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# Phenyl iodonium bis(perfluoroalkanesulphonyl) methide–dimethyl sulphoxide adduct. Its formation and X-ray structural analysis

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## Abstract

Irradiation of phenyl iodonium bis(perfluoroalkanesulphonyl)methide in DMSO yields a 1:1 adduct, DMSO·$PhI \equiv C(SO_2R_F)_2$. Its X-ray crystal structure is reported together with that of DMSO·$PhI \equiv \overline{CSO_2(CF_2)_3S}O_2$.

## Introduction

During the study of the photoreaction of phenyl iodonium bis(perfluoroalkanesulphonyl)methides [1], $PhI=C(SO_2CF_3)_2$ (**1a**), $PhI=\overline{CSO_2(CF_2)_3S}O_2$ (**1b**), it was interesting to find that a transylidation reaction occurred when **1** was treated with pyridine, methyl sulphide or triphenyl phosphine, giving a series of new ylides containing the bis(perfluoroalkanesulfonyl) functionality $Y^+ \ ^-C(SO_2R_F)_2$ [2] ($Y=C_5H_5N$, $Me_2S$, $Ph_3P$). Hadjiarapoglou and Varvoglis [3] have reported that $(PhSO_2)_2C=S(O)Me_2$ could be obtained by irradiation of $PhI=C(SO_2Ph)_2$ in DMSO. In our case, however, under the same reaction conditions, none of the corresponding $(R_FSO_2)C=S(O)Me_2$ was obtained, the only product being a 1:1 adduct. A recent publication [4] on the crystal structure of an alcohol–DMSO coordinate complex has prompted us to report our work.

## Experimental

### Materials

The complexes DMSO·$PhI \equiv C(SO_2CF_3)_2$ (**2a**) and DMSO·$PhI \equiv \overline{CSO_2(CF_2)_3S}O_2$ (**2b**) were obtained as fine colorless solids. Both were stable at room temperature and in air.

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## *Methods*

### *Infrared and NMR spectra*

$^1H$ NMR and $^{19}F$ NMR spectra were recorded on a Varian-360L instrument with $Me_4Si$ and $CF_3Cl$ as internal and external standards, respectively. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer.

### *Crystal data*

Intensity data were collected at 20 °C with an Enraf–Nonius CAD4 diffractometer using graphite-monochromated MoK$\alpha$ radiation. For **2a**, 1944 unique reflections were measured in the range $2° < 2\theta < 50°$, with $0 < h < 12$, $0 < k < 14$, $0 < l < 18$. For **2b**, 3756 unique reflections were measured in the range $2° < 2\theta < 50°$ with $0 < h < 10$, $0 < k < 12$, $-25 < l < 25$. The correction of LP and absorption was applied for the reflection data. The structures were solved using the direct MULTAN11/82 method. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by a full-matrix least-squares technique. For **2a**, the final $R$, $Rw$ and $S$ values were 0.053, 0.096 and 5.14, respectively, for 1544 observed reflections ($F^* > 3\sigma(F^*)$). For **2b**, the final $R$, $Rw$ and $S$ values were 0.040, 0.048 and 2.79, respectively, for 2158 observed reflections ($F^* > 3\sigma(F^*)$). All calculations

