

Trichorabdal F Acetate, C₂₂H₂₈O₇

BY RAM P. KASHYAP,* WILLIAM H. WATSON AND DAVID A. GROSSIE

FASTBIOS Laboratory, Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129, USA

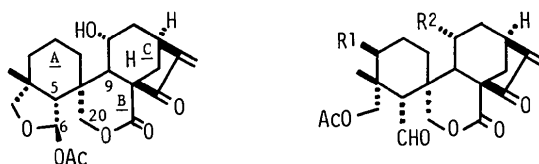
AND MANABU NODE, MIDORI SAI, EIICHI FUJITA AND KAORU FUJI

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

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Abstract. $M_r = 404.46$, orthorhombic, $P2_12_12_1$, $a = 15.199$ (8), $b = 17.334$ (7), $c = 7.576$ (3) Å, $V = 1996$ (2) Å³, $Z = 4$, $D_x = 1.346$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.07$ cm⁻¹, $F(000) = 864$, room temperature, $R = 0.040$ based on 914 unique reflections. The trichorabdal skeleton contains spiro-fused bicyclic and tricyclic ring systems. The bicyclic system is composed of a cyclohexane ring in a chair conformation *cis*-fused to a five-membered hemiacetal in a half-chair conformation. The tricyclic ring system contains a cyclohexane ring in a skew-boat conformation, a six-membered lactone ring in a 1,3-diplanar conformation and a five-membered ketone in an envelope conformation with an exocyclic double bond.

Introduction. Trichorabdal F acetate (1), which possesses potent antitumor activity against Ehrlich ascites carcinoma and P-388 lymphocytic leukemia, has been isolated from a methanol extract of *Rabdosia trichocarpa* Hara after acetylation with acetic anhydride and pyridine. Although structure (1) was elucidated by means of chemical correlation with trichorabdal B (2) (Fujita, Fuji, Sai, Node, Watson, & Zabel, 1981), an ambiguity concerning the stereochemistry at C(5) and C(6) still remained. Another point needing clarification was the conformation of ring A. Ring A of trichorabdal C (3) has a chair conformation with C(9) axial and C(2) equatorial, while ring A in trichorabdal B (2) exhibits an alternate chair conformation (Node, Sai, Fuji, Fujita, Shingu, Watson & Grossie, 1982).



(1)

(2) R¹ = H, R² = OH(3) R¹ = OH, R² = H

* GND University, Amritsar, India.

Experimental. Approximately cubic-shaped crystal, 0.2 × 0.2 × 0.2 mm, Syntex P2₁ diffractometer, θ : 2θ scan, variable scan rate, $2\theta_{\max} = 120^\circ$, graphite-monochromated radiation, lattice parameters from least squares of 15 medium-angle reflections, angles measured by a centering routine associated with the diffractometer system, systematic absences $h = 2n+1$ for $h00$, $k = 2n+1$ for $0k0$ and $l = 2n+1$ for $00l$; monitored reflection showed no significant change in intensity; 1886 independent reflections measured ($0 \leq h \leq 16$, $0 \leq k \leq 18$, $0 \leq l \leq 8$), 914 intensities greater than $3\sigma(I)$, Lorentz and polarization corrections applied, no absorption; direct methods, hydrogen atoms from difference Fourier and by calculation, full-matrix least-squares anisotropic refinement (H-atom coordinates not refined), $R = 0.040$, $R_w = 0.036$, $S = 1.29$, $\sum \omega(|F_o| - |F_c|)^2$ minimized, $\omega = 1/\sigma^2(F_o)$, largest $\Delta\rho$ excursion in final difference Fourier 0.17 e Å⁻³, av. and max. Δ/σ 0.11 and 0.96. Locally written programs were used for data reduction and initial block-diagonal least-squares refinement, MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) was used for the direct-methods calculations and XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used for all other computations.† Atomic scattering factors from XRAY76, anomalous dispersion corrections from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1 lists atomic positional parameters and U_{eq} values while Table 2 gives bond lengths and torsion angles.

