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# $N$-Trifluoromethylsulfonylimino derivatives of carbonyl-containing donor–acceptor systems

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**Abstract**—Imination of carbonyl compounds, containing electron donor groups, with trifluoromethylsulfonyl isocyanate to give the corresponding $N$-trifluoromethylsulfonylimino derivatives causes a strong bathochromic shift in their UV absorption maxima amounting to 150–200 nm. © 2002 Elsevier Science Ltd. All rights reserved.

The colors of many organic compounds are determined by electron transfer from an electron donor, e.g. a dimethylamino substituent, to an electron acceptor, in particular a carbonyl group.

We have conjectured that replacement of the oxygen atom in such donor–acceptor systems by the $=NSO_2CF_3$ group should lead to a considerable bathochromic shift in their absorption maxima due to the greater electron-withdrawing power of the introduced substituent,[1–4] as compared to the $sp^2$ oxygen, owing to the increase in polarity of the molecule.

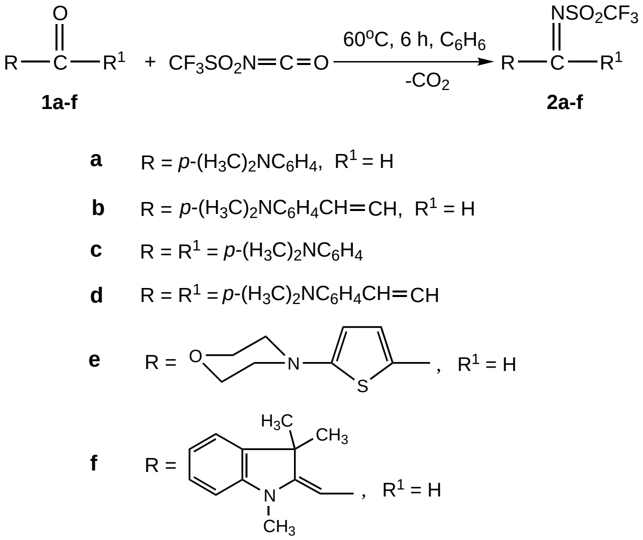
Trifluoromethylsulfonyl isocyanate has been reported as reacting with benzaldehyde with elimination of carbon dioxide to give $N$-trifluoromethylsulfonylbenzalimine in 40% yield.[5]

We have found that trifluoromethylsulfonyl isocyanate readily reacts with carbonyl compounds **1a**–**f** containing electron-releasing substituents to give the corresponding $N$-trifluoromethylsulfonylimino derivatives **2a**–**f** in 60–70% yields (Scheme 1).[6] Absorption maxima of the products are shifted 44–140 nm towards longer wavelengths relative to the parent compounds, the shift being increased with lengthening of the conjugation chain (Table 1).

It was of interest to ascertain the effect on the absorption maxima of ketocyanine dyes, containing cyclopentanone or cyclohexanone moieties in the polymethyne chain, on imination (Scheme 2).[6]

It was established that replacement of the carbonyl oxygen in ketocyanine dyes **1g**–**j** by the imino group $=NSO_2CF_3$ resulted in very strong bathochromic shifts (150–200 nm). The values of $\lambda_{max}$ for imines **2g**–**j** are 546–683 nm in benzene and 596–712 nm in acetonitrile, that is, they approach the near-IR region (Table 1). For comparison, the red shifts of the tosylimino derivatives of **1a** and **1i** in benzene are 46 and 92 nm only.

Upon protonation, ketocyanine derivatives **1i** and **1j** form *meso*-substituted tricarbocyanines, whose absorption maxima are shifted to longer wavelengths, e.g. for **1i**, from 530 to 717 nm.[7,8] In the case of imine **2i**, acidification of its solution in $CH_2Cl_2$ with $p$-toluene-



