

sont peu inclinés par rapport à *P*1: 2,1 (DPCA) et 1,7° (DPCB). On trouve 7° dans FPAMCA et 8° dans TRFLOC 10. Ceci entraîne des contacts courts N(1)—O(1) = 2,659 (3) et N(21)—O(21) = 2,645 (3) Å, indiquant une interaction entre ces atomes à laquelle participe l'hydrogène lié à N. Les paramètres géométriques en sont les suivants: N(1)—H(14): 1,03 (3), N(21)—H(15): 0,94 (3), O(1)—H(14): 1,98 (3), O(21)—H(15): 2,00 (3) Å, N(1)—H(14)—O(1): 121 (2) et N(21)—H(15)—O(21): 124°. Il y a dimérisation dans la maille par l'intermédiaire d'une paire de liaisons hydrogène entre les groupes carboxyliques des molécules *A* et *B*. La distance O(1)—O(22) est égale à 2,670 (3) Å et O(21)—O(2), à 2,668 (3) Å. Il y a dissymétrie au niveau des angles C(7)—O(2)—O(21) = 110,8 (2) et C(7)—O(1)—O(22) = 127,9 (2), de même C(27)—O(22)—O(1) = 110,7 (2) et C(27)—O(21)—O(2) = 127,3 (2)°. Les positions précises des atomes H de ces liaisons n'ont pu être déterminées par Fourier-différence.

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## Dimethyl(dimethylaminomethylene)ammonium 2,6-Dinitro-4-trifluoromethylbenzene-sulfonate

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**Abstract.** C<sub>5</sub>H<sub>13</sub>N<sub>2</sub><sup>+</sup>·C<sub>7</sub>H<sub>2</sub>F<sub>3</sub>N<sub>2</sub>O<sub>7</sub>S<sup>-</sup>, *M<sub>r</sub>* = 416.33, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 16.573 (3), *b* = 8.418 (2), *c* = 12.942 (3) Å, β = 101.52 (3)°, *U* = 1769 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.57, *D<sub>x</sub>* = 1.563 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ(Mo *K*α) = 2.07 cm<sup>-1</sup>, *F*(000) = 856, room temperature, *R* = 0.041 for 1515 independent reflections with *I* ≥ 3σ(*I*). In the anion the phenyl ring shows noticeable angular distortions with S 0.203 (1) Å out of the aromatic plane and the nitro groups tilted by 64.5 (2) and 61.2 (2)° respectively with respect to that plane. In the cation the methyl groups lie on opposite

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sides with respect to the central N(3)—C(8)—N(4) plane.

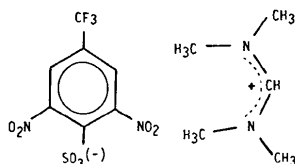
**Introduction.** Studies dealing with the synthesis of arylsulfonates of *N,N,N',N'*-tetramethylmethanedi-amine are of particular interest because of their possible use as tensioactives (Bagley & Poshkus, 1972). This class of compounds is generally prepared from the appropriate arylsulfoxide.

We now report details of the preparation and the structural analysis of the title compound which has

been obtained with good yields by using sodium 2,6-dinitro-4-trifluoromethylbenzenesulfonate as starting material.

**Experimental.** The sodium salt was prepared by adding a solution of  $\text{Na}_2\text{SO}_3$  (93 g, 0.74 mol) in water (800 ml) to a solution of sodium 3,5-dinitro-4-chlorobenzotrifluoride (200 g, 0.74 mol) in ethanol. After 4 h of stirring the solution was cooled to room temperature, the solid was filtered off and washed with ethanol. The compound was dried at 333 K with a yield of 93%.

The title compound was synthesized by adding *N,N*-dimethylformamidethionylchloride (71 g, 0.6 mol) drop by drop to a refluxing solution of sodium 2,6-dinitro-4-trifluoromethylbenzenesulfonate (100 g, 0.3 mol). The solution was then cooled in a mixture of water and ice, allowing the salt to precipitate. The solid was filtered off and vacuum dried. Analysis calc. for  $\text{C}_{12}\text{H}_{15}\text{F}_3\text{N}_4\text{O}_7\text{S}$ : C, 34.61; O, 26.92; N, 13.46; F, 13.7; S, 7.69; H, 3.6%; found: C, 34.8; O, 28.14; N, 13.38; F, 12.28; S, 7.75; H, 3.65%.



