

## 2-[[3-Fluorophenyl)amino]methylidene]-3-oxobutanenitrile and 5-[[3-fluorophenyl)amino]methylidene]-2,2-dimethyl-1,3-dioxane-4,6-dione: X-ray and DFT studies

Vratislav Langer,<sup>a\*</sup> Pavol Mach,<sup>b</sup> Ľubomír Smrčok,<sup>b</sup> Viktor Milata<sup>c</sup> and Kristína Plevová<sup>c</sup>

<sup>a</sup>Environmental Inorganic Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, SE-412 96 Göteborg, Sweden,

<sup>b</sup>Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic, and <sup>c</sup>Faculty of Food and Chemical Technology, Slovak Technical University, Radlinského 9, SK-812 37 Bratislava, Slovak Republic

Correspondence e-mail: langer@chalmers.se

Received 2 June 2010

Accepted 16 June 2010

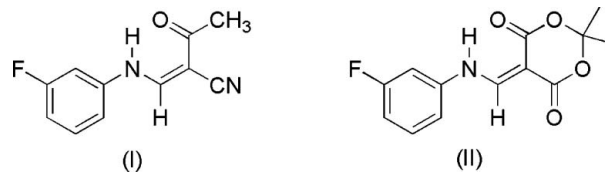
Online 7 July 2010

In the crystal structures of the title compounds,  $C_{11}H_9FN_2O$ , (I), and  $C_{13}H_{12}FNO_4$ , (II), the molecules are joined pairwise *via* different hydrogen bonds and the constituent pairs are crosslinked by weak  $C-H\cdots O$  hydrogen bonds. The basic structural motif in (I), which is partially disordered, comprises pairs of molecules arranged in an antiparallel fashion which enables  $C-H\cdots N\equiv C$  interactions. The pairs of molecules are crosslinked by two weak  $C-H\cdots O$  hydrogen bonds. The constituent pair in (II) is formed by intramolecular bifurcated  $C-H\cdots O/O'$  and combined inter- and intramolecular  $N-H\cdots O$  hydrogen bonds. In both structures, F atoms form weak  $C-F\cdots H-C$  interactions with the H atoms of the two neighbouring methyl groups, the  $H\cdots F$  separations being 2.59/2.80 and 2.63/2.71 Å in (I) and (II), respectively. The bond orders in the molecules, estimated using the natural bond orbitals (NBO) formalism, correlate with the changes in bond lengths. Deviations from the ideal molecular geometry are explained by the concept of non-equivalent hybrid orbitals. The existence of possible conformers of (I) and (II) is analysed by molecular calculations at the B3LYP/6-31+G\*\* level of theory.

### Comment

Heteroaryl aminoethylene compounds substituted with fluorine are not only excellent precursors for the synthesis of biologically active 4-quinolones, but they are also biologically active themselves as they show, for example, photobleaching activity towards cells of *Nicotiana tabacum*, and fungicidal, germicidal or herbicidal properties. The title compounds were

synthesized within the framework of our ongoing study (Langer *et al.*, 2006, 2009; Smrčok *et al.*, 2007) of the structure and properties of potential precursors of fluoroquinolones, knowledge of which has proven essential in reaction pathway considerations and planning.



Perspective drawings of the title molecules are shown in Fig. 1 for (I) and in Fig. 2 for (II). The structure of (I) shows disorder of the benzene ring (rotation by  $180^\circ$ ), with an occupancy of 0.890 (1) for the main component, and the methyl group at C10 has been refined with an occupancy of 50% for two orientations rotated  $60^\circ$  relative to each other. Considering the calculated dipole moments for the molecules of (I) and (II) (4.5 and 2.3 D, respectively), it can be assumed that the main packing force in both structures is electrostatic. The basic building unit in both structures comprises molecules joined pairwise *via* different hydrogen bonds and the constituent pairs are crosslinked to form hydrogen-bonded networks. The fundamental structural motif in the structure of (I) is pairs of molecules arranged in an antiparallel fashion which enables  $C-H\cdots N\equiv C$  interactions (Fig. 3). Every N atom is an acceptor of two hydrogen bonds of two slightly different lengths (Table 1). The pairs of molecules are crosslinked by two weak  $C-H\cdots O$  hydrogen bonds pointing at the O1 atom, which is also involved in the very bent intra-

