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1-(4-Chlorophenylsulfanyl)-2-nitro-4-(trifluoromethyl)benzene and 1-(4-chlorophenylsulfanyl)-4-nitro-2-(trifluoromethyl)benzene

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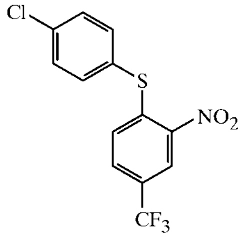
Two chemical isomers of 3-nitrobenzotrifluoride, namely 1-(4-chlorophenylsulfanyl)-2-nitro-4-(trifluoromethyl)benzene, $C_{13}H_7ClF_3NO_2S$, (I), and 1-(4-chlorophenylsulfanyl)-4-nitro-2-(trifluoromethyl)benzene, $C_{13}H_7ClF_3NO_2S$, (II), have been prepared and their crystal structures determined with the specific purpose of forming a cocrystal of the two. The two compounds display a similar conformation, with dihedral angles between the benzene rings of 83.1 (1) and 76.2 (1)°, respectively, but (I) packs in $P\overline{1}$ while (II) packs in $P2_1/c$, with C—H···O interactions. No cocrystal could be formed, and it is suggested that the C—H···O associations in (II) prevent intermolecular mixing and promote phase separation.

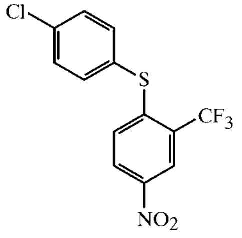
Comment

The crystal structure of the 1:1 molecular adduct of (+)-2-(3-methoxyphenoxy)propionic acid with (−)-2-(3-bromophenoxy)propionic acid, determined by Karle & Karle (1966), was the first crystallographic example of a designed cocrystal. The idea behind this combination was based on the use of two chemically similar optically active compounds to prepare a quasi-racemate. The existence of such species had been identified previously, but by techniques other than crystallography [as reviewed by Fredga (1973)]. More recently, Wheeler and co-workers have published similar studies using phenoxy- (Hendi *et al.*, 2001) or anilino-substituted propanoic acids (Fomulu *et al.*, 2002*b*). In these structural studies, the components associate *via* a heteromolecular carboxylic acid dimer, giving each component a mutual site for strong hydrogen-bonding interaction. Opposing chirality in the two enantiomers is also essential when producing a quasi-racemate. In addition, Fomulu *et al.* (2002*a*) have recently produced quasi-racemates using benzoyl-substituted benzylamines.

We posed the question that, if neither strong hydrogen-bonding sites nor chemical chirality were present, would, or could, two structurally similar chemical isomers still cocrystallize. To study this question, we chose isomeric pairs of compounds containing 3-nitrobenzotrifluoride, such that the nitro and trifluoromethyl groups were structurally interchanged. Both groups are known to be weak hydrogen-bond acceptors from strong hydrogen-bond donors (Allen *et al.*, 1997; Brammer *et al.*, 2001), but in the absence of such donors, the packing can be influenced only, if at all, by weak C—H interactions. A search of the April 2003 release of the Cambridge Structural Database (Allen, 2002) revealed 13 structures with a 3-nitrobenzotrifluoride moiety, although only four had one other substituent on the benzene ring, and two of these were bis(nitrotrifluoromethylphenyl) compounds that were bridged by either disulfide (Glidewell *et al.*, 2000) or bis(sulfonyl)imide (Bombicz *et al.*, 1995). Of the other two compounds, the additional substituents consisted of amine- (Glidewell *et al.*, 2002) or amide-containing groups (He *et al.*, 2001). Analyses of the crystal structures of the two individual components were essential in order to validate any comparisons with the cocrystal. Initial syntheses focused on thiophenol-substituted 3-nitrobenzotrifluoride. Again, the S atom in the thiophenol is not considered a strong hydrogen-bonding acceptor, and substituents on the thiophenol ring were limited to methyl and halogen groups. The first isomeric pair to simultaneously crystallize were 1-(4-chlorophenylsulfanyl)-2-nitro-4-(trifluoromethyl)benzene, (I), and 1-(4-chlorophenylsulfanyl)-4-nitro-2-(trifluoromethyl)benzene, (II), whose respective crystal structures are reported here.



