$\theta/2\theta$ scans
Absorption correction: refined from ΔF (Walker & Stuart, 1983)
3335 measured reflections
3233 independent reflections
2926 observed reflections [$I > \sigma(I)$]
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 21$
2 standard reflections frequency: 30 min intensity decay: 6.69%

Refinement

Refinement on F
$R = 0.060$
$wR = 0.055$
$S = 0.928$
2926 reflections
173 parameters
H atoms treated using a riding model
$w = 1/\sigma^2(F_o)$ where $\sigma(F_o^2) = [\sigma^2(I) + (pF_o^2)^2]$ and $p = 0.04$
$(\Delta/\sigma)_{max} = 0.011$
$\Delta\rho_{max} = 0.71$ e Å^{-3}
$\Delta\rho_{min} = -1.48$ e Å^{-3}
Extinction correction: Zachariasen (1977)
Extinction coefficient: 5.1×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Br	0.75155 (8)	0.27720 (7)	0.11826 (3)	0.0701 (3)
O1	0.4360 (5)	0.8761 (5)	0.1544 (2)	0.088 (2)
O2	0.3848 (5)	1.1096 (5)	0.0802 (2)	0.081 (2)
N1	0.0755 (6)	0.7504 (5)	0.1107 (2)	0.062 (2)
C1	−0.0060 (9)	0.8059 (8)	0.1921 (3)	0.090 (4)
C2	−0.1455 (9)	0.7007 (9)	0.2292 (3)	0.093 (4)
C3	−0.2202 (9)	0.7698 (9)	0.3052 (3)	0.090 (4)
C4	−0.397 (1)	0.698 (1)	0.3404 (3)	0.103 (5)
C5	−0.474 (1)	0.7654 (9)	0.4150 (3)	0.097 (4)
C6	−0.665 (1)	0.708 (1)	0.4480 (4)	0.112 (5)
C7	−0.744 (1)	0.772 (1)	0.5213 (3)	0.102 (5)
C8	−0.934 (1)	0.717 (1)	0.5537 (4)	0.125 (6)
C9	−1.016 (1)	0.776 (1)	0.6269 (4)	0.120 (6)
C10	−1.204 (1)	0.719 (2)	0.6583 (5)	0.163 (8)
C11	−1.285 (2)	0.770 (1)	0.7249 (5)	0.19 (1)
C31	0.3429 (7)	0.9587 (7)	0.1096 (3)	0.067 (3)
C32	0.1660 (7)	0.9037 (6)	0.0775 (3)	0.060 (3)
C33	−0.0962 (7)	0.7282 (7)	0.0687 (3)	0.071 (3)
C34	0.2196 (9)	0.5832 (7)	0.1040 (4)	0.094 (4)

Table 2. *Selected geometric parameters* (Å, °)

O1—C31	1.207 (6)	C4—C5	1.476 (8)
O2—C31	1.314 (6)	C5—C6	1.50 (1)
N1—C1	1.572 (6)	C6—C7	1.451 (9)
N1—C32	1.486 (6)	C7—C8	1.47 (1)
N1—C33	1.489 (7)	C8—C9	1.44 (1)
N1—C34	1.482 (6)	C9—C10	1.47 (1)
C1—C2	1.438 (9)	C10—C11	1.32 (1)
C2—C3	1.499 (8)	C31—C32	1.499 (7)
C3—C4	1.48 (1)		
C1—N1—C32	106.9 (4)	N1—C1—C2	116.9 (5)
C1—N1—C33	109.0 (4)	C1—C2—C3	112.5 (6)
C1—N1—C34	113.8 (4)	O1—C31—O2	124.8 (5)
C32—N1—C33	106.4 (4)	O1—C31—C32	125.6 (5)
C32—N1—C34	111.5 (4)	O2—C31—C32	109.6 (4)
C33—N1—C34	108.9 (4)	N1—C32—C31	118.4 (4)
C32—N1—C1—C2	163.9 (5)	O1—C31—C32—N1	9.8 (8)
C1—N1—C32—C31	63.0 (5)	O2—C31—C32—N1	−171.4 (4)
N1—C1—C2—C3	−177.5 (5)		

