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Structure of the 1:1 Complex between Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and Tetrahydrothiophene 1,1-Dioxide (Sulfolane), $C_3H_6N_6O_6 \cdot C_4H_8O_2S$

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Abstract. $M_r = 342.28$, triclinic, $P\bar{1}$, $a = 6.238$ (2), $b = 10.241$ (3), $c = 11.271$ (3) Å, $\alpha = 100.65$ (2), $\beta = 100.50$ (3), $\gamma = 94.193$ (3)°, $V = 691.5$ (4) Å³, $Z = 2$, $D_x = 1.64$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 2.66$ cm⁻¹, $F(000) = 340$, $T = 298$ K, $R_F = 0.040$ for 1605 observed reflections. The RDX molecule contains all of the three possible orientations of the NO₂ groups (axial, equatorial, and planar). The ring conformation is chair. The sulfolane molecule is regular and normal, but may be partly responsible for the rather unusual positioning of the NO₂ groups of the RDX molecule.

Introduction. As part of an effort to understand how energetic nitramines are able to accommodate dopant molecules in their crystal lattice (Brill & Karpowicz, 1982; Haller, Rheingold & Brill, 1983), the structure of the 1:1 complex of RDX and sulfolane, shown in Fig. 1, is of interest (Selig, 1966; Michaud, Merx, Poulain & Lepage, 1968). A structure determination without anisotropic refinement ($R = 0.12$) of this complex has been briefly described (Rerat, Barthou, Laurent & Rerat, 1968), but is not sufficiently complete to characterize all of the pertinent details. Herein is presented a redetermination of the structure in which some important features of the RDX molecule are revealed.

Experimental. RDX–sulfolane crystallized from a solution 5.4 mmol of RDX in 10 mL of sulfolane which had been heated to a temperature not exceeding 323 K. Crystal 0.15 × 0.23 × 0.38 mm epoxied to a glass fiber and coated with varnish to prevent solvent evaporation. Nicolet R3 diffractometer, graphite monochromator, Mo $K\alpha$. 24 reflections used to refine orientation matrix. No absorption correction. 1888

reflections collected scanning ω ($4^\circ \leq 2\theta \leq 45^\circ$), $R_{\text{merge}} = 0.0233$, 1781 unique, 1605 observed [$I \geq 2.5\sigma(I)$], 200 parameters. *SHELXTL* direct method *SOLV* (Sheldrick, 1978). Blocked-cascade procedure. $R_F = 0.0398$, $R_{wF} = 0.0437$; $w^{-1} = \sigma^2(F_o) + G|F_o|^2$, $G = 0.00048$. H atoms located in idealized positions on all C atoms. Final goodness-of-fit 1.525. Max. peak 0.21 e Å⁻³ in final $\Delta\rho$ map. (Δ/σ)_{max} 0.167. Inspection of F_o vs F_c values for intense low-angle reflections indicated that a correction for secondary extinction was required in the final cycles of refinement $\{F_{\text{corr}} = F_c[1.0 + 0.002x(F_c)^2/\sin(2\theta)]^{-0.25}$; x refined to 0.00583 in final run}. All form factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1 arrays the atomic coordinates and Table 2 the important bond distances and angles.† The lattice consists of discrete RDX and sulfolane molecules, which pack as shown in Fig. 2.

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39028 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

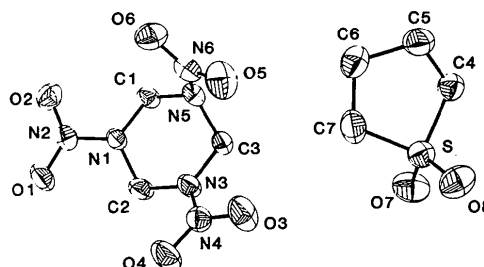


Fig. 1. Projections of RDX (left) and sulfolane (right) molecules.

