C4	0.5297 (3)	0.1579 (3)	0.4410 (10)	0.0235 (10)
C5	0.6030 (3)	0.1121 (3)	0.2534 (10)	0.0241 (10)
C6	0.6817 (3)	0.1749 (3)	0.1667 (10)	0.0232 (10)

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

S1—C2	1.798 (4)	O2—N	1.227 (5)
S1—S2	2.0595 (14)	N—C1	1.455 (5)
O1—N	1.235 (4)		
C2—S1—S2	104.69 (14)	C2—C1—N	121.4 (3)
$S1^i$—S2—S1	110.57 (9)	C6—C1—N	116.7 (3)
O2—N—O1	122.3 (3)	C1—C2—C3	117.1 (3)
O2—N—C1	119.8 (3)	C1—C2—S1	121.4 (3)
O1—N—C1	118.0 (3)	C3—C2—S1	121.6 (3)
C2—C1—C6	121.9 (3)		
C2—S1—S2—$S1^i$	−79.58 (12)	O1—N—C1—C6	−173.1 (3)
O2—N—C1—C2	−173.6 (3)	S2—S1—C2—C1	−177.3 (3)
O1—N—C1—C2	6.8 (5)	S2—S1—C2—C3	3.1 (4)
O2—N—C1—C6	6.5 (6)		

Symmetry code: (i) $1 - x, 1 - y, z$.

The unit cell was determined and the intensity data were collected on a Delft Instruments FAST diffractometer using the routines *ENDEX*, *REFINE* and *MADONL* in the *MADNES* software (Pflugrath & Messerschmidt, 1989), and processed using *ABSMAD* (Karaulov, 1992); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). The S, O, N and C atoms were refined with anisotropic displacement parameters. The H atoms were allowed to ride on their attached C atoms and refined with isotropic displacement parameters.

Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1996).

The use of the EPSRC X-ray crystallographic service at the University of Wales, Cardiff, is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 124–126

1-(4-Bromophenyl)-2-fluoroethanone (2,4-Dinitrophenyl)hydrazone Containing a Particularly Short Fluorine–Hydrogen Bond

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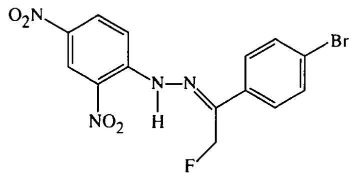
Abstract

The title compound, 4-bromophenyl fluoromethyl ketone (2,4-dinitrophenyl)hydrazone, $C_{14}H_{10}BrFN_4O_4$, contains a short F···H contact [2.02 (3) Å] indicating an optimal stabilizing interaction.

Comment

We have a current interest (Howard, Hoy, O'Hagan & Smith, 1996) in exploring the ability of fluorine bound to carbon in organic compounds to act as a hydrogen-bond acceptor. Systematic analyses of the Cambridge Structural Database (Allen *et al.*, 1987; Howard *et al.*, 1996; Shimoni & Glusker, 1994; Murray-Rust, Stallings, Monti, Preston & Glusker, 1983) reveal very few situations where such F atoms form short F···H contacts to acidic H atoms and in general these interactions are overridden by stronger hydrogen-bonding interactions between OH and NH groups.

In attempts to design a system which may exhibit fluorine–hydrogen bonding, we have prepared the dinitrophenylhydrazone of 4-bromo-α-fluoroacetophenone, (I). The fluoromethyl group was selected following our calculations (Howard *et al.*, 1996), which suggest that fluorine attached to an sp^3 carbon will act as a better hydrogen-bond acceptor than fluorine attached to an sp^2 carbon. The title compound is shown to possess a particularly short F···H contact of 2.02 (3) Å to the hydrogen of the hydrazone group, as part of a three-centred interaction with an O atom of the *ortho*-nitro group. This length is close to the calculated equilibrium distance (1.9 Å) of an optimal C_{sp^3}—F···H bond (Howard *et al.*, 1996) which makes it particularly unusual.



(I)

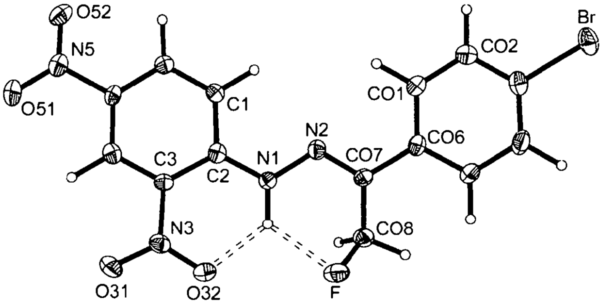


Fig. 1. View of $C_{14}H_{10}BrFN_4O_4$ showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii.