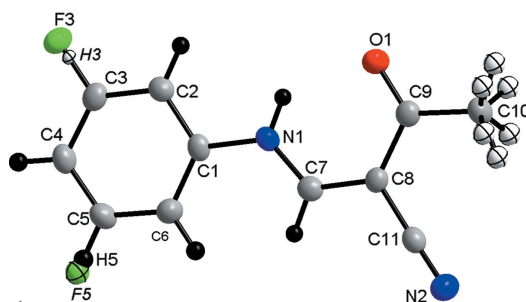


Figure 1

The atom-numbering scheme for (I), with atomic displacement ellipsoids drawn at the 50% probability level. Note that F3 and H5 have 0.890 (1) occupancy, while F5/H3 has an occupancy of 0.110 (1). The occupancies of the H atoms attached to C10 were fixed to 50%.

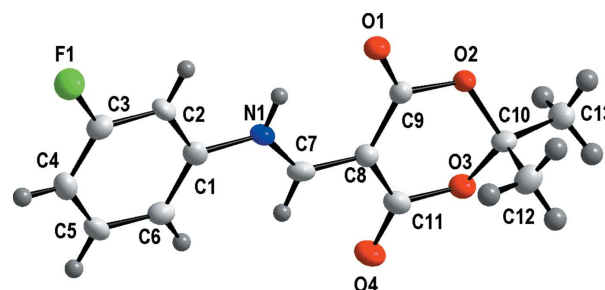
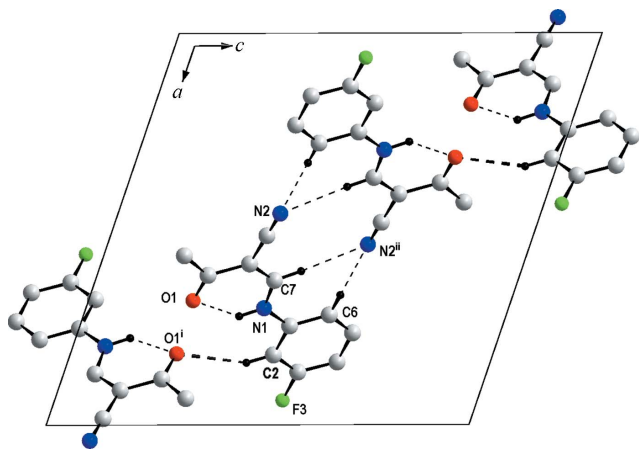


Figure 2

The atom-numbering scheme for (II), with atomic displacement ellipsoids drawn at the 50% probability level.

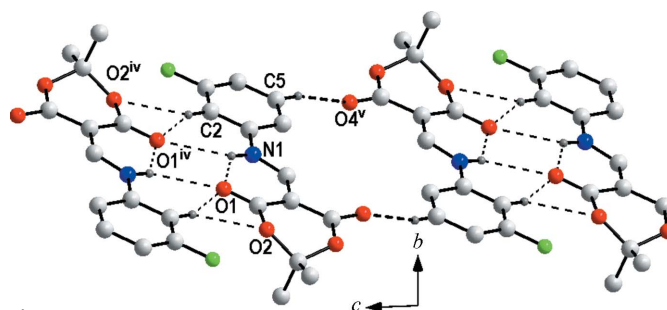
**Figure 3**

Pairs of molecules in the structure of (I) are linked by  $C2-H2 \cdots O1^i$  hydrogen bonds. The  $C10-H10C \cdots O1^{iii}$  hydrogen bond is not shown for the sake of clarity and H atoms not involved in the hydrogen-bonding scheme have been omitted. Symmetry codes are as in Table 1. Note that only the main component present in the structure of (I) is shown.

molecular  $N1-H1 \cdots O1$  hydrogen bond (Table 1). This arrangement can be described as a ribbon of molecules running approximately parallel to [101]. The pair of molecules in the structure of (II) is formed by the intermolecular bifurcated  $C2-H2 \cdots O1^{iv}/O2^{iv}$  and the combined inter- and intramolecular  $N1-H1 \cdots O1/O1^{iv}$  hydrogen bonds (Fig. 4). These basic pairs of molecules form ribbons through the  $C5-H5 \cdots O4^v$  hydrogen bond. Although the arrangement of neighboring ribbons is dictated mainly by electrostatic forces, they are also connected through weak  $C12-H12B \cdots O^{vi}$  interactions.