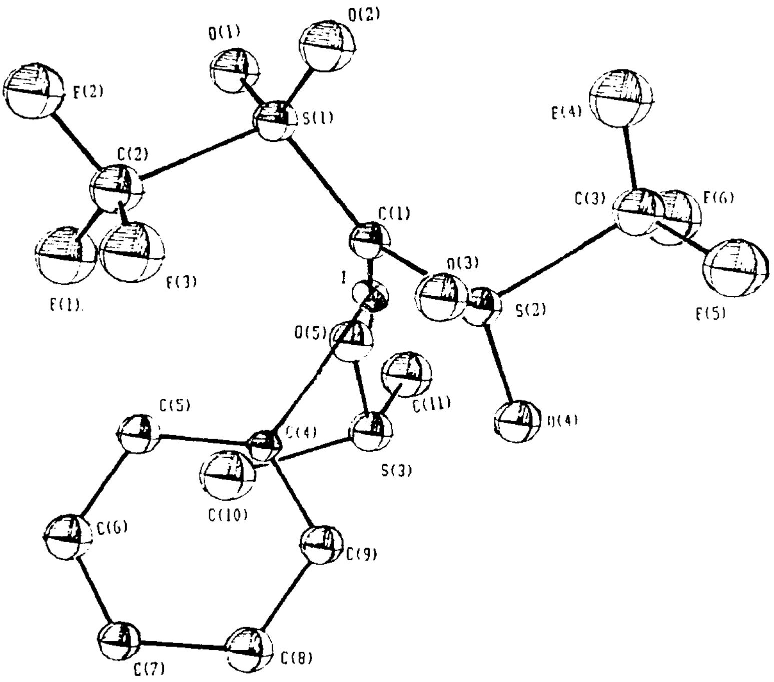


Fig. 1. The structure of **2a** (hydrogen atoms omitted). Selected bond lengths (Å) and bond angles (°). I–O(5), 2.59(2); I–C(1), 2.08(1); I–C(4), 2.11(1); C(1)–S(1), 1.67(1); C(1)–S(2), 1.68(1); C(2)–S(1), 1.86(2); C(3)–S(2), 1.84(2); C(1)–I–C(4), 98.9(4); O(5)–I–C(1), 173.5(4); O(5)–I–C(4), 81.8(4); S(1)–C(1)–S(2), 124.2(7).

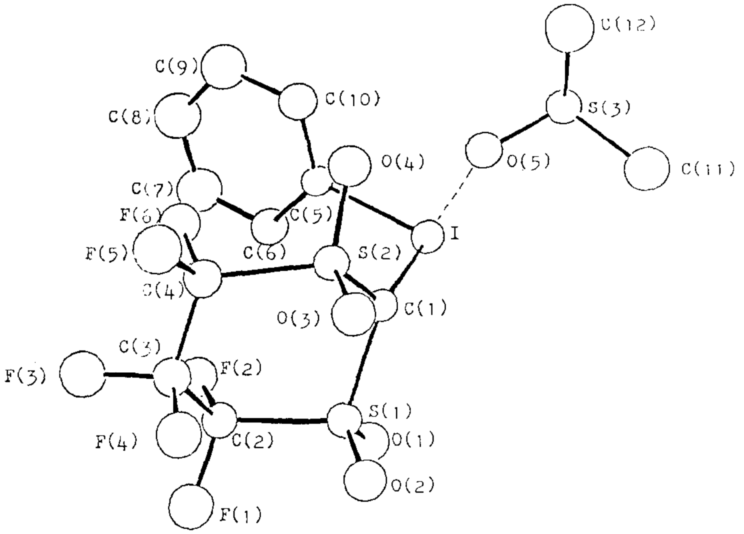
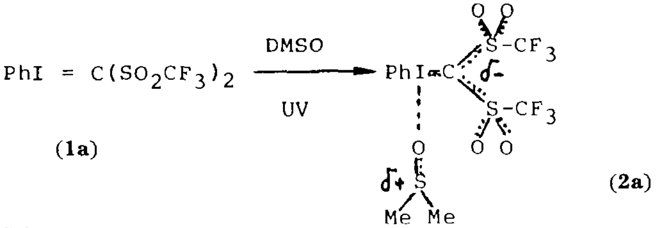


Fig. 2. The structure of **2b** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and bond angles (°). I–O(5), 2.564(4); I–C(1), 2.058(5); I–C(5), 2.110(6); S(1)–C(1), 1.686(5); S(2)–C(1), 1.678(6); O(5)–I–C(1), 176.1(2); O(5)–I–C(5), 77.1(2); C(1)–I–C(5), 99.0(2); S(1)–C(1)–S(2), 117.6(3); S(1)–C(1)–S(2), 117.6(3).