Orange crystals obtained from water; crystal used of dimensions  $0.12 \times 0.24 \times 0.30$  mm, density measured by flotation, PW 1100 diffractometer with monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71069$  Å); 25 reflections,  $8 < \theta < 10.4^\circ$ , used for refinement of cell dimensions; index ranges measured  $h - 19$  to  $19$ ,  $k 0$  to  $10$ ,  $l 0$  to  $15$ , two reflections (121 and 502) measured after every 180 min of X-ray exposure time. Scan width  $1.20^\circ$ , scan speed  $0.03^\circ \text{ s}^{-1}$ , total background measuring time 20 s;  $2\theta$  range  $5-50^\circ$ , total number of reflections measured 3505, 1515 reflections having  $I \geq 3\sigma(I)$  used in the analysis, corrections for Lorentz and polarization effects. Structure solved by direct methods (Hull, Viterbo, Woolfson & Shao-Hui, 1981) and refined by full-matrix least-squares procedure, with anisotropic thermal parameters for all non-H atoms;  $\sum w(\Delta F)^2$  minimized,  $R = 0.041$ ,  $wR = 0.041$ ,  $w = 2.2184[\sigma^2(F_o) + 0.000457(F_o)^2]^{-1}$ , H atoms located by difference Fourier maps, refined with isotropic temperature factors,  $S = 2.16$ ,  $(\Delta/\sigma)_{\text{max}} = 0.46$  maximum,  $\Delta\rho$  excursions  $0.54$  and  $-0.55 \text{ e } \text{Å}^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974); no corrections for absorption or secondary extinction. All calculations performed on a VAX 11/750 computer with *SHELX76* program package (Sheldrick, 1976). All geometrical calculations carried out with *PARST* (Nardelli, 1973). Drawings by *PLUTO78* (Motherwell & Clegg, 1978).

**Discussion.** Atomic coordinates and equivalent isotropic temperature factors are given in Table 1.\*

Bond lengths and angles are given in Table 2. Fig. 1 presents a view of the asymmetric unit: the tetramethylformamidinium cation and the 2,6-dinitro-4-trifluoromethylbenzenesulfonate anion. Cations and anions are hydrogen-bonded through H(8) of the formamidinium moiety and O(2') of the sulfonic group of the anion (as shown in Fig. 2).  $[\text{H}(8)\cdots\text{O}(2')] (1-x, -\frac{1}{2}+y, \frac{1}{2}-z) 2.24(4)$ ,  $[\text{C}(8)\cdots\text{O}(2')] 3.19(1) \text{ Å}$  and  $[\text{C}(8)-\text{H}(8)\cdots\text{O}(2')] 171(4)^\circ$ .

In addition the centrosymmetrically related anionic units are connected through hydrogen bonds involving the H(3) of the phenyl group and O(5<sup>ii</sup>) belonging to the nitro group in  $-x, -y, -z$ ; this results in the formation of ten-membered rings  $[\text{C}(3)\cdots\text{O}(5^{\text{ii}}) 3.40(1)$ ,  $[\text{H}(3)\cdots\text{O}(5^{\text{ii}}) 2.61(5) \text{ Å}$ ,  $[\text{C}(3)-\text{H}(3)\cdots\text{O}(5^{\text{ii}}) 152(4)^\circ]$ . Other inter- and intramolecular contacts present in the structure involving methyl H are not in an orientation favourable for being considered as hydrogen bonds (a list of such contacts has been deposited).

In the anion the geometry of the phenyl carbon skeleton is very sensitive to the electronic properties of the substituents. The two  $\text{NO}_2$  groups (electron-withdrawing) increase noticeably the internal angles  $[\text{C}(1)-\text{C}(2)-\text{C}(3) 124.1(4)$ ,  $[\text{C}(1)-\text{C}(6)-\text{C}(5) 124.2(4)^\circ]$  while the  $\text{SO}_3$  group decreases the endocyclic angle at C(1) to  $113.6(4)^\circ$ ; the  $\text{CF}_3$  group does not seem to have any influence, the endocyclic angle at C(4) being  $119.4(4)^\circ$ . The average C—C bond distance in the ring,  $1.376(6) \text{ Å}$ , is not significantly different from the value usually accepted. The C(1)—S bond distance,  $1.813(4) \text{ Å}$ , corresponds to the commonly accepted value for a C—S single bond and the S atom is displaced from the mean plane of the phenyl ring by  $0.216(3) \text{ Å}$ . The N—C bond distances of the two nitro groups are comparable  $[\text{N}(2)-\text{C}(6) 1.492(6)$  and  $[\text{N}(1)-\text{C}(2) 1.488(6) \text{ Å}]$  and slightly longer than expected [when compared with analogous bonds in 2,4,6-trinitro-1,3-benzenediol 2/3-hydrate and 2,4,6-trinitro-1,3,5-benzenetriol 2/3-hydrate (Pierce-Butler, 1982)].