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *MULTAN* (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976), *SCHAKAL*92 (Keller, 1992). Software used to prepare material for publication: *MolEN BTABLE*, *PTABLE* and *CIF IN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances involving H atoms, angles involving non-H atoms, torsion angles and contact distances have been deposited with the IUCr (Reference: SE1072). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Abrahamsson, S., Dahlén, B., Löfgren, H. & Pascher, I. (1978). *Prog. Chem. Fats Other Lipids*, **16**, 125–143.
Enraf–Nonius (1977). *CAD-4 Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Keller, E. (1992). *SCHAKAL*92. *A Computer Program for the Graphic Representation of Molecular and Crystallographic Models*. Univ. of Freiburg, Germany.
Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
Müller-Fahrnow, A., Hilgenfeld, R., Hesse, H., Saenger, W. & Pfannemüller, B. (1988). *Carbohydr. Res.* **176**, 165–174.
Rudert, R., Schulz, B., Reck, G., Vollhardt, D. & Kriwanek, J. (1995). *Acta Cryst.* C**51**, 766–768.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.
Wüstneck, R., Kriwanek, J., Herbst, M., Wasow, G. & Haage, K. (1992). *Colloids Surf.* **66**, 1–9.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1995). C**51**, 770-772

1-Trifluoroacetyl-3-trifluoromethyl-3a,8b-dihydro-1*H*,4*H*-indeno[1,2-*c*]pyrazole

M. Abdul-Ghani, R. G. Pritchard and A. E. Tipping

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

(*Received* 16 *September* 1994; *accepted* 18 *October* 1994)

Abstract

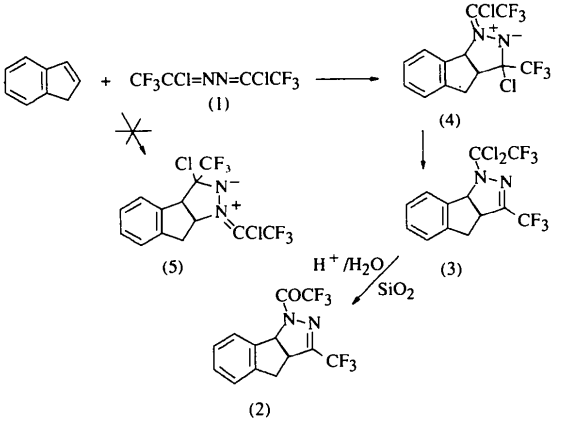
The title structure, $C_{13}H_8F_6N_2O$, is the hydrolysis product of the rearranged 1,3-dipolar cycloadduct of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene

©1995 International Union of Crystallography
Printed in Great Britain – all rights reserved

and indene, and comprises approximately planar moieties meeting at a dihedral angle of 119.7 (1)° along the shared C—C bond between the five-membered rings. One plane contains the carbonyl substituent, which lies *trans* to the N—N bond [O=C—N—N 179.2 (3)°] and completes a delocalization pathway extending from the ring C=N bond [C—N—N=C −176.3 (3)°]. However, as the latter bond is only 1.248 (4) Å long, any delocalization must be limited to the O=C—N—N region.

Comment

This structure determination, which forms part of a general investigation into 1,3-dipolar cycloaddition reactions of the dichloroazine (1) with a variety of cyclic alkenes, dienes and trienes (Abdul-Ghani, 1992; Abdul-Ghani & Tipping, 1993), was undertaken to identify the hydrolyzed product (2) and hence relate it to its precursor, the rearranged 1:1 cycloadduct (3). This study proved that the initial cycloaddition had afforded the 1:1 adduct (4) and not the alternative 1:1 adduct (5).



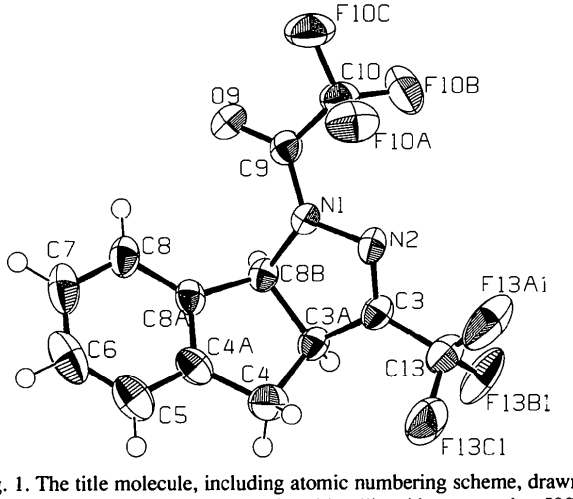


Fig. 1. The title molecule, including atomic numbering scheme, drawn using *ORTEP*II (Johnson, 1976) with ellipsoids set at the 50% probability level.