In both structures, the F atoms appear in such positions that they are able to form weak  $C-F \cdots H-C$  interactions (Howard *et al.*, 1996; Dunitz & Taylor, 1997) with the H atoms of the two neighbouring methyl groups, *i.e.* two H10A atoms in the structure of (I), and the H12C and H13C atoms in the structure of (II). The  $H \cdots F$  separations [2.59/2.80 Å in (I) and 2.63/2.71 Å (II)] are well within the limits found for this type of nonbonded contact (Shimoni & Glusker, 1994).

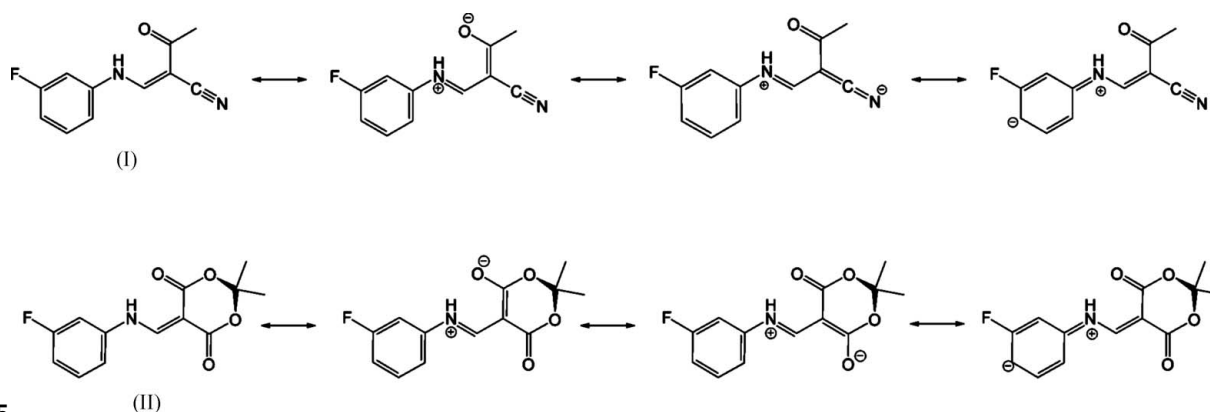
NBO (natural bond orbitals) analysis (Foster & Weinhold, 1980) carried out for the isolated molecules reveals a general

**Figure 4**

Hydrogen bonds within the constituent pair of molecules and the hydrogen bonds linking the pairs into sheets in the structure of (II). H atoms not involved in the hydrogen-bonding scheme have been omitted. Symmetry codes are as in Table 1.

delocalization pattern, which can be characterized (i) by delocalization of the lone pair of the N atom into the  $C=C$  antibonding orbital, resulting in the lowering of the bond order of this bond and in the increase of the bond order of the  $N1-C7$  bond, and (ii) by shifting of the electrons from the  $C=O$  double bonds towards the  $p_\pi$  orbital of the O atoms, resulting in the relatively large partial negative charge on O1 [NBO charges are  $-0.621$  |e| in (I) and  $-0.622$  |e| in (II)] and also in a decrease of its bond order (Tables 2 and 3). This shift is further enhanced by formation of an intramolecular  $O1 \cdots H1-N1$  hydrogen bond. All these changes are qualitatively described by a superposition of resonance structures, depicted in Fig. 5. The most obvious geometric consequences of such electron delocalizations are shortening of the formally single  $N1-C7$  bond and also lengthening of the formally double  $C7=C8$  bond, reflected in the decrease of the bond order (Tables 2 and 3). Another consequence of electron redistribution is structural rigidity of the  $N1-C7-C8-(C9-O1)(C11-N2)$  moiety in (I), which is further enhanced by the formation of an intramolecular  $N1-H1 \cdots O1$  hydrogen bond.