(I)



(II)

The similar conformations of (I) and (II) are shown in Figs. 1 and 2, respectively. The compounds have a similar dihedral angle between the two benzene rings [83.1 (1) and 76.2 (1)°, respectively] but differ in their C6—C1—S1—C7 torsion angle [15.4 (4) and 1.3 (5)°, respectively]. The low value of the torsion angle in (II) is a result of the orientation of the trifluoromethyl group and the lateral positions of atoms F22 and F23. The most significant difference between the two structures is in their packing, with (I) (Fig. 3) being triclinic ($P\overline{1}$) and (II) (Fig. 4) being monoclinic ($P2_1/c$). The 4-nitro group in (II) is involved in C—H···O interactions (Table 1), whereas no such associations are recorded in (I), nor are there any similar C—H close contacts recorded for either of the trifluoromethyl groups. However, in (I) there is a short contact

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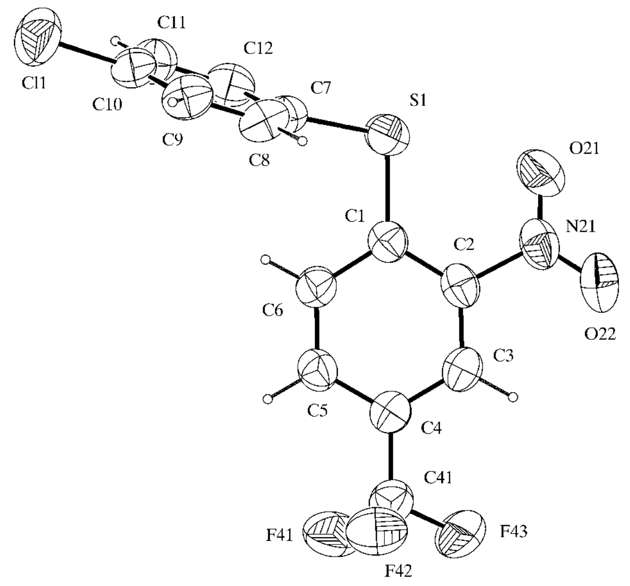

Figure 1
The molecular configuration and atom-numbering scheme for (I). Displacement ellipsoids are drawn at the 50% probability level.

[3.193 (5) Å] between atoms Cl1 and F43($-1 + x$, y, $-1 + z$). Attempts to cocrystallize (I) and (II) by dissolving equimolar amounts of each component in various solvents, with warming, and then allowing evaporation to dryness led to the recrystallization in each case of the individual compounds. This result was confirmed by distinct differences in the crystal morphology and the IR analysis of each crystal type. The inability of (I) and (II) to cocrystallize may be a result of the C—H···O interactions in (II), meaning that one molecule of (II) will preferentially associate with another molecule of (II) rather than a molecule of (I), thus propagating phase separation. Few conclusions can be drawn from just one isomeric pair, but the C—H···O interactions will be examined more closely as these studies into isomers of 3-nitrobenzotrifluoride progress.

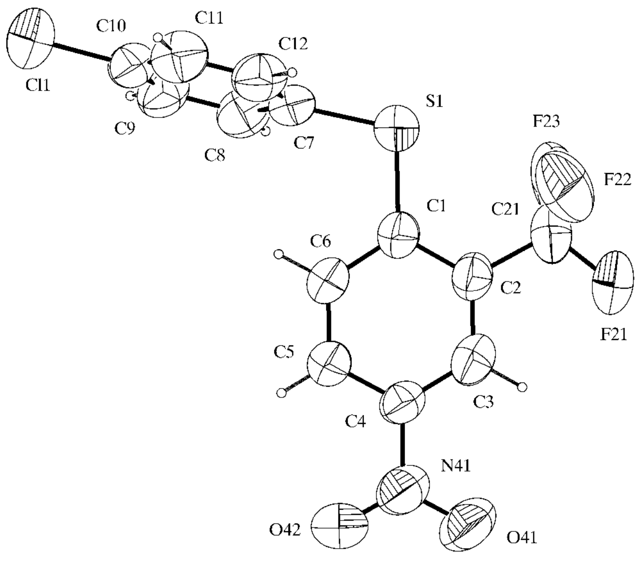

Figure 2
The molecular configuration and atom-numbering scheme for (II). Displacement ellipsoids are drawn at the 50% probability level.

