

The space group was determined to be $P2_1/c$ from the systematic absences. The data were measured using a variable scan rate with a maximum scan time of 60 s per reflection. The final drift correction factors were between 1.00 and 1.03. Profile analysis (Lehmann & Larsen, 1974; Grant & Gabe, 1978) was performed on all reflections. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985). Isotropic least-squares refinement using a local version of *SHELX76* (Sheldrick, 1976; van der Maelen Uría, 1990). Further anisotropic refinement followed by a difference Fourier synthesis allowed the location of all H atoms. During the final stages of the refinement the positional and anisotropic displacement parameters of the non-H atoms were refined. All H atoms were refined isotropically with individual displacement parameters. The function minimized was $\sum w(F_o - F_c)^2$. Geometrical calculations were carried out with *PARST* (Nardelli, 1983). All calculations were made at the University of Oviedo on the VAX computers of the Scientific Computer Center and X-ray group.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *DIRDIF* (Beurskens *et al.*, 1992). Data reduction: *DATAR*, local program. Molecular graphics: *EUCLID* (Spek, 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1190). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4,5-Bis(fluorodinitromethyl)-2-methoxy-1,3-dioxolane

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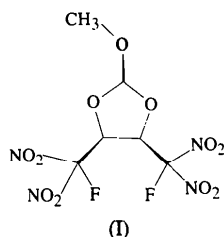
Abstract

The 1,3-dioxolane ring of the title compound, $C_6H_6F_2N_4O_{11}$, is in a slightly distorted 'twist' conformation. The largest deviations from the least-squares plane of the ring are exhibited by a C and an adjacent O atom which are displaced in opposite directions by about 0.23 Å. Bond distances agree well with those of the analogous formate ester, the major differences arising from the change in hybridization of the C5 atom from sp^2 in the ester to sp^3 in the present compound. The closest intermolecular interactions arise from nitro group O...O contacts of 2.9 Å between pairs of layers of molecules. Sublimed crystals 'jump' up to 1 cm and crack when gently heated (313 K).

Comment

The low-temperature structure determination of 4,5-bis-(fluorodinitromethyl)-2-methoxy-1,3-dioxolane, (I), was performed as part of a study of energetic materials containing the fluorodinitromethyl group. Details of the synthetic work have been discussed elsewhere (Koppes, 1995) and will be published separately (Koppes, 1996). The crystal structure of the analogous formate ester, 4,5-bis(fluorodinitromethyl)-1,3-dioxolan-2-one is known (Ammon & Bhattacharjee, 1984). In the ester, the ring conformation is determined by the planarity of the sp^2 -hybridized C5 atom with the three O atoms bound to it. The other two ring atoms, C1 and C3, are then displaced out of this plane in opposite directions by about 0.2 Å. In contrast, the 1,3-dioxolane ring in (I) has the C3 and O10 atoms displaced by 0.23 Å in

opposite directions from the ring least-squares plane. The complete least-squares-plane displacements are C1 0.140 (1), C3 -0.227 (1), C5 -0.128 (1), O9 -0.017 (1) and O10 0.233 (1) Å. Thus, the ring is in a slightly distorted 'twist' conformation.



The bond distances in (I) generally agree with those of the chemically similar bonds in the ester. The molecular packing for (I) consists of layers in the *bc* plane, with nitro O...O contacts of 2.9 Å between pairs of layers and some intralayer nitro O...O contacts as well. Crystals of (I) on a glass slide placed on a warm (313 K) microscope stage 'jumped' off the slide. Subsequent microscopic examination revealed cracks in crystals that had jumped. The maximum jump height

was about 1 cm. Crystals of other compounds have been observed to jump (Dunitz & Bernstein, 1995) and at least some of these also have layered structures (Ding, Herbst, Praefcke, Kohne & Saenger, 1991).

Experimental

A sample of (I) was obtained from Dr William M. Koppes, Naval Surface Warfare Center, Indian Head Division, Indian Head, MD 20640-5035, USA. Crystals were grown by sublimation in a sealed tube under reduced pressure.