In the cation the N(4)—C(8) and N(3)—C(8) bond distances,  $1.312(7)$  and  $1.299(6) \text{ Å}$  respectively, are comparable, which indicates a mesomeric effect. The value  $[131.3(5)^\circ]$  of the N(4)—C(8)—N(3) angle is larger than expected, and could be explained by the presence of the bulky methyl substituents which are twisted with respect to the central N(4), C(8), N(3)

\* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving hydrogen atoms, and intramolecular contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43616 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

plane [deviations are: C(9) 0.07 (1), C(10) -0.15 (1), C(11) -0.08 (1) and C(12) 0.20 (1) Å]. The N—C (methyl) distances are as expected.

Table 1. Atomic coordinates ( $\times 10^4$ ) and  $U_{eq}$  ( $\text{\AA}^2 \times 10^3$ ) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

|       | x        | y          | z         | $U_{eq}(\text{\AA}^2)$ |
|-------|----------|------------|-----------|------------------------|
| S     | 3051 (1) | -1467 (2)  | 636 (1)   | 45.1 (4)               |
| O(1)  | 3080 (2) | -3156 (4)  | 732 (3)   | 68 (2)                 |
| O(2)  | 2696 (2) | -666 (5)   | 1427 (2)  | 70 (1)                 |
| O(3)  | 3794 (2) | -737 (4)   | 465 (2)   | 54 (1)                 |
| C(1)  | 2315 (3) | -1055 (5)  | -571 (3)  | 36 (2)                 |
| C(2)  | 1497 (3) | -676 (6)   | -578 (3)  | 39 (2)                 |
| N(1)  | 1150 (3) | -830 (8)   | 392 (4)   | 66 (2)                 |
| O(4)  | 1109 (3) | -2131 (7)  | 740 (3)   | 105 (2)                |
| O(5)  | 907 (3)  | 385 (7)    | 730 (3)   | 101 (2)                |
| C(3)  | 952 (3)  | -179 (6)   | -1448 (4) | 46 (2)                 |
| C(4)  | 1201 (3) | -54 (6)    | -2396 (3) | 42 (2)                 |
| C(7)  | 596 (3)  | 514 (8)    | -3340 (4) | 64 (2)                 |
| F(1)  | -16 (2)  | -516 (5)   | -3622 (2) | 102 (2)                |
| F(2)  | 238 (2)  | 1849 (5)   | -3141 (3) | 120 (2)                |
| F(3)  | 921 (2)  | 738 (5)    | -4168 (2) | 92 (2)                 |
| C(5)  | 1997 (3) | -426 (6)   | -2448 (3) | 41 (2)                 |
| C(6)  | 2529 (2) | -906 (5)   | -1548 (3) | 36 (2)                 |
| N(2)  | 3386 (2) | -1254 (6)  | -1681 (3) | 47 (2)                 |
| O(6)  | 3637 (2) | -2600 (5)  | -1501 (3) | 64 (1)                 |
| O(7)  | 3755 (2) | -159 (5)   | -1981 (3) | 72 (2)                 |
| C(8)  | 6613 (3) | -3813 (6)  | 1433 (4)  | 48 (2)                 |
| N(3)  | 5838 (2) | -3434 (5)  | 1190 (3)  | 50 (2)                 |
| C(9)  | 5388 (4) | -2871 (10) | 176 (5)   | 75 (3)                 |
| C(10) | 5349 (5) | -3498 (14) | 2025 (6)  | 81 (3)                 |
| N(4)  | 7199 (2) | -3734 (5)  | 888 (3)   | 52 (2)                 |
| C(11) | 7141 (5) | -3079 (9)  | -166 (6)  | 71 (3)                 |
| C(12) | 7993 (4) | -4479 (12) | 1329 (8)  | 82 (3)                 |

Table 2. Bond lengths (Å) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

|           |           |            |            |
|-----------|-----------|------------|------------|
| S—O(1)    | 1.427 (4) | C(7)—F(3)  | 1.306 (7)  |
| S—O(2)    | 1.444 (4) | C(4)—C(5)  | 1.371 (6)  |
| S—O(3)    | 1.433 (3) | C(5)—C(6)  | 1.374 (5)  |
| S—C(1)    | 1.813 (4) | C(6)—N(2)  | 1.492 (6)  |
| C(1)—C(2) | 1.390 (6) | N(2)—O(6)  | 1.213 (6)  |
| C(2)—N(1) | 1.488 (6) | N(2)—O(7)  | 1.213 (6)  |
| N(1)—O(4) | 1.191 (9) | C(6)—C(1)  | 1.386 (6)  |
| N(1)—O(5) | 1.212 (8) | C(8)—N(3)  | 1.299 (6)  |
| C(2)—C(3) | 1.362 (6) | N(3)—C(9)  | 1.454 (8)  |
| C(3)—C(4) | 1.374 (7) | N(3)—C(10) | 1.476 (10) |
| C(4)—C(7) | 1.495 (6) | C(8)—N(4)  | 1.312 (7)  |
| C(7)—F(1) | 1.329 (7) | N(4)—C(11) | 1.457 (9)  |
| C(7)—F(2) | 1.320 (8) | N(4)—C(12) | 1.466 (8)  |

