Structure of *O*-Benzyl-*N*,*N'*-diisopropyluronium Trifluoromethanesulfonate
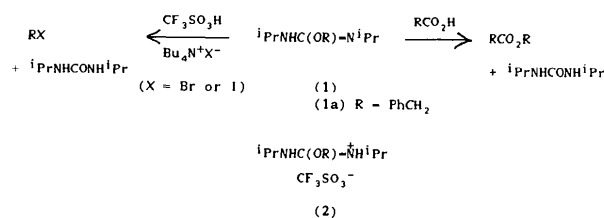
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Abstract. $C_{14}H_{23}N_2O^+.CF_3SO_3^-$, $M_r = 384.4$, monoclinic, $P2_1/c$, $a = 20.488$ (2), $b = 13.358$ (1), $c = 15.643$ (1) Å, $\beta = 111.813$ (4)°, $V = 3974.6$ Å^3, $Z = 8$, $D_x = 1.285$ Mg m^{-3}, $F(000) = 1616$, $\lambda(\text{Cu } K\alpha) = 1.54184$ Å, $\mu = 1.86$ mm^{-1}, $T = 293$ K. $R = 0.090$ for 3127 observed reflections. The structure contains two independent anions and two independent cations. The CN–C(O)–NC unit of the cations is essentially planar, as in the urea which results from nucleophilic attack at the C–O bond, so little geometrical rearrangement is necessary when the bond is broken. Nucleophilic attack along the line of the C–O bond is relatively unimpeded by substituents. An (*E,Z*) configuration is observed for the arrangement of the isopropyl groups about the central N–C(O)–N unit.

Introduction. *O*-Alkylisoureas (1) are valuable reagents for the preparation of carboxylic and phosphoric esters, ethers and alkyl halides (Mathias, 1979; Collingwood, Davies & Golding, 1987). It is postulated that these reactions proceed by protonation of (1) at the imino N atom, followed by nucleophilic attack (carboxylate or halide) at the *O*-alkyl group of the protonated (1). The salt (2), prepared from the isourea (1a), is an example of such a protonated *O*-alkylisourea stabilized by the non-nucleophilic counter ion trifluoromethanesulfonate. We have determined the structure of (2) to investigate its suitability for nucleophilic attack in geometrical terms.

Experimental. (2) was prepared by slow addition of trifluoromethanesulfonic acid (316 µl, 3.57 mmol) to a stirred solution of *O*-benzyl-*N*,*N'*-diisopropylisourea [(1a); 835 mg, 3.57 mmol] in dichloromethane (15 ml). After 30 min, concentration gave (2) in quantitative yield. Colourless platelets (m.p. 408.7–410.2 K, satisfactory elemental analysis) were obtained by

recrystallization from a dichloromethane–light petroleum mixture.

Siemens AED2 diffractometer with graphite monochromator, crystal size $0.1 \times 0.4 \times 0.45$ mm, cell parameters from 2θ values of 32 reflections ($25 < 2\theta < 35°$) measured at $\pm\omega$. Intensities measured in ω/θ scan mode, width 0.77° below α_1 to 0.77° above α_2, scan time 18 s, $2\theta_{max} = 110°$, $h -21 \rightarrow 21$, $k \, 0 \rightarrow 14$, $l \, 0 \rightarrow 16$, no significant changes in three standard reflections, no absorption correction. 5659 reflections, 4983 unique ($R_{int} = 0.051$), 3127 with $F > 4\sigma_c(F)$, σ_c based on counting statistics. Structure determination by direct methods, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) - 19 + 257G + 297G^2 + 62S - 26S^2 - 632GS$ determined empirically from analysis of variance, where $G = F_o/F_{max}$ and $S = \sin\theta/\sin\theta_{max}$ (Hong & Robertson, 1985). Anisotropic thermal parameters, H atoms constrained [C–H = 0.96 Å, H–C–H = 109.5°, aromatic H on ring angle external bisectors, $U(\text{H}) = 1.2U_{eq}(\text{C})$], isotropic extinction parameter $x = 1.8$ (4) $\times 10^{-6}$ [$F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$]. 452 parameters, $R = 0.090$, $wR = 0.061$, slope of normal probability plot = 1.01, mean (Δ/σ) = 0.06, max. = 0.24, max. ($\Delta\rho$) = 0.38, min. = -0.38 e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974); *SHELXTL* (Sheldrick, 1985) and local computer programs.