Crystal data

C₆H₆F₂N₄O₁₁

M_r = 348.15

Monoclinic

*C*2/*c*

a = 17.816 (2) Å

b = 9.0500 (10) Å

c = 15.468 (3) Å

β = 98.700 (10)°

V = 2465.3 (6) Å³

Z = 8

D_x = 1.876 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 26 reflections

θ = 12–12.5°

μ = 0.198 mm⁻¹

T = 173 (2) K

Prism

0.20 × 0.20 × 0.20 mm

Colourless

Data collection

Siemens P4/RA four-circle diffractometer

θ/2θ scans

Absorption correction:

none

6014 measured reflections

2829 independent reflections

2068 observed reflections

[*I* > 2σ(*I*)]

*R*_{int} = 0.0537

θ_{max} = 27.50°

h = -1 → 23

k = -11 → 11

l = -20 → 19

3 standard reflections

monitored every 97

reflections

intensity decay: 8%

Refinement

Refinement on *F*²

R(*F*) = 0.0408

wR(*F*²) = 0.1063

S = 1.038

2828 reflections

232 parameters

H atoms refined isotropically

w = 1/[σ²(*F*_o²) + (0.0500*P*)²

+ 0.2100*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} = 0.067

Δρ_{max} = 0.294 e Å⁻³

Δρ_{min} = -0.232 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

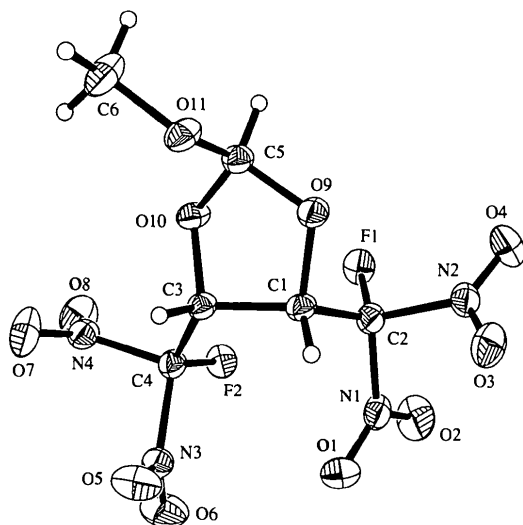


Fig. 1. View of C₆H₆F₂N₄O₁₁ showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

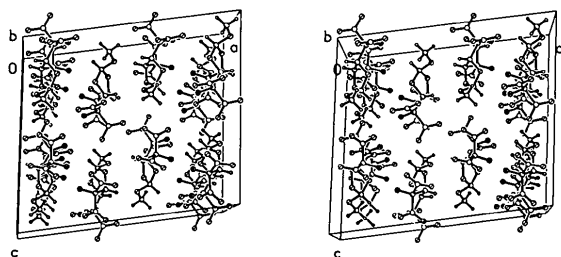


Fig. 2. Stereoview of the unit-cell packing viewed along the *b* axis.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C1	0.08749 (11)	0.0618 (2)	0.18566 (11)	0.0196 (4)
C2	0.14253 (10)	-0.0597 (2)	0.16889 (11)	0.0213 (4)
C3	0.10725 (10)	0.2232 (2)	0.16579 (11)	0.0186 (4)
C4	0.14539 (10)	0.2631 (2)	0.08822 (11)	0.0212 (4)
C5	0.12768 (10)	0.1985 (2)	0.31103 (11)	0.0217 (4)
C6	0.0987 (2)	0.4211 (2)	0.3763 (2)	0.0374 (5)
O1	0.08746 (9)	-0.0461 (2)	0.02149 (9)	0.0361 (4)
O2	0.19068 (9)	-0.1757 (2)	0.05342 (10)	0.0432 (4)
O3	0.05303 (8)	-0.2394 (2)	0.18685 (10)	0.0335 (3)

