

1,3-Bis(4-fluorobenzenesulfonyl)-5-methylene-1,2,3,4,5,6-hexahydropyrimidine

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Key indicators

Single-crystal X-ray study

T = 294 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.045

wR factor = 0.124

Data-to-parameter ratio = 10.3

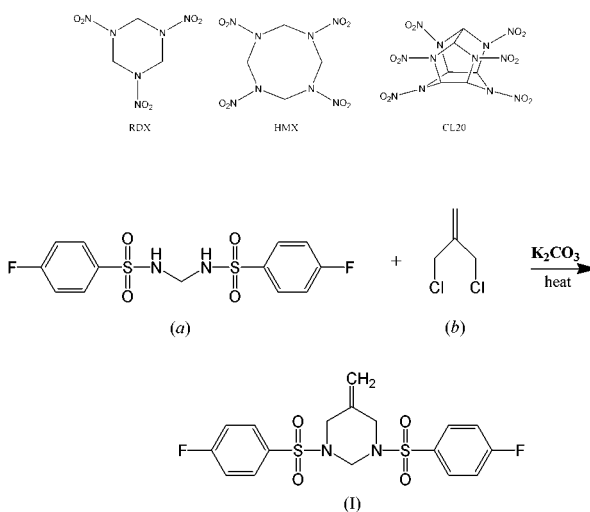
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title molecule, $\text{C}_{17}\text{H}_{16}\text{F}_2\text{N}_2\text{O}_4\text{S}_2$, contains a diazacyclohexane ring with fluorobenzenesulfonamide groups, and an exocyclic double bond. This polyamine ring was synthesized to be a precursor for novel energetic analogs of 1,3,5-trinitrotriazacyclohexane (RDX), from a complex condensation reaction. The structure contains several weak intermolecular and intramolecular $\text{C}-\text{H} \cdots \text{O}$ contacts.

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Comment

Polyamine rings, or ring systems, are necessary precursors for several of the most potent energetic materials known, such as RDX, HMX, and CL20. The $\text{C}-\text{N}$ bonds holding these molecules together are weaker than $\text{C}-\text{C}$ bonds, and thus release more energy when they are dissociated and recombined to form gaseous products, such as N_2 and CO_2 . The backbone rings in these molecules are first synthesized with no energetic substituents, often through fairly simple condensation reactions between amines and a reactive carbonyl compound (*e.g.* glyoxal or formaldehyde). However, (I) results from a more complex condensation wherein the two N atoms seen in the central ring of the product (I) are already linked together in reactant (a). This reaction produces a diazacyclohexane ring with the amino N atoms already protected or stabilized by fluorobenzenesulfonamide groups, and an exocyclic double bond. This particular 'designed' product, (I), was targeted as a precursor for further synthetic addition of energetic groups to produce novel analogs of 1,3,5-trinitrotriazacyclohexane (RDX).



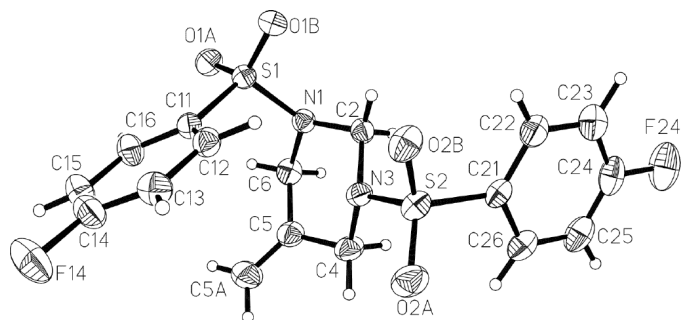


Figure 1
A view of (I), with 25% probability displacement ellipsoids.