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

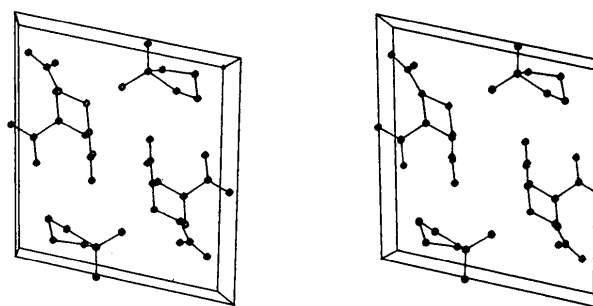
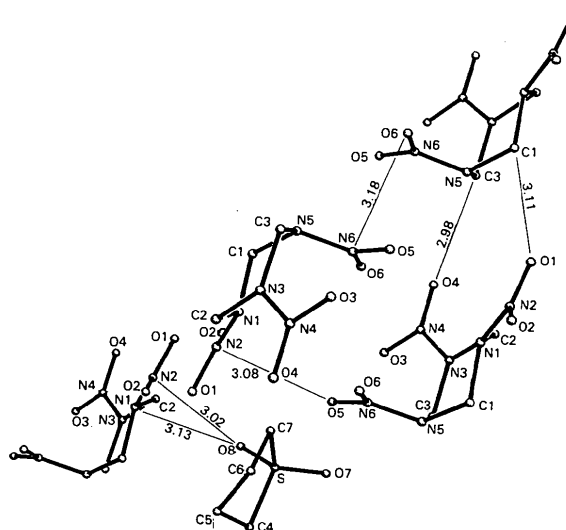
	x	y	z	U_{eq}
C(1)	2913 (4)	1869 (3)	7227 (2)	38 (1)
C(2)	-192 (5)	3218 (3)	6908 (3)	47 (1)
C(3)	2714 (4)	3214 (3)	5668 (3)	36 (1)
O(1)	-2119 (3)	1802 (2)	8205 (2)	56 (1)
O(2)	605 (3)	622 (2)	8519 (2)	53 (1)
O(3)	-444 (4)	3492 (3)	3827 (2)	71 (1)
O(4)	-2972 (3)	3481 (3)	4904 (2)	64 (1)
O(5)	2336 (4)	957 (2)	4046 (2)	65 (1)
O(6)	2613 (4)	-243 (2)	5438 (2)	63 (1)
N(1)	581 (3)	1980 (2)	7200 (2)	34 (1)
N(2)	-358 (4)	1450 (2)	8036 (2)	39 (1)
N(3)	462 (4)	3364 (3)	5765 (2)	46 (1)
N(4)	-1078 (4)	3420 (2)	4775 (2)	44 (1)
N(5)	3353 (3)	1986 (2)	6036 (2)	36 (1)
N(6)	2679 (4)	814 (2)	5103 (2)	45 (1)
C(4)	6305 (5)	3235 (3)	924 (3)	46 (1)
C(5)	5940 (5)	1751 (3)	854 (3)	55 (1)
C(6)	4463 (5)	1538 (3)	1744 (3)	59 (1)
C(7)	2609 (5)	2392 (3)	1543 (3)	53 (1)
O(7)	3879 (4)	5001 (2)	1904 (2)	65 (1)
O(8)	2490 (4)	3773 (2)	-205 (2)	58 (1)
S	3691 (1)	3782 (1)	1009 (1)	40 (1)

Table 2. Interatomic distances (\AA) and angles ($^\circ$)

C(1)-N(1)	1.463 (3)	N(2)-O(1)	1.217 (3)
C(1)-N(5)	1.442 (4)	N(2)-O(2)	1.225 (3)
C(2)-N(1)	1.460 (4)	N(4)-O(3)	1.218 (3)
C(2)-N(3)	1.450 (4)	N(4)-O(4)	1.221 (3)
C(3)-N(3)	1.446 (4)	N(6)-O(5)	1.210 (4)
C(3)-N(5)	1.455 (4)	N(6)-O(6)	1.210 (4)
N(1)-N(2)	1.368 (3)	C(4)-C(5)	1.505 (4)
N(3)-N(4)	1.346 (3)	C(5)-C(6)	1.514 (5)
N(5)-N(6)	1.422 (3)	C(6)-C(7)	1.510 (5)
		C(4)-S	1.775 (3)
		C(7)-S	1.779 (3)
		O(7)-S	1.435 (2)
		O(8)-S	1.434 (2)
N(2)-N(1)-C(1)	117.8 (2)	N(6)-N(5)-C(1)	114.6 (2)
N(2)-N(1)-C(2)	116.4 (2)	N(6)-N(5)-C(3)	114.5 (2)
C(1)-N(1)-C(2)	115.5 (2)	C(1)-N(5)-C(3)	113.0 (2)
N(4)-N(3)-C(2)	119.6 (2)	N(1)-C(2)-N(3)	106.7 (2)
N(4)-N(3)-C(3)	121.5 (2)	N(1)-C(1)-N(5)	108.2 (2)
C(2)-N(3)-C(3)	118.0 (2)	N(3)-C(3)-N(5)	110.3 (2)
N(1)-N(2)-O(1)	117.3 (2)	S-C(4)-C(5)	103.9 (2)
N(1)-N(2)-O(2)	117.2 (2)	C(4)-C(5)-C(6)	106.9 (3)
O(1)-N(2)-O(2)	125.4 (3)	C(5)-C(6)-C(7)	107.5 (3)
N(3)-N(4)-O(3)	116.9 (2)	C(6)-C(7)-S	105.9 (2)
N(3)-N(4)-O(4)	118.4 (2)	C(4)-S-C(7)	96.8 (1)
O(3)-N(4)-O(4)	124.5 (2)	C(4)-S-O(7)	111.2 (1)
N(5)-N(6)-O(5)	117.2 (2)	C(7)-S-O(7)	111.5 (1)
N(5)-N(6)-O(6)	116.9 (2)	C(4)-S-O(8)	109.8 (1)
O(5)-N(6)-O(6)	125.9 (2)	C(7)-S-O(8)	108.9 (1)
		O(7)-S-O(8)	116.8 (1)