An additional characteristic feature of the  $C1-N1-C7-C8$  fragment is increased values of the skeletal angles, namely  $C1-N1-C7$  [ $125.15$  ( $14^\circ$ ) in (I) and  $125.6$  ( $2^\circ$ ) in (II)] and  $N1-C7-C8$  [ $124.79$  ( $15^\circ$ ) in (I) and  $127.4$  ( $3^\circ$ ) in (II)] relative to the expected ideal value of  $120^\circ$ . The main reason is the increased  $s$  content in the hybrid orbitals on the N1 and C7 atoms as a consequence of the shortening of the  $N1-C7$  bond.

**Figure 5**

Possible resonance structures of the title compounds. All principal geometry features are compatible with a superposition of these resonance structures.

This increase in *s* character in turn brings about an increase in the *p* character in two other formally *sp*<sup>2</sup> hybrids and thus lowers the angle between them (Bent, 1961; Langer *et al.*, 2009).

The benzene ring connected to the aminomethylene group is, in both structures, only slightly rotated from the plane of the N1—C7—C8—C9—C11 atoms, the torsion angle C7—N1—C1—C6 being  $-1.6(2)^\circ$  in (I) and  $-2.7(4)^\circ$  in (II). Full optimizations of the molecular geometry in a vacuum, however, give remarkably larger torsion angles, *viz.*  $13^\circ$  in (I) and  $11^\circ$  in (II), but a closer inspection of the torsion potential around the C1—N1 bond reveals that it is, in both cases, very flat. Its flatness can be documented by the fact that the strictly planar structure of (I) has a total energy of only  $0.06 \text{ kJ mol}^{-1}$  higher than the minimum and the calculated harmonic torsion frequency is only  $14 \text{ cm}^{-1}$ . Such flatness of the torsion potentials is a compromise between the two competing interactions: on the one hand, repulsion of the H1—H2 and the H6—H7 H atoms tending to rotate the ring from the planar position and, on the other hand, delocalization of the lone pair of the N atom into the phenyl ring, stabilizing the planar arrangement.

An interesting feature of this torsion potential is the low barrier for  $180^\circ$  rotation of the substituted benzene ring, leading to conformations (Ia) and (IIa). According to the molecular calculation in a vacuum, these conformations are even slightly more stable than the molecules of (I) and (II), *i.e.* by  $0.6$  and  $0.4 \text{ kJ mol}^{-1}$ , respectively. In (I), conformation (Ia) is present as a minor component with an occupancy of  $0.110(1)$ . The rotation barriers separating these conformers are also rather small, *i.e.*  $14.7$  and  $15.0 \text{ kJ mol}^{-1}$ , respectively, and are further reduced by a polar medium. For instance, our polarizable continuum model (PCM; Miertuš *et al.*, 1981; Foresman *et al.*, 1996) calculation revealed that in water the barrier further reduces to  $10.2$  and  $11.7 \text{ kJ mol}^{-1}$ , respectively. The preference of the conformations of (I) and (II) over (Ia) and (IIa) in the real structures is thus apparently a result of the packing forces in the crystals.

## Experimental

The title compounds could be easily prepared by nucleophilic vinylic substitution of equimolar amounts of 2-ethoxymethylene-3-oxobutanenitrile or 5-ethoxymethylene-2,2-dimethyl-1,3-dioxane-4,6-dione with 3-fluoroaniline in boiling ethanol (Leya *et al.*, 1999). Both compounds were recrystallized from methanol (25 ml) in an Erlenmeyer flask by slow evaporation at room temperature over a period of a week. The melting points were  $461\text{--}463$  and  $434\text{--}436 \text{ K}$  for (I) and (II), respectively.