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* Fig. 1 shows one of the two crystallographically independent cations; the other does not differ significantly from it.

The structure of the cation displays features which indicate its suitability for nucleophilic attack at the *O*-alkyl group. As expected, the isopropyl groups and benzyl group adopt positions that minimize steric interactions. For the isopropyl groups this is achieved by *Z* and *E* configurations about the N–C(O)–N unit. An (*E,E*)-configuration is clearly improbable, whilst (*Z,Z*) would be destabilized by an interaction between

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44360 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

$U_{eq} = \frac{1}{3}(\text{trace of orthogonalized } U_{ij} \text{ matrix}).$

	x	y	z	U_{eq}
S(1)	4243 (1)	1149 (1)	3133 (1)	65 (1)
O(11)	4401 (3)	791 (3)	4045 (3)	92 (2)
O(12)	4212 (3)	2214 (3)	3042 (3)	97 (3)
O(13)	4630 (3)	659 (4)	2647 (4)	114 (3)
C(1)	3393 (6)	798 (11)	2549 (7)	150 (6)
F(11)	2962 (3)	1099 (7)	2922 (5)	223 (5)
F(12)	3346 (5)	−249 (7)	2616 (6)	224 (5)
F(13)	3143 (3)	958 (9)	1700 (4)	296 (6)
S(2)	855 (1)	1031 (1)	3978 (1)	57 (1)
O(21)	535 (3)	478 (4)	3148 (3)	112 (3)
O(22)	867 (3)	2085 (3)	3853 (3)	98 (3)
O(23)	646 (2)	736 (3)	4708 (3)	80 (2)
C(2)	1741 (5)	665 (8)	4367 (6)	116 (5)
F(21)	2113 (3)	1109 (6)	5138 (4)	177 (4)
F(22)	1822 (4)	−315 (5)	4563 (5)	186 (5)
F(23)	2039 (3)	853 (8)	3798 (5)	239 (6)
O(3)	1236 (2)	5249 (3)	2326 (2)	60 (2)
N(31)	764 (3)	3772 (3)	1599 (3)	58 (2)
N(32)	1060 (3)	4004 (4)	3153 (3)	79 (3)
C(301)	1154 (3)	5710 (4)	1454 (3)	54 (2)
C(302)	1362 (3)	6785 (4)	1649 (3)	56 (2)
C(303)	1878 (4)	7199 (5)	1392 (4)	77 (3)
C(304)	2036 (5)	8199 (5)	1515 (5)	111 (5)
C(305)	1704 (4)	8784 (5)	1911 (5)	99 (4)
C(306)	1180 (4)	8420 (5)	2169 (5)	92 (4)
C(307)	1016 (4)	7408 (4)	2041 (4)	72 (3)
C(308)	1001 (3)	4318 (4)	2344 (4)	56 (3)
C(309)	488 (4)	2764 (4)	1548 (4)	67 (3)
C(310)	1023 (5)	2025 (5)	1517 (6)	129 (6)
C(311)	−196 (4)	2677 (6)	753 (5)	124 (5)
C(312)	1261 (4)	4644 (5)	3993 (4)	94 (4)
C(313)	1863 (4)	4147 (7)	4746 (4)	116 (4)
C(314)	640 (5)	4745 (7)	4271 (5)	131 (5)
O(4)	3674 (2)	5268 (3)	973 (3)	66 (2)
N(41)	4170 (3)	3791 (3)	766 (3)	61 (2)
N(42)	3872 (3)	4081 (4)	2016 (3)	89 (3)
C(401)	3756 (3)	5698 (4)	168 (4)	63 (3)
C(402)	3538 (3)	6783 (4)	123 (4)	61 (3)
C(403)	3006 (4)	7126 (5)	−619 (5)	82 (3)
C(404)	2842 (5)	8161 (6)	−685 (6)	120 (5)
C(405)	3225 (5)	8768 (6)	24 (5)	119 (5)
C(406)	3751 (5)	8444 (6)	782 (6)	102 (4)
C(407)	3914 (4)	7430 (5)	815 (5)	80 (4)
C(408)	3927 (4)	4359 (4)	1248 (4)	58 (3)
C(409)	4484 (4)	2793 (4)	1057 (4)	79 (4)
C(410)	5227 (5)	2800 (8)	1148 (9)	219 (11)
C(411)	4081 (7)	2048 (6)	370 (7)	199 (9)
C(412)	3630 (6)	4746 (7)	2623 (6)	127 (6)
C(413)	4220 (6)	4831 (7)	3506 (7)	157 (8)
C(414)	2979 (5)	4232 (9)	2720 (6)	167 (7)