**Scheme 1.**

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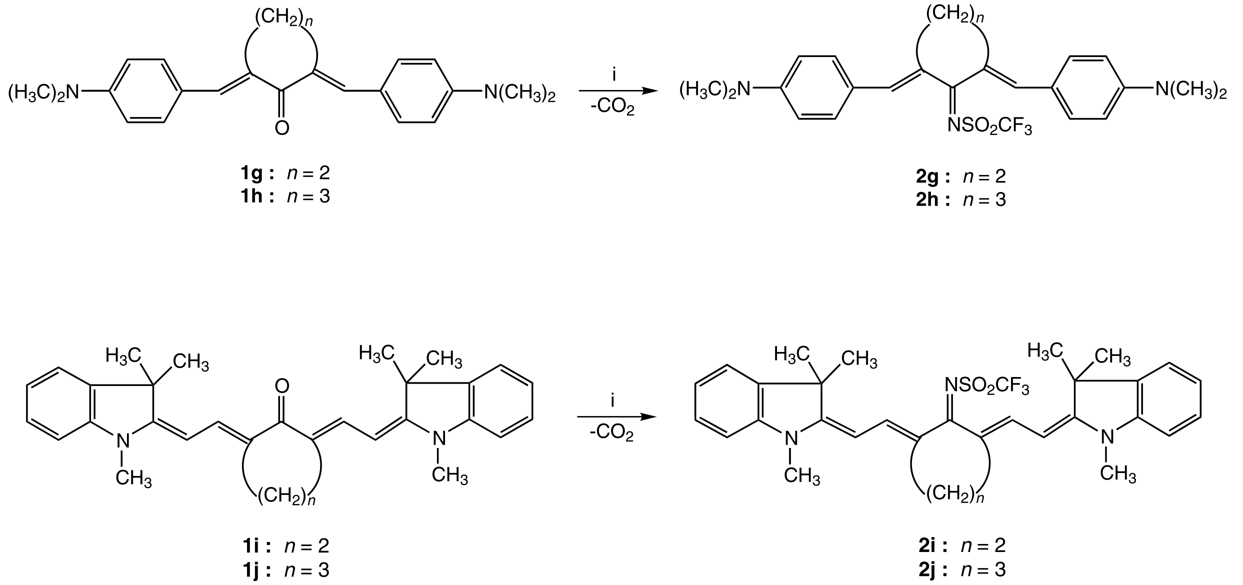
**Table 1.** Absorption maxima and yields of imines **2a–j**

| Entry | **1** | $\lambda_{max}$/nm ($C_6H_6$) | $\lambda_{max}$/nm ($CH_3CN$) | **2** | $\lambda_{max}$/nm ($C_6H_6$) | $\Delta\lambda_{max}$/nm[a] ($C_6H_6$) | $\varepsilon$ ($\times 10^{-4}$) | $\lambda_{max}$/nm ($CH_3CN$) | $\Delta\lambda_{max}$/nm[a] ($CH_3CN$) | $\varepsilon$ ($\times 10^{-4}$) | Yield **2** (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **1a** | 334 | 336 | **2a** | 401 | 67 | 5.22 | 409 | 73 | 5.83 | 76 |
| 2 | **1b** | 377 | 372 | **2b** | 469 | 92 | 2.47 | 482 | 110 | 4.80 | 65 |
| 3 | **1c** | 348 | 354 | **2c** | 435 | 87 | 2.94 | 455 | 101 | 3.59 | 70 |
| 4 | **1d** | 431 | 434 | **2d** | 535 | 104 | 2.70 | 574 | 140 | 4.90 | 52 |
| 5 | **1e** | 354 | 360 | **2e** | 418 | 64 | 2.37 | 421 | 61 | 4.85 | 67 |
| 6 | **1f** | 334 | 335 | **2f** | 381 | 47 | 4.53 | 379 | 44 | 5.98 | 62 |
| 7 | **1g** | 457 | 459 | **2g** | 584 | 127 | 1.04 | 619 | 160 | 2.90 | 60 |
| 8 | **1h** | 426 | 429 | **2h** | 546 | 120 | 4.0 | 596 | 167 | 3.79 | 63 |
| 9 | **1i** | 508 | 530 | **2i** | 646 | 138 | 7.5 | 678 | 148 | 5.5 | 60 |
| 10 | **1j** | 492 | 513 | **2j** | 683 | 191 | 2.0 | 712 | 199 | 7.76 | 55 |

[a] The difference in $\lambda_{max}$ between **1** and **2** in $C_6H_6$ or $CH_3CN$.



**1g :** *n* = 2
**1h :** *n* = 3

**2g :** *n* = 2
**2h :** *n* = 3

**1i :** *n* = 2
**1j :** *n* = 3

**2i :** *n* = 2
**2j :** *n* = 3

**Scheme 2.** *Reagents and conditions*: (i) $CF_3SO_2NCO$, $C_6H_6$, 60°C, 6 h.

sulfonic or trifluoromethanesulfonic acid causes a shift in $\lambda_{max}$ to even longer wavelengths, from 678 to 819 nm. These shifts can be explained by the fact that in the acid medium both **1i** and **2i** form tricarbocyanine dyes possessing nuclear substituents of a different electronic nature in the *meso*-position of the polymethyne chain, i.e. the electron donor HO group in **1i** and the electron acceptor $NHSO_2CF_3$ group ($\sigma_p$ 0.49) in **2i**, which produce the hypsochromic and bathochromic effects, respectively. These effects are relative to the reference dye which is unsubstituted at this position ($\lambda_{max}$ 798 nm in $CH_2Cl_2$), and is in agreement with the Dewar–Knott color rules.[9]

In conclusion, the proposed method allows the synthesis of deeply colored dyes by imination of the carbonyl group as $=NSO_2CF_3$.