### Compound (I)

#### Crystal data

$\text{C}_{11}\text{H}_9\text{FN}_2\text{O}$	$V = 942.8(3) \text{ \AA}^3$
$M_r = 204.20$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 13.907(2) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$b = 5.0357(8) \text{ \AA}$	$T = 153 \text{ K}$
$c = 14.233(2) \text{ \AA}$	$0.49 \times 0.12 \times 0.08 \text{ mm}$
$\beta = 108.946(4)^\circ$	

#### Data collection

Siemens SMART CCD area-detector diffractometer	13411 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2554 independent reflections
$T_{\min} = 0.949$ , $T_{\max} = 0.991$	1650 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.072$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$	2 restraints
$wR(F^2) = 0.128$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
2554 reflections	$\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$
148 parameters	

### Compound (II)

#### Crystal data

$\text{C}_{13}\text{H}_{12}\text{FNO}_4$	$\gamma = 71.931(4)^\circ$
$M_r = 265.24$	$V = 600.8(2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 6.3000(12) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.4753(18) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$c = 10.765(2) \text{ \AA}$	$T = 153 \text{ K}$
$\alpha = 88.947(5)^\circ$	$0.38 \times 0.11 \times 0.06 \text{ mm}$
$\beta = 79.810(4)^\circ$	

#### Data collection

Siemens SMART CCD area-detector diffractometer	6091 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2132 independent reflections
$T_{\min} = 0.956$ , $T_{\max} = 0.993$	1244 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.071$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$	174 parameters
$wR(F^2) = 0.147$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
2132 reflections	$\Delta\rho_{\text{min}} = -0.25 \text{ e \AA}^{-3}$

For (I), a rotational disorder of the benzene ring was resolved on the F3/F5 positions with the C—F distance restrained to a common value (refined) having an s.u. of  $0.02 \text{ \AA}$ . The positions of the aromatic H atoms were constrained to ideal geometry and refined using an appropriate riding model, with N—H =  $0.88 \text{ \AA}$  and C—H =  $0.95 \text{ \AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ . For methyl groups [ $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  and C—H =  $0.98 \text{ \AA}$ ], C—C—H angles ( $109.5^\circ$ ) were kept

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
(I)				
N1—H1 $\cdots$ O1	0.88	2.05	2.765 (17)	131
C7—H7 $\cdots$ N2 <sup>ii</sup>	0.95	2.46	3.395 (2)	167
C6—H6 $\cdots$ N2 <sup>ii</sup>	0.95	2.67	3.618 (2)	173
C2—H2 $\cdots$ O1 <sup>i</sup>	0.95	2.41	3.300 (2)	156
C10—H10C $\cdots$ O1 <sup>iii</sup>	0.98	2.58	3.554 (2)	172
(II)				
N1—H1 $\cdots$ O1	0.86	2.15	2.775 (3)	129
N1—H1 $\cdots$ O1 <sup>iv</sup>	0.86	2.53	3.334 (3)	156
C2—H2 $\cdots$ O1 <sup>iv</sup>	0.93	2.44	3.296 (4)	153
C2—H2 $\cdots$ O2 <sup>iv</sup>	0.93	2.59	3.449 (4)	154
C5—H5 $\cdots$ O4 <sup>v</sup>	0.93	2.46	3.372 (3)	165
C12—H12B $\cdots$ O3 <sup>vi</sup>	0.96	2.67	3.584 (4)	160

Symmetry codes: (i)  $-x + \frac{3}{2}$ ,  $y + \frac{1}{2}$ ,  $-z + \frac{1}{2}$ ; (ii)  $-x + 1$ ,  $-y + 1$ ,  $-z + 1$ ; (iii)  $x$ ,  $y - 1$ ,  $z$ ; (iv)  $-x + 2$ ,  $-y + 2$ ,  $-z + 2$ ; (v)  $-x + 1$ ,  $-y + 2$ ,  $-z + 1$ ; (vi)  $-x + 3$ ,  $-y + 1$ ,  $-z + 1$ .

**Table 2**

Selected bond distances (Å) and Wiberg bond orders (WBO; Wiberg, 1968) in (I).

Note that the N1–H1 and C7–H7 bond distances (in bold) are taken from the molecular calculations rather than from the structure refinement.