Fig. 1 is an ORTEP (Johnson, 1971) drawing of the title compound. A bicyclic ring system is spiro-fused to a tricyclic ring system. The bicyclic system contains a cyclohexane ring (A) in a chair conformation and a

† Lists of structure factors, thermal parameters, hydrogen-atom coordinates and valence angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39026 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positional parameters ($\times 10^4$) for non-hydrogen atoms and equivalent isotropic thermal parameters U_{eq} ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

	x	y	z	U_{eq}^*
C(1)	7228 (4)	1422 (4)	8249 (9)	52 (4)
C(2)	6244 (5)	1253 (4)	8281 (9)	61 (5)
C(3)	5986 (4)	869 (4)	10003 (9)	51 (5)
C(4)	6218 (4)	1370 (3)	11617 (9)	39 (4)
C(5)	7179 (3)	1661 (3)	11524 (7)	31 (3)
C(6)	7697 (4)	968 (4)	12279 (8)	42 (4)
O(6)	8269 (3)	1252 (2)	13644 (6)	47 (3)
C(7)	8479 (4)	3036 (4)	11772 (9)	43 (4)
O(7)	8738 (3)	3348 (2)	13098 (6)	61 (3)
C(8)	7740 (4)	3368 (3)	10693 (7)	30 (4)
C(9)	7186 (4)	2808 (3)	9470 (8)	34 (4)
C(10)	7519 (4)	1965 (4)	9720 (8)	31 (4)
C(11)	7159 (5)	3113 (4)	7557 (8)	46 (5)
O(11)	7990 (3)	3032 (3)	6745 (6)	59 (3)
C(12)	6825 (5)	3943 (4)	7553 (8)	51 (5)
C(13)	7197 (5)	4429 (4)	9055 (9)	43 (4)
C(14)	8069 (4)	4087 (4)	9673 (8)	43 (4)
C(15)	7027 (4)	3752 (4)	11848 (9)	38 (4)
O(15)	6800 (3)	3577 (3)	13313 (6)	51 (3)
C(16)	6647 (5)	4377 (4)	10734 (9)	39 (4)
C(17)	5966 (5)	4811 (4)	11201 (10)	65 (6)
C(18)	5539 (4)	2009 (4)	11885 (9)	53 (4)
C(19)	6274 (4)	873 (4)	13271 (9)	54 (5)
O(19)	7088 (3)	474 (3)	13097 (6)	62 (3)
C(20)	8520 (4)	1989 (4)	9712 (8)	46 (4)
O(20)	8890 (3)	2410 (3)	11174 (6)	44 (3)
C(21)	9135 (5)	1078 (4)	13506 (11)	47 (5)
O(21)	9461 (3)	692 (3)	12420 (7)	65 (4)
C(22)	9612 (5)	1464 (5)	15017 (11)	86 (6)

$$* U_{eq} = \frac{1}{3} [U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}a^*b^*abc\cos\gamma + 2U_{13}a^*c^*acc\cos\beta + 2U_{23}bcb^*c^*cosa].$$

Table 2. Interatomic distances (\AA) and torsion angles ($^\circ$) for (1)

C(1)–C(2)	1.524 (10)	C(8)–C(15)	1.544 (9)
C(1)–C(10)	1.524 (9)	C(9)–C(10)	1.558 (9)
C(2)–C(3)	1.516 (10)	C(9)–C(11)	1.543 (9)
C(3)–C(4)	1.541 (9)	C(10)–C(20)	1.522 (9)
C(4)–C(5)	1.547 (8)	C(11)–O(11)	1.412 (9)
C(4)–C(18)	1.528 (9)	C(11)–C(12)	1.526 (10)
C(4)–C(19)	1.523 (9)	C(12)–C(13)	1.525 (10)
C(5)–C(6)	1.546 (8)	C(13)–C(14)	1.526 (10)
C(5)–C(10)	1.553 (8)	C(13)–C(16)	1.525 (10)
C(6)–O(6)	1.438 (8)	C(15)–O(15)	1.201 (8)
C(6)–O(19)	1.405 (8)	C(15)–C(16)	1.490 (10)
O(6)–C(21)	1.354 (9)	C(16)–C(17)	1.328 (10)
C(7)–O(7)	1.207 (8)	C(19)–O(19)	1.424 (8)
C(7)–C(8)	1.504 (9)	C(20)–O(20)	1.441 (8)
C(7)–O(20)	1.332 (8)	C(21)–O(21)	1.171 (9)
C(8)–C(9)	1.584 (8)	C(21)–C(22)	1.511 (11)
C(8)–C(14)	1.549 (9)		
C(1)C(2)C(3)C(4)	58.5 (7)	C(13)C(14)C(8)C(15)	–49.2 (5)
C(2)C(3)C(4)C(5)	–49.2 (7)	C(14)C(8)C(15)C(16)	34.4 (6)
C(3)C(4)C(5)C(10)	43.3 (7)	C(8)C(15)C(16)C(13)	–6.9 (7)
C(4)C(5)C(10)C(1)	–44.1 (7)	C(15)C(16)C(13)C(14)	–24.1 (7)
C(5)C(10)C(1)C(2)	51.6 (7)	C(16)C(13)C(14)C(8)	45.3 (6)
C(10)C(1)C(2)C(3)	–60.8 (7)	C(8)C(15)C(16)C(17)	174.9 (7)
C(10)C(20)O(20)C(7)	–36.1 (8)	O(15)C(15)C(16)C(17)	–3.1 (12)
C(20)O(20)C(7)C(8)	–11.4 (8)	C(4)C(5)C(6)O(19)	–14.0 (6)
O(20)C(7)C(8)C(9)	28.3 (8)	C(5)C(6)O(19)C(19)	–12.9 (6)
C(7)C(8)C(9)C(10)	2.6 (7)	C(6)O(19)C(19)C(4)	35.4 (6)
C(8)C(9)C(10)C(20)	–44.3 (6)	O(19)C(19)C(4)C(5)	–42.1 (6)
C(9)C(10)C(20)O(20)	64.6 (6)	C(19)C(4)C(5)C(6)	33.0 (5)
C(20)O(20)C(7)O(7)	172.9 (6)	O(7)C(7)C(8)C(15)	–36.1 (8)
C(8)C(9)C(11)C(12)	–54.0 (7)	O(15)C(15)C(8)C(7)	–31.7 (9)
C(9)C(11)C(12)C(13)	40.9 (8)	C(10)C(9)C(11)O(11)	–54.5 (7)
C(11)C(12)C(13)C(14)	24.1 (8)	C(8)C(9)C(11)O(11)	71.1 (6)
C(12)C(13)C(14)C(8)	–74.1 (6)		
C(13)C(14)C(8)C(9)	58.8 (6)		
C(14)C(8)C(9)C(11)	2.6 (7)		