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6. General procedure for **2a–j**: To a stirred suspension or solution of **1a–j** (2 mmol) in anhydrous benzene (5 ml) was added dropwise, at 2–5°C, under a flow of dry argon, a solution of trifluoromethylsulfonyl isocyanate (2.2 mmol) in anhydrous benzene (4 ml). The mixture was stirred for 6 h at 60°C then filtered and the solvent was distilled off. The residue was washed with hot hexane and purified by crystallization or chromatography on silica gel (eluent: benzene/ethyl acetate, 5:2).
Compound **2a**: Mp 182–184°C (benzene; dec.); $^1H$ NMR (300 MHz, $CDCl_3$, TMS): $\delta$ 3.15 (s, 6H, $N(CH_3)_2$), 6.72

(m, 2H, $C_6H_4$), 7.86 (m, 2H, $C_6H_4$), 8.75 (s, 1H, HC=N); $^{19}$F NMR (288 MHz, $CDCl_3$, $CFCl_3$): $\delta$ −77.94 (s, $CF_3$); IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 1590 (C=N). Anal. calcd for $C_{10}H_{11}F_3N_2O_2S$: C, 42.86; H, 3.96; N, 10.00. Found: C, 43.16; H, 4.04; N, 10.22.

Compound **2b**: Mp 161–162°C (benzene/hexane; dec.); $^1$H NMR (300 MHz, acetone-$d_6$, TMS): $\delta$ 3.21 (s, 6H, $N(CH_3)_2$), 6.88 (m, 2H, $C_6H_4$), 7.02 (dd, 1H, $J$ = 15 Hz, 10 Hz, HC=), 7.77 (m, 2H, $C_6H_4$), 8.08 (d, 1H, $J$ = 15 Hz, HC=), 8.77 (d, 1H, $J$ = 10 Hz, HC=N); $^{19}$F NMR (288 MHz, acetone-$d_6$, $CFCl_3$): $\delta$ −77.89 (s, $CF_3$); IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 1580 (C=N). Anal. calcd for $C_{12}H_{13}F_3N_2O_2S$: C, 47.06; H, 4.28; N, 9.15. Found: C, 46.98; H, 4.27; N, 9.16%.

Compound **2c**: Mp 196–198°C (benzene/hexane); $^1$H NMR (300 MHz, acetone-$d_6$, TMS): $\delta$ 3.18 (s, 12H, $2N(CH_3)_2$), 6.84 (m, 4H, $2C_6H_4$), 7.61 (m, 4H, $2C_6H_4$); $^{19}$F NMR (288 MHz, acetone-$d_6$, $CFCl_3$): $\delta$ −79.10 (s, $CF_3$); IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 1600 (C=N). Anal. calcd for $C_{18}H_{20}F_3N_3O_2S$: C, 54.13; H, 5.05; N, 10.52. Found: C, 54.20; H, 5.17; N, 10.56%.

Compound **2d**: Mp 214–216°C; $^1$H NMR (300 MHz, acetone-$d_6$, TMS): $\delta$ 3.14 (s, 12H, $2N(CH_3)_2$), 6.85 (m, 4H, $2C_6H_4$), 7.50 (d, 2H, $J$ = 15.2 Hz, 2HC=), 7.69 (m, 4H, $2C_6H_4$), 8.06 (d, 2H, $J$ = 15.2 Hz, 2HC=); $^{19}$F NMR (288 MHz, acetone-$d_6$, $CFCl_3$): $\delta$ −79.27 (s, $CF_3$); IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 1580 (C=N). Anal. calcd for $C_{22}H_{24}F_3N_3O_2S$: C, 42.86; H, 3.96; N, 10.00. Found: C, 43.16; H, 4.04; N, 10.22%.