Experimental

The synthesis of (I) was carried out by treatment of 1-(4-bromophenyl)-2-fluoroethanone and a solution of 2,4-dinitrophenylhydrazine in ethanol:sulfuric acid (10:1). The orange compound was recrystallized from ethyl acetate.

Crystal data

$C_{14}H_{10}BrFN_4O_4$
$M_r = 397.17$
Orthorhombic
Pbca
$a = 13.366\,(1)$ Å
$b = 7.3869\,(7)$ Å
$c = 29.892\,(3)$ Å
$V = 2951.4\,(5)$ Å^3
$Z = 8$
$D_x = 1.788$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 274 reflections
$\theta = 19.09$–$28.84°$
$\mu = 2.826$ mm^{-1}
$T = 150\,(2)$ K
Slab
0.4 × 0.2 × 0.1 mm
Orange

Data collection

Siemens SMART–CCD diffractometer
ω scans
Absorption correction: by integration from crystal shape (*XPREP* in *SHELXTL*; Sheldrick, 1995)
$T_{\min} = 0.5260$, $T_{\max} = 0.8011$

19823 measured reflections
3382 independent reflections
2830 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0441$
$\theta_{\max} = 27.49°$
$h = -17 \rightarrow 17$
$k = -8 \rightarrow 9$
$l = -33 \rightarrow 38$
Data 99.5% complete at $\theta_{\max}$

Refinement

Refinement on F^2
$R(F) = 0.0373$
$wR(F^2) = 0.0771$
$S = 1.215$
3375 reflections
257 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 4.2451P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.039$
$\Delta\rho_{\max} = 0.408$ e Å^{-3}
$\Delta\rho_{\min} = -0.786$ 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)

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

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

	x	y	z	$U_{\rm eq}$
Br	0.74483 (2)	0.02400 (4)	0.26238 (1)	0.0330 (1)
F	1.1779 (1)	−0.4310 (2)	0.11438 (6)	0.0299 (4)
O31	1.2375 (2)	−0.5529 (3)	−0.05514 (7)	0.0377 (5)
O32	1.2292 (1)	−0.4701 (3)	0.01409 (6)	0.0296 (4)
O51	1.0103 (2)	−0.3540 (3)	−0.16433 (6)	0.0402 (6)
O52	0.8837 (1)	−0.1814 (3)	−0.14697 (6)	0.0299 (4)
N1	1.0750 (2)	−0.2882 (3)	0.04366 (7)	0.0199 (4)
N2	1.0075 (2)	−0.2344 (3)	0.07586 (7)	0.0202 (4)
N3	1.1964 (2)	−0.4689 (3)	−0.02468 (8)	0.0227 (5)
N5	0.9589 (2)	−0.2699 (3)	−0.13725 (8)	0.0251 (5)
C1	0.9562 (2)	−0.2029 (3)	−0.01344 (8)	0.0194 (5)
C2	1.0468 (2)	−0.2876 (3)	−0.00009 (8)	0.0185 (5)
C3	1.1052 (2)	−0.3694 (3)	−0.03441 (8)	0.0184 (5)
C4	1.0765 (2)	−0.3627 (3)	−0.07904 (9)	0.0207 (5)
C5	0.9890 (2)	−0.2768 (3)	−0.09010 (8)	0.0196 (5)
C6	0.9277 (2)	−0.1972 (3)	−0.05762 (9)	0.0204 (5)
C01	0.8774 (2)	−0.0901 (4)	0.13988 (9)	0.0269 (6)
C02	0.8103 (2)	−0.0329 (4)	0.1726 (1)	0.0288 (6)
C03	0.8360 (2)	−0.0516 (4)	0.21732 (9)	0.0245 (5)
C04	0.9267 (2)	−0.1257 (4)	0.22998 (9)	0.0305 (6)
C05	0.9936 (2)	−0.1825 (4)	0.19714 (9)	0.0278 (6)
C06	0.9701 (2)	−0.1654 (3)	0.15149 (8)	0.0203 (5)
C07	1.0414 (2)	−0.2220 (3)	0.11631 (8)	0.0191 (5)
C08	1.1506 (2)	−0.2541 (4)	0.12767 (9)	0.0248 (6)