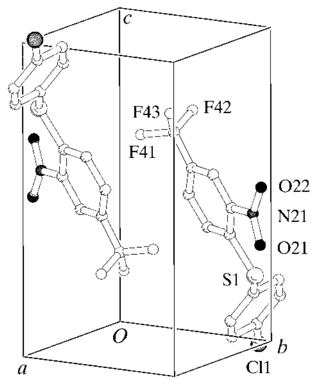

Figure 3
Packing diagram of (I).

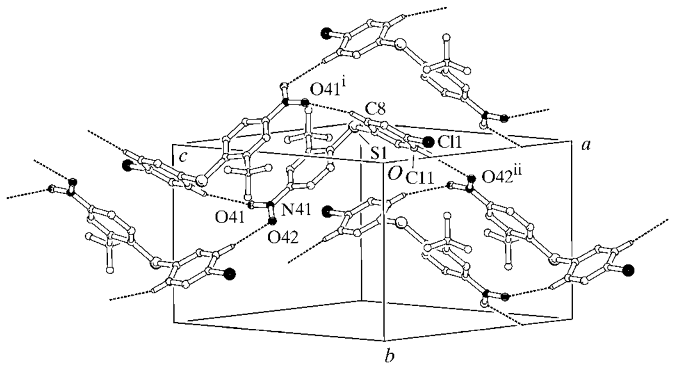

Figure 4
Packing diagram of (II), viewed along the *a* axis. [Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $x - \frac{1}{2}, -\frac{1}{2} - y, \frac{1}{2} + z$.]

Experimental

Both compounds were obtained from Key Organics Ltd and crystals were grown from ethanol solutions.

Compound (I)

Crystal data

$C_{13}H_7ClF_3NO_2S$
$M_r = 333.71$
Triclinic, $P\overline{1}$
$a = 7.1953$ (14) Å
$b = 8.4763$ (17) Å
$c = 11.811$ (2) Å
$\alpha = 84.35$ (3)°
$\beta = 88.05$ (3)°
$\gamma = 70.06$ (3)°
$V = 673.8$ (2) Å^3

$Z = 2$
$D_x = 1.645$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2771 reflections
$\theta = 2.9$–30.5°
$\mu = 0.48$ mm^{-1}
$T = 150$ (2) K
Needle, yellow
0.20 × 0.06 × 0.06 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.911$, $T_{\max} = 0.972$
4967 measured reflections

2336 independent reflections
1564 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.057$
$\theta_{\max} = 25.0°$
$h = -8 \rightarrow 8$
$k = -9 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.202$
$S = 1.03$
2336 reflections
190 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1266P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}

Compound (II)

Crystal data

$C_{13}H_7ClF_3NO_2S$
$M_r = 333.71$
Monoclinic, $P2_1/n$
$a = 12.335$ (3) Å
$b = 9.2477$ (18) Å
$c = 12.929$ (3) Å
$\beta = 108.32$ (3)°
$V = 1400.1$ (5) Å^3
$Z = 4$

$D_x = 1.583$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11 965 reflections
$\theta = 2.9$–$27.5°$
$\mu = 0.46$ mm^{-1}
$T = 568$ (2) K
Plate, colourless
0.30 × 0.27 × 0.02 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.875$, $T_{\max} = 0.991$
10 187 measured reflections

3183 independent reflections
1305 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.091$
$\theta_{\max} = 27.5°$
$h = -15 \rightarrow 15$
$k = -11 \rightarrow 11$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.083$
$wR(F^2) = 0.258$
$S = 0.99$
3183 reflections
191 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1331P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.66$ e Å^{-3}
$\Delta\rho_{\min} = -0.39$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.051 (8)

Table 1
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C8—H8$\cdots$O41$^{\text{i}}$	0.93	2.50	3.397 (6)	161
C11—H11$\cdots$O42$^{\text{ii}}$	0.93	2.47	3.392 (6)	174

Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $x - \frac{1}{2}, -\frac{1}{2} - y, \frac{1}{2} + z$.

All H atoms were included in the refinement, at calculated positions, in the riding-model approximation, with C—H distances of 0.95 Å (aromatic H). The isotropic displacement parameters were set at $1.25U_{\text{eq}}$ of the carrier atom. The high weighting values for both (I) and (II) were the result of the soft poor quality crystals obtained. There is no discernible disorder in the CF_3 group in the structure of (II).

For both compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTON*94 (Spek, 1994) and *PLATON*97 (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1187). Services for accessing these data are described at the back of the journal.

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