Experimental

A mixture of the dichloroazine (1) (4.00 g, 15.32 mmol) and indene (1.78 g, 15.34 mmol) heated *in vacuo* in a Rotaflo tube (*ca* 100 ml) at 343 K (4 d), gave volatile material identified as unchanged dichloroazine (1) (0.89 g, 3.41 mmol, 22% recovered) and a non-volatile residue (4.81 g). The residue was introduced onto the top of a DCFC column (silica Merck Kieselgel 60H) as a solution in petroleum ether (b.p. 313–333 K) and CH_2Cl_2 in the ratio 2:1 *v/v*, and hydrogen chloride was immediately evolved from the surface of the silica. After a short time (10 min) the material was eluted (same eluant) to afford unchanged indene (0.33 g, 2.84 mmol, 19% recovered) and the title compound, (2) (3.58 g, 11.12 mmol, 93%), m.p. 378–380 K (found: C 48.7, H 2.4, N 8.6, F 35.7%, M^+ 322; $C_{13}H_8F_6N_2O$ requires C 48.8, H 2.5, N 8.7, F 35.4%, M^+ 322). Crystals for the X-ray study were obtained by recrystallization from a mixture of CH_2Cl_2 and *n*-pentane in the ratio 1:1 *v/v*.

Crystal data

$C_{13}H_8F_6N_2O$	Mo $K\alpha$ radiation
M_r = 322.21	λ = 0.71069 Å
Orthorhombic	Cell parameters from 25 reflections
Pbca	θ = 13.3–21.3°
a = 10.648 (2) Å	μ = 0.164 mm^{-1}
b = 12.589 (3) Å	T = 233 K
c = 18.594 (4) Å	Plate
V = 2492 (1) Å^3	0.40 × 0.30 × 0.10 mm
Z = 8	Colourless
D_x = 1.717 Mg m^{-3}	

Data collection

Siemens *R3m/V* diffractometer	θ_{max} = 24.5°
$\omega/2\theta$ scans	$h = 0 \rightarrow 12$
Absorption correction: none	$k = 0 \rightarrow 14$
2393 measured reflections	$l = 0 \rightarrow 21$
2393 independent reflections	3 standard reflections monitored every 150 reflections
1075 observed reflections [$I > 3\sigma(I)$]	intensity decay: insignificant

Refinement

Refinement on F	$(\Delta/\sigma)_{max}$ = 0.09
R = 0.0387	$\Delta\rho_{max}$ = 0.19 e Å^{-3}
wR = 0.0458	$\Delta\rho_{min}$ = −0.16 e Å^{-3}
S = 1.150	Extinction correction: none
1075 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
227 parameters	
H-atom parameters not refined	
Weighting scheme based on measured e.s.d.'s	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
F10*A*	0.4777 (2)	0.4432 (2)	0.6999 (1)	0.066 (2)
F10*B*	0.3884 (2)	0.5544 (2)	0.6319 (1)	0.068 (2)
F10*C*	0.3774 (2)	0.3903 (2)	0.6090 (1)	0.068 (2)

F13*A*1	0.663 (2)	0.736 (2)	0.772 (1)	0.11 (1)
F13*B*1	0.746 (2)	0.8366 (7)	0.6982 (7)	0.076 (5)
F13*C*1	0.857 (2)	0.737 (1)	0.7588 (9)	0.085 (7)
F13*A*2	0.628 (1)	0.772 (2)	0.742 (2)	0.10 (1)
F13*B*2	0.793 (4)	0.829 (2)	0.702 (1)	0.14 (3)
F13*C*2	0.787 (4)	0.710 (2)	0.7766 (9)	0.08 (1)
O9	0.5766 (2)	0.4128 (2)	0.5345 (2)	0.048 (2)
N1	0.6565 (3)	0.5386 (2)	0.6048 (2)	0.033 (2)
N2	0.6423 (3)	0.6037 (2)	0.6632 (2)	0.036 (2)
C3	0.7363 (3)	0.6629 (3)	0.6654 (2)	0.035 (2)
C3A	0.8333 (3)	0.6462 (3)	0.6099 (2)	0.036 (2)
C4	0.9567 (4)	0.6016 (3)	0.6386 (2)	0.048 (3)
C4A	0.9637 (3)	0.4933 (3)	0.6079 (2)	0.041 (2)
C5	1.0589 (4)	0.4208 (3)	0.6182 (2)	0.056 (3)
C6	1.0522 (4)	0.3266 (4)	0.5830 (3)	0.065 (3)
C7	0.9541 (5)	0.3042 (3)	0.5387 (3)	0.057 (3)
C8	0.8583 (4)	0.3753 (3)	0.5288 (2)	0.044 (2)
C8A	0.8643 (3)	0.4697 (3)	0.5654 (2)	0.034 (2)
C8B	0.7727 (3)	0.5593 (3)	0.5643 (2)	0.033 (2)
C9	0.5679 (3)	0.4702 (3)	0.5858 (2)	0.036 (2)
C10	0.4523 (4)	0.4657 (3)	0.6330 (2)	0.045 (3)
C13	0.7436 (5)	0.7433 (4)	0.7226 (3)	0.050 (3)

