; F, 21·3; N, 5·3%), τ 2·56 (1H, d, J_o 9·0 Hz, 5-H), 3·06 (1H, d, J_m 3·0 Hz, 2-H), 3·37 (1H, dd, J_o 9·0, J_m 3·0 Hz, 6-H), and 7·05 (6H, s, NMe_2).

The bromo-amine (5·4 g), copper(I) cyanide (2·2 g), and dimethylformamide (10 ml) were boiled for 6 h. The partially cooled solution was shaken with sodium cyanide (4 g) in water (20 ml) and twice extracted with benzene (20 ml). The organic layer was washed with 10% aqueous sodium cyanide and then with water. Removal of the solvent yielded a solid which was first distilled, b.p. 185—186 °C at 15 mmHg, and then recrystallised from light petroleum (b.p. 80—100 °C) to give needles of *4-dimethylamino-2-trifluoromethylbenzonitrile* (3·3 g), m.p. 91·5—92 °C (Found: C, 56·0; H, 4·1; F, 26·4; N, 13·2. $C_{10}H_9F_3N_2$ requires C, 56·1; H, 4·2; F, 26·6; N, 13·1%), τ 2·44 (1H, d, J_o 9·0 Hz, 6-H), 3·10 (1H, d, J_m 3·0 Hz, 3-H), 3·26 (1H, dd, J_o 9·0, J_m 3·0 Hz, 5-H), and 6·91 (6H, s, NMe_2).

Ethereal 4-dimethylamino-2-trifluoromethylphenyl-lithium, from 4-bromo-*NN*-dimethyl-3-trifluoromethylaniline

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[20] P. Tarrant and M. R. Lilyquist, *J. Amer. Chem. Soc.*, 1953, **75**, 3034.

[21] L. Friedman and H. Shechter, *J. Org. Chem.*, 1961, **26**, 2522.

[22] V. Caló, F. Ciminale, L. Lopez, and P. E. Todesco, *J. Chem. Soc. (C)*, 1971, 3652.

[23] G. Hallas and D. R. Waring, *Chem. and Ind.*, 1969, 620.

[24] G. Hallas and A. Schofield, *J. Chem. Soc. (B)*, 1968, 933.

(2·7 g) and the n-butyl-lithium–1,2-bisdimethylaminoethane complex, was added under nitrogen to 4-dimethylamino-2-trifluoromethylbenzonitrile (2·1 g) in ether (30 ml), and the mixture was boiled for 2 h. The cold solution was thrice extracted with 3M-hydrochloric acid (30 ml) and the aqueous layer was boiled for 7 h, basified, and distilled in steam. Elution of the residue from alumina with benzene–chloroform (2 : 1) and crystallisation of the product from ethanol gave needles of the *ketone* (2·3 g), m.p. 132·5—133·5 °C (Found: C, 56·3; H, 4·6; F, 28·5; N, 6·9. $C_{19}H_{18}F_6N_2O$ requires C, 56·4; H, 4·5; F, 28·2; N, 6·9%), τ 2·74 (2H, d, J_o 8·5 Hz, 6- and 6′-H), 2·99 (2H, d, J_m 2·5 Hz, 3- and 3′-H), 3·36 (2H, dd, J_o 8·5, J_m 2·5 Hz, 5- and 5′-H), and 6·95 (12H, s, NMe_2).

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