**(1a)**

**(2a)**

Scheme 1.

were performed on a MICROVAX II computer with SDP, MULTAN11/82 and ORTEP programs. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

## Results and discussion

The following crystal data were obtained:

Compound **2a**: $C_{11}H_{11}O_5F_6S_3I$: $M = 560.29$; orthorhombic; space group, $P212121$; $a = 10.180(3)$, $b = 11.768(3)$, $c = 15.808(2)$ Å, $V = 1893.8$ Å$^3$, $Z = 4$, $D_c = 1.965$ g cm$^{-3}$; $F(000) = 1088$; (MoK$\alpha$) $= 20.63$ cm$^{-1}$; crystal dimensions, 0.2×0.2×0.2 mm.

Compound **2b**: $C_{12}H_{11}O_5F_6S_3I$: $M = 572.30$; monoclinic; space group, $P21/n$; $a = 8.733(1)$, $b = 10.239(2)$, $c = 21.101(1)$ Å, $\beta = 94.47(4)°$; $V = 1881.0$ Å$^3$, $z = 4$, $D_c = 2.021$ g cm$^{-3}$; $F(000) = 1112$; (MoK$\alpha$) $= 20.794$ cm$^{-1}$; crystal dimensions, 0.2×0.2×0.1 mm.

TABLE 1

Physical data for compounds **1** and **2**

| Compound | M.p. (°C) | IR data ($\nu_{as}SO_2$) (cm$^{-1}$) | $^1$H NMR data ($\delta$ ppm) | Analysis [Found (Calcd.)] | | |
|---|---|---|---|---|---|---|
| | | | | C | H | F |
| **1a** | 140 | 1360 | 7.6–7.8 (m, 3H);<br>8.8–8.4 (m, 2H) | 22.42<br>(22.41) | 0.86<br>(1.03) | 24.17<br>(23.65) |
| **2a** | 116–118 | 1351 | 7.5–7.6 (m, 3H);<br>8.1–8.2 (m, 2H);<br>3.5 (s, 2 × $CH_3$)[a] | 23.09<br>(23.56) | 1.91<br>(1.96) | 20.43<br>(20.34) |
| **1b** | 193 | 1360 | 7.6–7.8 (m, 3H);<br>8.2–8.4 (m, 2H) | 24.00<br>(24.29) | 0.77<br>(1.01) | 23.73<br>(23.08) |
| **2b** | 180–182 | 1352 | 7.5–7.8 (m, 3H);<br>8.0–8.1 (m, 2H);<br>3.5 (s, 2 × $CH_3$)[a] | 25.20<br>(25.17) | 1.72<br>(1.92) | 19.85<br>(19.93) |

[a] The downfield chemical shift of the methyl group in **2** relative to that in $(CH_3)_2SO$ indicates that it is attached to a positively charged sulphur atom.

The spectral data and X-ray analyses reveal that both materials are 1:1 adducts, as shown in Figs. 1 and 2. From the X-ray structural analysis of **1a** [1], we proposed that the C–I bond (1.89 Å) has some double-bond character. In complex **2a** the C–I bond is somewhat longer (2.08 Å), whereas the two C–S bonds (1.69 Å and 1.66 Å) are shorter than in **1a** (1.72 Å and 1.77 Å) due to interaction between the iodine atom and the oxygen atom of DMSO. This interaction is also apparent from a comparison of some physical data for **1a** and **2a** (Table 1). From these data, the adducts **2** could also be considered as charge-transfer complexes (see Scheme 1).

Because the distance between the sulphur atom of DMSO and any sulphonyl oxygen atom of **2a** is larger than 3.5 Å, an intramolecular six-membered ring structure is ruled out.

## Conclusions

The 1:1 addition products **2a** and **2b** are formed during the photoreaction of **1** with DMSO. Their structures are fully supported by the spectral data and X-ray analyses.

## References

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