Table 2. *Bond lengths* (Å) *and angles* (°)

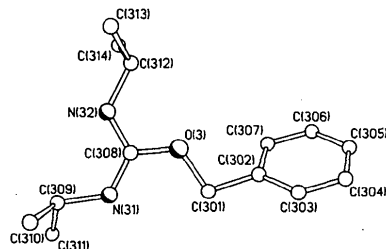|			
S(1)–O(11)	1·424 (4)	S(2)–O(21)	1·425 (5)
S(1)–O(12)	1·429 (5)	S(2)–O(22)	1·422 (5)
S(1)–O(13)	1·443 (7)	S(2)–O(23)	1·417 (5)
S(1)–C(1)	1·705 (11)	S(2)–C(2)	1·755 (10)
C(1)–F(11)	1·290 (16)	C(2)–F(21)	1·305 (11)
C(1)–F(12)	1·408 (17)	C(2)–F(22)	1·341 (13)
C(1)–F(13)	1·251 (12)	C(2)–F(23)	1·278 (14)
O(3)–C(301)	1·449 (7)	O(4)–C(401)	1·450 (8)
O(3)–C(308)	1·339 (7)	O(4)–C(408)	1·328 (7)
N(31)–C(308)	1·305 (7)	N(41)–C(408)	1·293 (9)
N(31)–C(309)	1·450 (8)	N(41)–C(409)	1·477 (8)
N(32)–C(308)	1·295 (8)	N(42)–C(408)	1·302 (9)
N(32)–C(312)	1·492 (7)	N(42)–C(412)	1·512 (13)
C(301)–C(302)	1·496 (7)	C(401)–C(402)	1·510 (8)
C(302)–C(303)	1·378 (11)	C(402)–C(403)	1·343 (8)
C(302)–C(307)	1·377 (10)	C(402)–C(407)	1·376 (8)
C(303)–C(304)	1·372 (10)	C(403)–C(404)	1·418 (11)
C(304)–C(305)	1·330 (13)	C(404)–C(405)	1·362 (11)
C(305)–C(306)	1·367 (13)	C(405)–C(406)	1·344 (10)
C(306)–C(307)	1·390 (9)	C(406)–C(407)	1·391 (10)
C(309)–C(310)	1·489 (12)	C(409)–C(410)	1·476 (15)
C(309)–C(311)	1·494 (9)	C(409)–C(411)	1·472 (11)
C(312)–C(313)	1·507 (9)	C(412)–C(413)	1·464 (12)
C(312)–C(314)	1·496 (14)	C(412)–C(414)	1·556 (16)
O(11)–S(1)–O(12)	114·8 (3)	O(21)–S(2)–O(22)	114·5 (3)
O(11)–S(1)–O(13)	114·3 (3)	O(21)–S(2)–O(23)	114·5 (3)
O(12)–S(1)–O(13)	114·3 (4)	O(22)–S(2)–O(23)	114·3 (3)
O(11)–S(1)–C(1)	104·6 (5)	O(21)–S(2)–C(2)	103·8 (4)
O(12)–S(1)–C(1)	102·8 (5)	O(22)–S(2)–C(2)	104·8 (4)
O(13)–S(1)–C(1)	104·2 (5)	O(23)–S(2)–C(2)	103·1 (4)
S(1)–C(1)–F(11)	113·9 (8)	S(2)–C(2)–F(21)	111·5 (8)
S(1)–C(1)–F(12)	108·5 (8)	S(2)–C(2)–F(22)	112·0 (8)
F(11)–C(1)–F(12)	101·5 (11)	F(21)–C(2)–F(22)	104·6 (8)
S(1)–C(1)–F(13)	117·1 (10)	S(2)–C(2)–F(23)	113·8 (7)
F(11)–C(1)–F(13)	110·4 (10)	F(21)–C(2)–F(23)	106·8 (9)
F(12)–C(1)–F(13)	103·7 (11)	F(22)–C(2)–F(23)	107·5 (10)
C(301)–O(3)–C(308)	119·9 (4)	C(401)–O(4)–C(408)	119·1 (5)
C(308)–N(31)–C(309)	125·2 (5)	C(408)–N(41)–C(409)	124·6 (5)
C(308)–N(32)–C(312)	124·8 (5)	C(408)–N(42)–C(412)	125·0 (6)
O(3)–C(301)–C(302)	107·0 (4)	O(4)–C(401)–C(402)	107·1 (5)
C(301)–C(302)–C(303)	121·1 (6)	C(401)–C(402)–C(403)	120·0 (5)
C(301)–C(302)–C(307)	121·1 (6)	C(401)–C(402)–C(407)	119·7 (5)
C(303)–C(302)–C(307)	117·7 (6)	C(403)–C(402)–C(407)	120·2 (6)
C(302)–C(303)–C(304)	121·1 (8)	C(402)–C(403)–C(404)	119·3 (6)
C(303)–C(304)–C(305)	120·1 (9)	C(403)–C(404)–C(405)	118·1 (7)
C(304)–C(305)–C(306)	121·5 (7)	C(404)–C(405)–C(406)	123·9 (7)
C(305)–C(306)–C(307)	118·5 (8)	C(405)–C(406)–C(407)	116·7 (7)
C(302)–C(307)–C(306)	121·0 (7)	C(402)–C(407)–C(406)	121·7 (6)
O(3)–C(308)–N(31)	121·2 (6)	O(4)–C(408)–N(41)	122·5 (6)
O(3)–C(308)–N(32)	114·7 (5)	O(4)–C(408)–N(42)	113·7 (6)
N(31)–C(308)–N(32)	124·0 (5)	N(41)–C(408)–N(42)	123·7 (5)
N(31)–C(309)–C(310)	110·0 (6)	N(41)–C(409)–C(410)	109·8 (7)
N(31)–C(309)–C(311)	110·1 (5)	N(41)–C(409)–C(411)	108·9 (6)
C(310)–C(309)–C(311)	113·3 (6)	C(410)–C(409)–C(411)	110·7 (9)
N(32)–C(312)–C(313)	108·3 (6)	N(42)–C(412)–C(413)	106·8 (9)
N(32)–C(312)–C(314)	108·7 (6)	N(42)–C(412)–C(414)	107·2 (7)
C(313)–C(312)–C(314)	110·5 (6)	C(413)–C(412)–C(414)	112·3 (9)