	Bond distance	WBO
F3–C3	1.3508 (19)	0.893
O1–C9	1.2361 (18)	1.654
N1–C7	1.3234 (19)	1.307
N1–C1	1.4240 (19)	1.041
N1–H1	<b>1.028</b>	0.694
N2–C11	1.151 (2)	2.842
C7–C8	1.386 (2)	1.460
C7–H7	<b>1.085</b>	0.904
C8–C11	1.429 (2)	1.108
C8–C9	1.455 (2)	1.107
C9–C10	1.498 (2)	1.023

**Table 3**

Selected bond distances (Å) and Wiberg bond orders (WBO) in (II).

Note that the N1–H1 bond distance (in bold) is taken from the molecular calculations rather than from the structure refinement.

	Bond distance	WBO
F1–C3	1.361 (3)	0.888
O1–C9	1.213 (3)	1.660
O4–C11	1.216 (3)	1.696
N1–C7	1.315 (3)	1.333
N1–C1	1.422 (3)	1.033
N1–H1	<b>1.028</b>	0.707
C7–C8	1.377 (3)	1.433
C8–C11	1.442 (4)	1.078
C8–C9	1.435 (4)	1.101

fixed, while the torsion angle was allowed to refine with the starting positions based on the circular Fourier synthesis averaged using the local threefold axis. In (I), the methyl group is also disordered and was refined with two components with 50% occupancy, rotated 60° relative to each other. Molecular calculations were carried out at the B3LYP/6–31+G\*\* level of theory using *GAUSSIAN98* (Frisch *et al.*, 1998). NBO (Foster & Weinhold, 1980) calculations were carried out using the *NBO* (Version 3.1; Glendening *et al.*, 1993) program included in the *GAUSSIAN* package.

For both compounds, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*, *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *PLATON* (Spek, 2009).

Financial support of this research by the Slovak Grant Agency (grants No. VEGA 1/0225/08 and 2/0150/09) and the Science and Technology Assistance Agency (APVV-0055/07) is acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3374). Services for accessing these data are described at the back of the journal.

## References

- Bent, H. A. (1961). *Chem. Rev.* **61**, 275–311.
- Brandenburg, K. (2009). *DIAMOND*. Version 3.2c. Crystal Impact GbR, Bonn, Germany.
- Bruker (2003). *SMART* (Version 5.63) and *SAINT* (Version 6.45). Bruker AXS Inc., Madison, Wisconsin, USA.
- Dunitz, J. D. & Taylor, R. (1997). *Chem. Eur. J.* **3**, 89–98.
- Foresman, J. B., Keith, T. A., Wiberg, K. B., Snoonian, J. & Frisch, M. J. (1996). *J. Phys. Chem.* **100**, 16098–16104.
- Foster, J. P. & Weinhold, F. (1980). *J. Am. Chem. Soc.* **102**, 7211–7218.
- Frisch, M. J., *et al.* (1998). *GAUSSIAN98*. Revision A.7. Gaussian Inc., Pittsburgh, PA, USA.
- Glendening, E. D., Reed, A. D., Carpenter, J. E. & Weinhold, F. (1993). *NBO*. Version 3.1. Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin, USA.
- Howard, J. A. K., Hoy, V. J., O'Hagan, D. & Smith, G. T. (1996). *Tetrahedron*, **32**, 12613–12622.
- Langer, V., Mach, P., Smrčok, Ľ. & Milata, V. (2009). *Acta Cryst.* **C65**, o183–o185.
- Langer, V., Scholtzová, E., Mach, P., Solčan, T. & Smrčok, Ľ. (2006). *Acta Cryst.* **C62**, o544–o546.
- Leya, E., Montreal, E. & Hernández, A. (1999). *J. Fluorine Chem.* **94**, 7–10.
- Miertuš, S., Scrocco, E. & Tomasi, J. (1981). *Chem. Phys.* **55**, 117–129.
- Sheldrick, G. M. (2003). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shimoni, L. & Glusker, J. P. (1994). *Struct. Chem.* **5**, 383–397.
- Smrčok, Ľ., Jorík, V., Scholtzová, E. & Milata, V. (2007). *Acta Cryst.* **B63**, 477–484.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Wiberg, K. B. (1968). *Tetrahedron*, **24**, 1083–1096.