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

F—C08	1.414 (3)	N2—C07	1.295 (3)
N1—C2	1.361 (3)	C06—C07	1.480 (3)
N1—N2	1.378 (3)	C07—C08	1.516 (3)
C2—N1—N2	119.3 (2)	N2—C07—C08	122.4 (2)
C07—N2—N1	116.3 (2)	C06—C07—C08	120.3 (2)
N2—C07—C06	117.2 (2)	F—C08—C07	109.3 (2)
O31—N3—C3—C2	172.1 (2)	N1—N2—C07—C06	−179.7 (2)
N3—C3—C2—N1	3.7 (4)	N2—C07—C06—C01	−13.9 (4)
C3—C2—N1—N2	−169.0 (2)	O51—N5—C5—C4	5.4 (4)
C2—N1—N2—C07	−173.9 (2)	F—C08—C07—N2	−58.7 (3)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···F	1.030 (1)	2.02 (3)	2.734 (4)	125 (2)
N1—H11···O32	1.030 (1)	1.86 (3)	2.614 (4)	127 (2)

H atoms were located from Fourier difference maps and refined with a riding model (including free rotation about C—C bonds for methyl groups) and with $U_{\rm iso}$ constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom. The C—H and N—H distances were adjusted to neutron-diffraction values (Allen *et al.*, 1987).

Data collection: *SMART* (Siemens, 1996*a*). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1996*b*). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1178). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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6-Oxo-6-phenyl-6-phospha-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene

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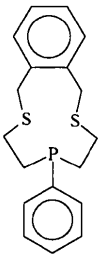
Abstract

The title molecule, 6-phenyl-6-phospha-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene 6-oxide, $C_{18}H_{21}OPS_2$, has an exodentate conformation, with the S and P atoms oriented away from the centre of the macrocyclic cavity.

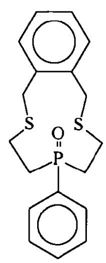
Comment

Tricoordinated P atom-containing macrocycles are of potential use as ligands in catalysis and ion-selective transport (Caminade & Majoral, 1994). It has been reported that the introduction of S donor atoms into these systems could modulate their complexing abilities towards transition metal ions (Kyba, Clubb, Larson, Schueler & Davis, 1985). These mixed macrocycles containing phosphorus and sulfur can be easily transformed into their phosphane or sulfoxide equivalents which are useful in molecular recognition and the complexation of anions (Izatt, Pawlak, Brandshaw & Bruening, 1991).

We have reported recently that $S_2P({=}O)$-containing macrocycles show good selectivity properties as neutral carriers in ion-selective electrodes (Casabó *et al.*, 1996). In this context and in order to clarify the relationships between the molecular conformations and selectivity properties, we report here the synthesis of the S_2P-containing macrocycle 6-phenyl-6-phospha-3,9-dithiabicyclo[9.4.0]pentadeca-1(11),12,14-triene, (1), and its phosphine oxide derivative, (2), together with the crystal structure determination of the latter.



(1)



(2)

The bond lengths and angles in compound (2) (Fig. 1) are normal. A comparison of the torsion angles of (2) with those of the 6-S derivative reveals only minor differences (at most 10°) and thus, the conformations of the two compounds are essentially similar (Lockhart *et al.*, 1992). Also, the intramolecular distances between the heavy atoms are almost the same. The longest S···S distance is 5.795 (1) Å in (2) and 5.772 (1) Å in the 6-S

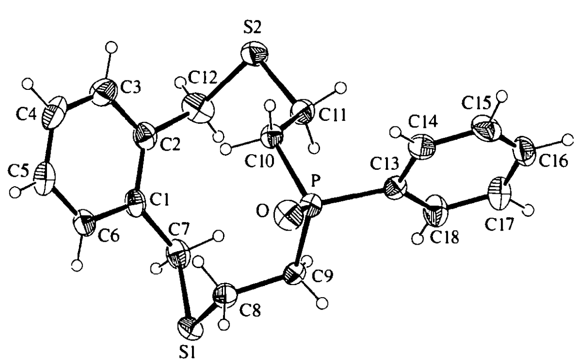


Fig. 1. The molecular structure of the title compound showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.