Fig. 1. One of the crystallographically independent cations, showing the numbering scheme. H atoms are omitted. The other cation follows a corresponding numbering scheme.

one isopropyl group and the benzyl methylene group. The torsion angle for the unit N(31)–C(308)–O(3)–C(301) is 7·3 (9)° [−8·4 (8)° in the other cation]; this indicates a strong interaction between the oxygen and the $R\text{NH}{=}\overset{+}{C}{=}\text{NH}R$ unit, *i.e.* essentially sp^2 hy-

bridization at O. The torsion angles 171·3 (5)° for C(308)–O(3)–C(301)–C(302) and 124·3 (6)° for O(3)–C(301)–C(302)–C(303) minimize steric interactions, but do not indicate any significant interaction between the aromatic π system and the σ^* orbital of the C(301)–O(3) bond [corresponding torsion angles in the other cation are −170·3 (5) and −120·4 (7)°]. Nucleophilic attack along the axis of this bond from behind C(301) is relatively unimpeded. Breakage of the bond leads to the formation of *N,N'*-diisopropylurea, with a planar urea unit; in the cation here, atoms O(3), N(31), N(32), C(308), C(309) and C(312) are essentially coplanar, with an r.m.s. deviation of 0·038 (2) Å [0·032 (2) Å for the other cation], so little geometrical rearrangement is involved in the formation of the urea.