As is the case in pure RDX (Choi & Prince, 1972), the RDX molecules in this structure adopt the chair conformation (Fig. 3). However, the molecular architecture in the pure and solvated RDX lattices differs with regard to the positions of the NO₂ groups. In pure RDX a pseudomirror plane exists in the molecules in which two of the NO₂ groups are essentially axial with respect to the ring, while the C₂NNO₂ fragment of the third is essentially planar and

is situated approximately in the plane of the ring. A greater variety of NO₂ positions is found in RDX-sulfolane as revealed in Fig. 3. The lone pair of electrons on N(5) appears to be partially active stereochemically and forces the attached NO₂ group into an axial orientation. The lone pair of N(1) is also partially active, but in the opposite direction and forces the attached NO₂ unit into an equatorial position. The lone pair on N(3) is not preferentially positioned on either side thereby producing an essentially planar C₂NNO₂ unit. Thus, each of the three extreme NO₂ positions with respect to the triazine ring is present in the RDX molecule of RDX-sulfolane. The structure demonstrates that the amine lone pair can be comfortably accommodated in any reasonable position, which, in turn, suggests that axial-equatorial interconversions of the NO₂ groups by stereochemical action of the amine lone pair might be facile. RDX molecules in solution and in the gas phase appear to have essentially C_{3v} symmetry (Karpowicz & Brill, 1983), which is consistent with dynamic time-averaged axial-equatorial NO₂ motion. The directional activity of the amine lone

Fig. 2. Stereoscopic view of the unit cell along the *a* axis.Fig. 3. View of the positions of the NO₂ groups of RDX. The shortest intermolecular contacts (e.s.d.'s ~ 0.004 \AA) are shown.

pair may be at least partly responsible for the variations in the N—N bond lengths.

Apart from the N—N bond, the bond distances and angles in RDX are similar to those found in pure RDX (Choi & Prince, 1972). The sulfolane molecule is structurally similar to that in other complexes (Swank & Willet, 1974), except that the bond distances and angles are more uniform in the RDX–sulfolane complex.

Because of the decrease in the density of the RDX–sulfolane lattice (1.64 g cm^{-3}) compared to pure RDX (1.8 g cm^{-3}), fewer short intermolecular contacts exist. The shortest intermolecular distances are given in Fig. 3. These tend to be O...N and O...C attractions between RDX molecules, and O...N attractions between RDX and sulfolane. RDX packs as interlocked molecules related by the inversion operation. The axial NO_2 of one molecule nests in the 'basket' of a neighbor in a manner similar to that in pure RDX. However, according to Fig. 3 the sulfolane molecule may also play a role in the stereochemistry of N(1). O(8) is positioned to repel the lone pair on N(1) and could be responsible for this lone pair preferring to localize in an equatorial rather than axial region of space.

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Structure of 1,4:3,6-Dianhydro-D-sorbitol,* $\text{C}_6\text{H}_{10}\text{O}_4$, at 100 K

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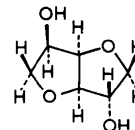
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Abstract. $M_r = 146.14$, orthorhombic, $P2_12_12_1$, $a = 5.313$ (2), $b = 7.006$ (3), $c = 17.174$ (5) Å, $V = 639.3$ Å³, $Z = 4$, $D_x = 1.52 \text{ Mg m}^{-3}$, D_m not measured, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.138 \text{ mm}^{-1}$, $F(000) = 312$, $T \approx 100 \text{ K}$. Final $R = 0.026$ for 1263 observed data. Evidence is obtained for the existence of a bifurcated hydrogen bond consisting of an intermolecular ($\text{O}\cdots\text{O} = 2.771$ Å) and an intramolecular ($\text{O}\cdots\text{O} = 2.826$ Å) hydrogen bond.

Introduction. In the course of an investigation of the complexation behaviour of 1,4:3,6-dianhydrohexitols with lanthanoid compounds, information was needed

about the conformation of 1,4:3,6-dianhydro-D-sorbitol (DIAN):



The compound has both an *endo*- and an *exo*-OH function. With the use of IR spectroscopy it has been shown that in dilute CCl_4 solution ($< 0.005 \text{ M}$) a strong intramolecular hydrogen bond exists between the *endo*-OH and the neighbouring ether O atom (Brimacombe, Foster, Stacey & Whiffen, 1958). The two fused five-membered rings of DIAN may adopt several envelope and half-chair conformations. A

* IUPAC name: 1,4:3,6-dianhydro-D-glucitol.