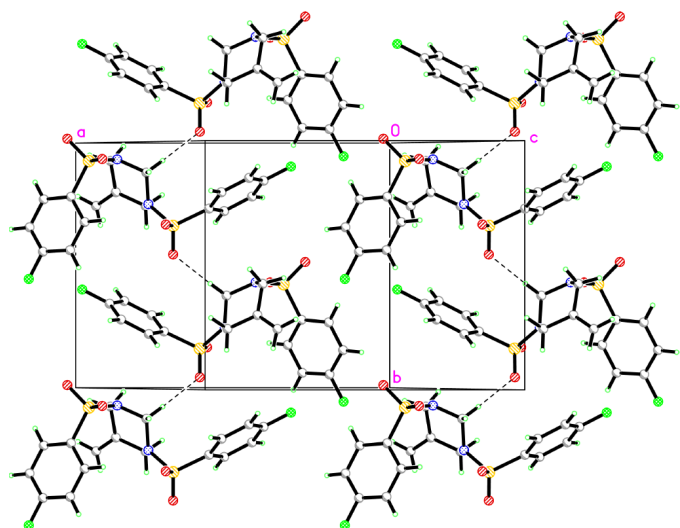


Figure 2
The packing of (I), viewed down a direction perpendicular to the (001) plane. Only half of the contents of the cell (from $z = 0$ to $z = \frac{1}{2}$) are shown, for clarity. The other half of the cell is related to that shown above by the inversion center at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Short C—H \cdots O contacts [H \cdots O distance = 2.53 (3) Å and C—H \cdots O angle = 173 (2) $^\circ$] link the screw-axis-related molecules along b , the vertical axis.

intramolecular C—H \cdots O contacts (Table 1), but they are not very short and are quite bent, so they may not be even weak 'hydrogen bonds' but just unavoidable contacts caused by substitution of two bulky groups on each sulfonyl group. The remaining two C—H \cdots O intermolecular bonds shown in Table 1 are close to linear [C—H \cdots O angles of 163 (2) and 173 (2) $^\circ$], and so appear to be hydrogen bonds, but weak ones, since their H \cdots O contact distances [2.53 (3) and 2.54 (3) Å] are very slightly less than the expected van der Waals H \cdots O contact of 2.62 Å (Rowland & Taylor, 1996).

Experimental

Potassium carbonate (0.1 g, 0.27 mmol) and methallyl dichloride (0.038 g, 0.30 mmol) were added to a solution of methylene bis(4-fluorobenzenesulfonamide) (0.1 g, 0.27 mmol) in acetonitrile. The reaction mixture was heated at reflux overnight and then the resulting mixture was cooled to room temperature, filtered and concentrated to obtain a crystalline residue, which was recrystallized from a mixture

of absolute ethanol and 2-butanone and dried to obtain (I) as colorless crystals with a melting point of 457–458 K.

Crystal data

$C_{17}H_{16}F_2N_2O_4S_2$
 $M_r = 414.44$
 Monoclinic, $P2_1/n$
 $a = 13.8591$ (2) Å
 $b = 10.8218$ (1) Å
 $c = 13.8946$ (2) Å
 $\beta = 114.751$ (1) $^\circ$
 $V = 1892.48$ (5) Å 3
 $Z = 4$

$D_x = 1.455$ Mg m $^{-3}$
 Cu $K\alpha$ radiation
 Cell parameters from 7044 reflections
 $\theta = 3.8$ –67.0 $^\circ$
 $\mu = 2.97$ mm $^{-1}$
 $T = 294$ (2) K
 Plate, colorless
 $0.18 \times 0.16 \times 0.05$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2001)
 $T_{\min} = 0.686$, $T_{\max} = 0.862$
 9044 measured reflections

3177 independent reflections
 2783 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 67.1$ $^\circ$
 $h = -15 \rightarrow 16$
 $k = -11 \rightarrow 12$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.124$
 $S = 1.07$
 3177 reflections
 309 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2 + 0.1403P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.24$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -0.35$ e Å $^{-3}$
 Extinction correction: SHELXTL
 Extinction coefficient: 0.0116 (7)

Table 1
Hydrogen-bonding geometry (Å, $^\circ$).

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
C2—H2A \cdots O1B	0.95 (2)	2.39 (2)	2.852 (3)	109 (2)
C22—H22 \cdots O2B	0.89 (3)	2.51 (3)	2.873 (3)	105 (1)
C16—H16 \cdots O1A	0.91 (3)	2.51 (3)	2.884 (3)	105 (2)
C4—H4B \cdots O2A	1.02 (3)	2.49 (3)	2.897 (3)	103 (2)
C2—H2A \cdots O2B	0.95 (2)	2.52 (2)	2.947 (3)	108 (2)
C13—H13 \cdots O2B ⁱ	0.87 (3)	2.54 (3)	3.386 (3)	163 (2)
C2—H2B \cdots O2A ⁱⁱ	0.95 (3)	2.53 (3)	3.476 (3)	173 (2)

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

All of the H atoms were refined freely. The C—H bond distances are 0.86 (4)–1.03 (3) Å.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXTL (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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