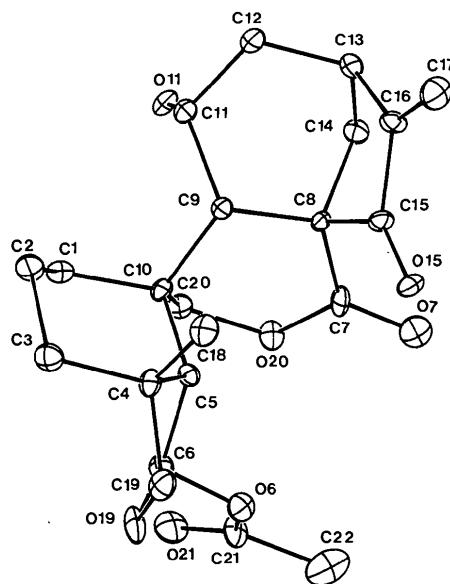


Fig. 1. ORTEP drawing of trichorabdal F acetate. Hydrogen atoms have been omitted for clarity.

cis-fused five-membered hemiacetal ring in a half-chair conformation (Bucourt, 1974). The two rings are essentially perpendicular. Bond lengths in the cyclohexane ring range from 1.516 (10) to 1.553 (8) \AA and the angles around the spiro fusion are 107.4 (5) to 113.3 (5) $^\circ$. The tricyclic ring system contains a cyclohexane ring (C) in a skew-boat or twist conformation (Toromanoff, 1980). This conformation is enforced by a 1,3-axial fusion to form a five-membered ketone ring with an exocyclic double bond and by a *cis*-fused six-membered lactone ring (B). The six-membered lactone ring is in a distorted 1,3-diplanar conformation. The variation in bond lengths (Table 2) can be rationalized in terms of atom hybridization, ring strain and steric factors.

There is an intermolecular hydrogen bond between O(11) and O(7); O(11)–H(11a) = 0.82 (4), H(11a) \cdots O(7) = 2.30 (4), O(11) \cdots O(7) = 3.038 (4) \AA , O(11)–H(11a) \cdots O(7) = 150.2 (6) $^\circ$.

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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), $C_3H_6N_6O_6 \cdot C_4H_8O_2S$

BY THOMAS M. HALLER, THOMAS B. BRILL* AND ARNOLD L. RHEINGOLD

Department of Chemistry, University of Delaware, Newark, DE 19711, USA

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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.

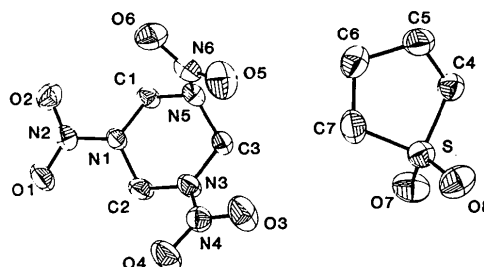


Fig. 1. Projections of RDX (left) and sulfolane (right) molecules.

* Author to whom correspondence should be addressed.