|                |           |                  |           |
|----------------|-----------|------------------|-----------|
| O(1)—S—O(2)    | 114.5 (2) | C(8)—N(3)—C(9)   | 127.0 (5) |
| O(1)—S—O(3)    | 115.2 (2) | C(8)—N(3)—C(10)  | 118.4 (5) |
| O(2)—S—O(3)    | 113.2 (2) | C(9)—N(3)—C(10)  | 114.5 (5) |
| C(1)—S—O(1)    | 105.7 (2) | C(8)—N(4)—C(11)  | 127.3 (5) |
| C(1)—S—O(2)    | 102.8 (2) | C(8)—N(4)—C(12)  | 118.2 (5) |
| C(1)—S—O(3)    | 103.6 (2) | C(11)—N(4)—C(12) | 114.4 (5) |
| S—C(1)—C(2)    | 122.4 (3) | C(4)—C(7)—F(1)   | 111.5 (5) |
| S—C(1)—C(6)    | 123.6 (3) | C(4)—C(7)—F(2)   | 111.5 (4) |
| C(2)—C(1)—C(6) | 113.6 (4) | C(4)—C(7)—F(3)   | 113.5 (4) |
| C(1)—C(2)—N(1) | 121.1 (4) | F(1)—C(7)—F(2)   | 105.1 (5) |
| C(1)—C(2)—C(3) | 124.1 (4) | F(1)—C(7)—F(3)   | 106.6 (5) |
| C(3)—C(2)—N(1) | 114.8 (4) | F(2)—C(7)—F(3)   | 108.2 (5) |
| C(2)—N(1)—O(4) | 117.4 (5) | C(4)—C(5)—C(6)   | 119.1 (4) |
| C(2)—N(1)—O(5) | 116.3 (5) | C(5)—C(6)—N(2)   | 115.1 (4) |
| O(4)—N(1)—O(5) | 126.3 (5) | C(5)—C(6)—C(1)   | 124.2 (4) |
| C(2)—C(3)—C(4) | 119.6 (5) | C(1)—C(6)—N(2)   | 120.7 (4) |
| C(3)—C(4)—C(7) | 118.8 (4) | C(6)—N(2)—O(6)   | 117.4 (4) |
| C(3)—C(4)—C(5) | 119.4 (4) | O(6)—N(2)—O(7)   | 126.5 (4) |
| C(5)—C(4)—C(7) | 121.8 (4) | C(6)—N(2)—O(7)   | 116.1 (4) |
| N(3)—C(8)—N(4) | 131.3 (5) |                  |           |

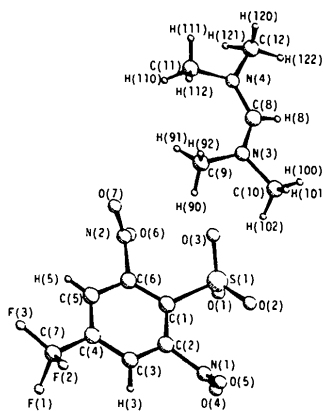


Fig. 1. Perspective view of the asymmetric units.

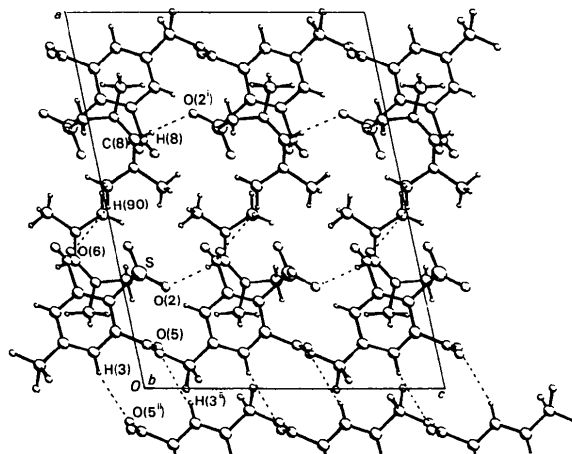


Fig. 2. Cell content viewed down b.

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