Table 2. *Selected geometric parameters* (Å, °)

O9—C9	1.202 (4)	C4—C4A	1.480 (5)
N1—N2	1.369 (4)	C4A—C5	1.378 (5)
N1—C8B	1.472 (4)	C4A—C8A	1.354 (5)
N1—C9	1.325 (4)	C5—C6	1.356 (6)
N2—C3	1.248 (4)	C6—C7	1.361 (7)
C3—C3A	1.476 (5)	C7—C8	1.369 (5)
C3—C13	1.470 (5)	C8—C8A	1.372 (5)
C3A—C4	1.526 (5)	C8A—C8B	1.491 (5)
C3A—C8B	1.527 (5)	C9—C10	1.513 (5)
N2—N1—C8B	113.2 (3)	C4A—C5—C6	118.3 (4)
N1—N2—C3	107.1 (3)	C4A—C8A—C8	121.1 (4)
N2—C3—C3A	116.9 (3)	C4A—C8A—C8B	110.7 (3)
C3—C3A—C4	114.2 (3)	C8—C8A—C8B	128.1 (3)
C3—C3A—C8B	101.2 (3)	N1—C8B—C3A	101.4 (3)
C4—C3A—C8B	107.1 (3)	N1—C8B—C8A	114.2 (3)
C3A—C4—C4A	104.3 (3)	C3A—C8B—C8A	104.9 (3)
C4—C4A—C5	126.5 (4)	O9—C9—N1	123.2 (4)
C4—C4A—C8A	112.8 (3)	O9—C9—C10	120.0 (3)
C5—C4A—C8A	120.7 (4)	N1—C9—C10	116.7 (3)

Each of the fluorine atoms attached to C13 is disordered over two sites, with the population of F13*A*1, F13*B*1 and F13*C*1 refining to 0.67 (3) and the occupancy of the alternative sites F13*A*2, F13*B*2 and F13*C*2 being constrained to one minus this value.

Data collection: *P3/PC Diffractometer Control Software* (Siemens, 1989). Cell refinement: *P3/PC Diffractometer Control Software*. Data reduction: *PROCESS TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *LS TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *FINISH TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Abdul-Ghani, M. (1992). PhD thesis, Univ. of Manchester, England.
Abdul-Ghani, M. & Tipping, A. E. (1993). *J. Fluorine Chem.* **63**, 5–11.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.
Siemens (1989). *P3/PC Diffractometer Program*. Version 3.13. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1995). C**51**, 772–775

2-(2,6-Difluorophenyl)-1,3-dithiane and 2-(2,6-Difluorophenyl)-1,3-dithiane 1,1,3,3-Tetraoxide. The Role of Oxidation in Locking a Molecular Conformation

A. J. Adamson, R. E. Banks, K. N. Mothersdale, R. G. Pritchard, T. Manley and A. E. Tipping

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

(*Received* 4 *July* 1994; *accepted* 5 *October* 1994)

Abstract

In 2-(2,6-difluorophenyl)-1,3-dithiane, (1), $C_{10}H_{10}F_2S_2$, described here, and its unfluorinated counterpart [Kalff & Romers (1966). *Acta Cryst.* **20**, 490–496], the conformation about the C—C bond joining the two rings is similar, with S—C—C_{ar}—C_{ar} torsion angles of 59.5 (2) and −67.6 (2)° in the former, and 59.7 and −66.0° in the latter. In the oxidation product 2-(2,6-difluorophenyl)-1,3-dithiane 1,1,3,3-tetraoxide, (2), $C_{10}H_{10}F_2O_4S_2$, the torsion angles become 42.8 (4) and −87.6 (3)°. There is a slight flattening of the tetrahedral geometry at atom C2, as indicated by the sum of the three non-H bond angles [335.7 (2) and 340.8 (3)° for (1) and (2), respectively]. Compound (2) is not unduly sterically congested since the shortest O···F contact of 2.712 (3) Å is close to the expected van der Waals distance of 2.75 Å. However, further twisting about the central bond would lead to an unacceptably short O···F contact of 1.501 Å, effectively blocking free rotation of the phenyl ring about this bond.

Comment

The structure determination of the title compounds, 2-(2,6-difluorophenyl)-1,3-dithiane, (1), and 2-(2,6-difluorophenyl)-1,3-dithiane 1,1,3,3-tetraoxide, (2), was carried out as part of a general investigation into the synthesis and chemistry of 2-fluoroaryl-1,3-dithianes, including studies of their hydrolysis and their oxidation to the corresponding bis(sulfone) compounds (Adamson

©1995 International Union of Crystallography
Printed in Great Britain – all rights reserved