O4	0.16711 (9)	-0.2700 (2)	0.25817 (10)	0.0403 (4)
O5	0.02444 (8)	0.2838 (2)	0.00527 (10)	0.0395 (4)
O6	0.11971 (9)	0.2419 (2)	-0.06356 (9)	0.0441 (4)
O7	0.12124 (10)	0.5138 (2)	0.10626 (11)	0.0428 (4)
O8	0.23660 (9)	0.4524 (2)	0.09227 (11)	0.0438 (4)
O9	0.09195 (7)	0.06570 (14)	0.27841 (8)	0.0235 (3)
O10	0.15906 (7)	0.26197 (14)	0.24155 (8)	0.0223 (3)
O11	0.07107 (7)	0.28425 (15)	0.33650 (8)	0.0260 (3)
N1	0.14015 (10)	-0.0979 (2)	0.07176 (10)	0.0261 (4)
N2	0.11884 (10)	-0.2052 (2)	0.20921 (10)	0.0251 (3)
N3	0.09059 (10)	0.2609 (2)	0.00106 (10)	0.0258 (3)
N4	0.17109 (10)	0.4265 (2)	0.09683 (10)	0.0269 (4)
F1	0.21429 (6)	-0.03382 (12)	0.20154 (7)	0.0272 (3)
F2	0.20568 (6)	0.18265 (12)	0.07850 (7)	0.0257 (3)

Table 2. Selected geometric parameters (Å, °)

C1—O9	1.425 (2)	C4—F2	1.325 (2)
C1—C2	1.522 (3)	C5—O11	1.376 (2)
C1—C3	1.544 (2)	C5—O10	1.407 (2)
C2—F1	1.323 (2)	C5—O9	1.417 (2)
C3—O10	1.421 (2)	C6—O11	1.437 (2)
C3—C4	1.509 (2)		
O9—C1—C2	104.48 (14)	F2—C4—C3	115.43 (15)
O9—C1—C3	101.39 (13)	F2—C4—N3	108.14 (14)
C2—C1—C3	118.54 (15)	C3—C4—N3	113.01 (14)
F1—C2—C1	114.66 (15)	F2—C4—N4	107.47 (14)
F1—C2—N1	107.18 (13)	C3—C4—N4	108.81 (14)
C1—C2—N1	113.97 (14)	N3—C4—N4	103.14 (13)
F1—C2—N2	107.75 (14)	O11—C5—O10	112.45 (15)
C1—C2—N2	108.98 (14)	O11—C5—O9	105.72 (14)
N1—C2—N2	103.58 (13)	O10—C5—O9	106.45 (13)
O10—C3—C4	106.39 (14)	C5—O9—C1	109.44 (13)
O10—C3—C1	102.02 (13)	C5—O10—C3	104.22 (13)
C4—C3—C1	121.85 (14)	C5—O11—C6	113.0 (2)

Table 3. Bond distances (Å) and angles (°) for the nitro groups with *e.s.d.*'s in parentheses and calculated standard deviations in square brackets

	Range	Mean
C—N	1.536 (2)–1.548 (2)	1.542 [5]
N—O	1.203 (2)–1.219 (2)	1.210 [5]
O—N—O	127.1 (2)–128.4 (2)	127.8 [5]
C—N—O	114.5 (2)–117.3 (2)	116 [1]

H atoms were refined in observed positions. One reflection (802) had an unusually large disagreement between F_o^2 and F_c^2 (10σ) and was excluded from the final stages of refinement. The next largest disagreement was 5.0σ and no other disagreements were larger than 3.9σ . The highest peaks in the final difference map were attributable to bonding electrons between C atoms.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXTL (Sheldrick, 1990b).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BK1205). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Phase Transition and Expected Non-Linear Polarizability of 1-Hydroxy-4-(4-methylphenylamino)-9,10-anthraquinone

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Abstract

The title compound, C₂₁H₁₅NO₃, shows a second-order phase transition above 313 K. Both phases are non-centrosymmetric. According to semi-empirical calculations, these polar crystals are liable to exhibit second-order hyperpolarizability.

Comment

In the framework of our investigation of anthraquinone dyes, we studied 1-hydroxy-4-(4-methylphenylamino)-9,10-anthraquinone, (I), which is also known as Solvent Violet 13 or Disperse Blue 72.