Compound **2e**: Mp 160–162°C; $^1$H NMR (300 MHz, acetone-$d_6$, TMS): $\delta$ 3.78 (m, 4H, $2CH_2$), 3.89 (m, 4H, $2CH_2$), 6.79 (m, 1H, $C_4H_2S$), 8.11 (m, 1H, $C_4H_2S$), 8.58 (s, 1H, HC=N); $^{19}$F NMR (288 MHz, acetone-$d_6$, $CFCl_3$): $\delta$ −79.20 (s, $CF_3$); IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 1585 (C=N). Anal. calcd for $C_{10}H_{11}F_3N_2O_3S_2$: C, 36.58; H, 3.35; N, 8.54. Found: C, 36.87; H, 3.44; N, 8.60%.

Compound **2f**: Mp 201–203°C; $^1$H NMR (300 MHz, acetone-$d_6$, TMS): $\delta$ 1.69 (s, 6H, $C(CH_3)_2$), 3.74 (s, 3H, $NCH_3$), 6.06 (d, 1H, $J$ = 12.9 Hz, HC=), 7.37–7.64 (m, 4H, $C_6H_4$), 8.90 (d, 1H, $J$ = 12.9 Hz, HC=N); $^{19}$F NMR (288 MHz, acetone-$d_6$, $CFCl_3$): $\delta$ −78.20 (s, $CF_3$); IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 1570 (C=N). Anal. calcd for $C_{14}H_{15}F_3N_2O_2S$: C, 50.60; H, 4.52; N, 8.43. Found: C, 50.68; H, 4.68; N, 8.23%.

Compound **2g**: Mp 226–228°C (dec.); $^{19}$F NMR (288 MHz, acetone-$d_6$, $CFCl_3$): $\delta$ −79.64 (s, $CF_3$); IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 1560 (C=N). Anal. calcd for $C_{24}H_{26}F_3N_3O_2S$: C, 60.36; H, 5.49; N, 8.80. Found: C, 60.54; H, 5.69; N, 8.86%.

Compound **2h**: Mp 231–233°C; $^1$H NMR (300 MHz, acetone-$d_6$, TMS): $\delta$ 2.84 (m, 4H, $2CH_2$), 2.92 (m, 2H, $CH_2$), 3.08 (s, 12H, $2N(CH_3)_2$), 6.69 (m, 4H, $2C_6H_4$), 7.50 (m, 4H, $2C_6H_4$), 7.88 (s, 2H, 2HC=); $^{19}$F NMR (288 MHz, acetone-$d_6$, $CFCl_3$): $\delta$ −78.72 (s, $CF_3$); IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 1570 (C=N). Anal. calcd for $C_{25}H_{28}F_3N_3O_2S$: C, 61.04; H, 5.70; N, 8.54. Found: C, 61.00; H, 5.66; N, 8.63%.

Compound **2i**: Mp 271–273°C (dec.); $^1$H NMR (300 MHz, acetone-$d_6$, TMS): $\delta$ 1.71 (s, 12H, $2C(CH_3)_2$), 2.78 (s, 4H, $2CH_2$), 3.49 (s, 6H, $2NCH_3$), 5.71 (d, 2H, $J$ = 13.7 Hz, 2HC=), 6.87–7.47 (m, 8H, $2C_6H_4$), 8.21 (d, 2H, $J$ = 13.7 Hz, 2HC=); $^{19}$F NMR (288 MHz, acetone-$d_6$, $CFCl_3$): $\delta$ −78.90 (s, $CF_3$); IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 1565 (C=N). Anal. calcd for $C_{32}H_{34}F_3N_3O_2S$: C, 66.09; H, 5.85; N, 7.23. Found: C, 66.15; H, 5.82; N, 7.39%.

Compound **2j**: Mp 232–234°C (dec.); $^1$H NMR (300 MHz, acetone-$d_6$, TMS): $\delta$ 1.79 (s, 12H, $2C(CH_3)_2$), 1.92 (m, 2H, $CH_2$), 2.79 (m, 4H, $2CH_2$), 3.82 (s, 6H, $2NCH_3$), 6.26 (d, 2H, $J$ = 14 Hz, 2HC=), 7.27–8.04 (m, 8H, $2C_6H_4$), 8.45 (d, 2H, $J$ = 14 Hz, 2HC=); $^{19}$F NMR (288 MHz, acetone-$d_6$, $CFCl_3$): $\delta$ −79.70 (s, $CF_3$); IR: $\nu_{max}$ (KBr)/cm$^{-1}$ 1560 (C=N). Anal. calcd for $C_{33}H_{36}F_3N_3O_2S$: C, 66.55; H, 6.05; N, 7.06. Found: C, 66.74; H, 6.24; N, 6.84%.

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