A planar arrangement has been observed for the N—C(O)—N unit and its nitrogen substituents in other isourea structures, with widely varying degrees of out-of-plane twist of the O-substituent (Plastas & Stewart, 1969; Brown & Meyers, 1970; Einstein & Field, 1979; Hegarty, McCormack, Brady, Ferguson & Roberts, 1980). In the simplest structure, that of [(H₂N)₂COCH₃]Cl (White & Mason, 1970; Brown & Meyers, 1970), the methyl substituent on oxygen also lies essentially in the molecular plane, as in the present case, with electronic effects not over-ridden by steric factors.

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Structures of the Conducting Salts of Pyrazinoethylenedithiotetrathiafulvalene (PEDTTTF) and Dimethylpyrazinoethylenedithiotetrathiafulvalene (DMPEDTTTF): β-(PEDTTTF)₃I₃ and β-(DMPEDTTTF)₃I₃

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Abstract. (*A*): 2-(Dithiolo[4,5-*b*]dithiin-2-ylidene)-dithiolo[4,5-*b*]pyrazinium iodide, $(C_{10}H_6N_2S_6)I$, $M_r = 473 \cdot 48$, triclinic, $P\bar{1}$, $a = 8 \cdot 179$ (2), $b = 5 \cdot 588$ (1), $c = 16 \cdot 735$ (2) Å, $\alpha = 104 \cdot 75$ (1), $\beta = 89 \cdot 02$ (2), $\gamma = 104 \cdot 82$ (2)°, $V = 714 \cdot 1$ Å³, $Z = 2$, $D_m = 2 \cdot 16$, $D_x = 2 \cdot 201$ g cm⁻³, Cu $K\bar{\alpha}$, $\lambda = 1 \cdot 54178$ Å, $\mu = 256 \cdot 4$ cm⁻¹, $F(000) = 458$, $T = 296$ (2) K. (*B*): 2-(Dithiolo[4,5-*b*]dithiin-2-ylidene)-5,6-dimethyldithiolo-[4,5-*b*]pyrazinium iodide, $(C_{12}H_{10}N_2S_6)I$, $M_r = 501 \cdot 50$, monoclinic, $C2$, $a = 34 \cdot 943$ (3), $b = 6 \cdot 610$ (1), $c = 7 \cdot 335$ (1) Å, $\beta = 92 \cdot 13$ (1)°, $V = 1693 \cdot 0$ Å³, $Z = 4$, $D_m = 2 \cdot 00$, $D_x = 1 \cdot 967$ g cm⁻³, Cu $K\bar{\alpha}$, $\lambda = 1 \cdot 54178$, $\mu = 216 \cdot 7$ cm⁻¹, $F(000) = 980$, $T = 296$ (2) K. Final *R* values are 0·045 (*A*) and 0·025 (*B*) for 2126 and 1615 reflections. Anions in both structures are disordered in the **b** direction. Cations pack side by side, in a planar arrangement, through S⋯S and S⋯N contacts, the shortest of which are S⋯S = 3·427, S⋯N = 3·315 (*A*), S⋯S = 3·375 Å (*B*). There is also partial (*A*) to good (*B*) stacking and intrastack S⋯S contacts of 3·724 (*A*) and 3·638 Å (*B*).

Introduction. With the discovery (Yagubskii, Shchegolev, Laukhin, Kononovich, Kartsovnik, Zvarykina & Buravov, 1984) of superconductivity at ambient pressure in the first sulfur-based organic metal, β-(ET)₂I₃, attempts are being made to modify the structural and physical properties of this material. One approach is to substitute the triiodide anion systematically by various other trihalide anions of differing sizes and polarizabilities (Leung, Emge, Schultz, Beno, Carlson, Wang, Firestone & Williams, 1986). Another approach is to modify the cation (Terzis, Hountas & Papavassiliou, 1986). In this paper we further modified the donor and report on the structures of the title compounds.

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