Acta Cryst. (1996). C**52**, 3127–3128

Ethyl 2-Fluoro-3-oxo-2-(*p*-toluoyl)-3-(*p*-tolyl)propanoate, $C_{20}H_{19}O_4F$

MOON-JIB KIM,[a] JOON-CHEOL SHIN,[a] JAE-HYUK LEE,[a] DAE-YONG RHIE,[b] DAE-YOUNG KIM,[b] IL-HWAN SUH,[c] SUNG-SAN CHOI,[c] WILLIAM P. JENSEN[d] AND DAVID E. LEWIS[d]

[a]*Department of Physics, Soonchunhyang University, POB 97, Asan, Chungnam, Seoul 336-600, Korea,* [b]*Department of Chemistry, Soonchunhyang University, POB 97, Asan, Chungnam, Seoul 336-600, Korea,* [c]*Department of Physics, Chungnam National University, Taejon 605-764, Korea, and* [d]*Department of Chemistry, South Dakota State University, Bookings, SD 57007, USA. E-mail: moonkim@asan.sch.ac.kr*

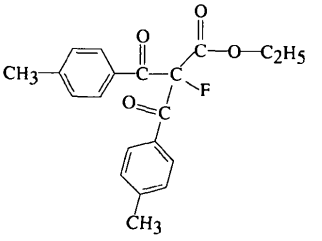
(*Received 21 November 1995; accepted 12 September 1996*)

Abstract

The structure of the title compound was determined by single-crystal X-ray methods. The carbonyl C=O bond distances are approximately 1.20 Å and van der Waals intermolecular contacts are normal. The bond distances are normal for all bonds in the molecule except for those involving C9: the C—F bond distance is 1.382 (6) Å and the C—C bond distances are 1.545 (8), 1.531 (8) and 1.529 (9) Å, all approximately 0.05 Å longer than normal for these bonds.

Comment

As part of our research programs, we have synthesized the title compound, (I), from the reaction of α-fluoro phosphonacetate with *p*-toluoyl chloride in the presence of magnesium chloride (Kim, Rhie & Oh, 1996). The X-ray crystallographic study of this compound has been undertaken to confirm its structure.



(I)

An *ORTEP* (Johnson, 1965) drawing of the molecule with the atom numbering is presented in Fig. 1. The bond distances are normal for all bonds in the molecule except for those involving C9, the α-C atom of the propanoic acid moiety; the C—F bond distance is 1.382 (6) Å, and the C—C lengths are all approximately 0.05 Å longer than normal for these bonds. The molecule adopts a conformation in which the three carbonyl-O atoms and the F atom are as far apart as possible, located at the vertices of a distorted tetrahedron. The atoms of the *p*-methylbenzoyl groups and ester group are each planar; O1, C1–C9 are coplanar within 0.116 (6) Å, O2, C9–C17 within 0.218 (6) Å and O3, O4, C9 and C18 within 0.002 (3) Å.

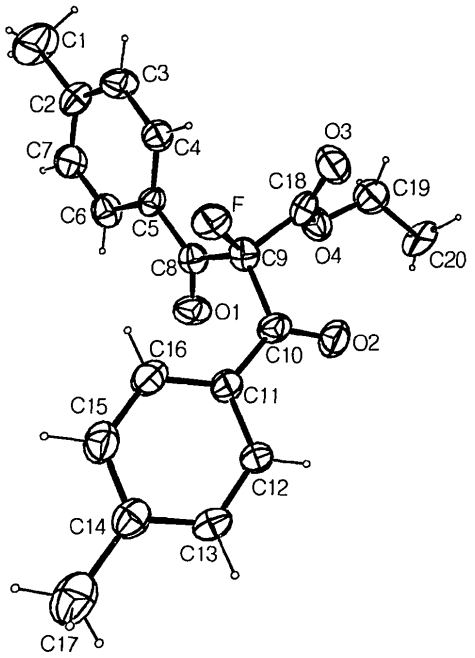


Fig. 1. *ORTEP* (Johnson, 1965) drawing and numbering scheme. The ellipsoids are drawn at the 50% probability level and H atoms are represented as spheres of arbitrary radii.

In this conformation, the C_s symmetry of the molecule is disrupted with the two *p*-toluoyl groups being superimposable on each other by a rotation of 120° about the C—F bond. The torsion angles F—C9—C8—O1, F—C9—C10—O2, F—C9—C18—O3 and F—C9—C18—O4 are −126.2 (8), −134.2 (8), 18.5 (7) and −161.2 (7)°, respectively, indicating that all three carbonyl groups are skewed from parallel by 19° or more. The unusually long bond distance involving C9 and the dihedral angles involving the three carbonyl groups bonded to C9 may be rationalized in terms of electrostatic repulsion between highly electronegative elements: the bond distances are expanded to reduce the repulsion between the O and F atoms, and the torsion angles are skewed to avoid the repulsive forces introduced by having the carbon–oxygen dipoles parallel, as would be required by C_s symmetry.

Experimental

Compound (I) was obtained from the reaction of α-fluoro phosphonacetate with *p*-toluoyl chloride in the presence of magnesium chloride (Kim, Rhie & Oh, 1996).

Crystal data

$C_{20}H_{19}O_4F$
M_r = 342.35
Monoclinic
$P2_1/n$
a = 14.790 (2) Å
b = 8.5620 (12) Å
c = 14.380 (3) Å
β = 98.8530 (13)°
V = 1799.3 (5) Å^3
Z = 4
D_x = 1.264 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 15.5–20.2°
μ = 0.094 mm^{-1}
T = 298 K
Needle
0.23 × 0.23 × 0.20 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2533 measured reflections
1815 independent reflections
934 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.023
θ_{max} = 23.97°
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 9$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 100 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0675
$wR(F^2)$ = 0.1321
S = 0.984
1815 reflections
254 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.246
$\Delta\rho_{max}$ = 0.171 e Å^{-3}
$\Delta\rho_{min}$ = −0.219 e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0143 (15)
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)*

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

	x	y	z	U_{eq}
C1	0.6135 (7)	0.8628 (13)	0.2106 (7)	0.094 (3)
C2	0.6170 (5)	0.7325 (9)	0.1422 (6)	0.063 (2)
C3	0.5850 (4)	0.7553 (8)	0.0482 (6)	0.062 (2)
C4	0.5927 (4)	0.6383 (8)	−0.0156 (5)	0.055 (2)
C5	0.6316 (4)	0.4948 (9)	0.0118 (5)	0.052 (2)
C6	0.6625 (4)	0.4733 (9)	0.1068 (5)	0.068 (2)
C7	0.6544 (5)	0.5913 (10)	0.1699 (5)	0.069 (2)
C8	0.6399 (4)	0.3784 (8)	−0.0624 (6)	0.060 (2)
O1	0.6117 (3)	0.4035 (5)	−0.1438 (3)	0.075 (2)
C9	0.6855 (4)	0.2189 (8)	−0.0354 (5)	0.052 (2)
C18	0.6681 (5)	0.1130 (10)	−0.1219 (5)	0.063 (2)
O3	0.6083 (4)	0.0172 (6)	−0.1339 (4)	0.089 (2)
O4	0.7288 (3)	0.1450 (5)	−0.1778 (3)	0.074 (2)
C19	0.7147 (6)	0.0725 (9)	−0.2701 (6)	0.099 (3)
C20	0.6780 (17)	0.1754 (18)	−0.3417 (10)	0.192 (12)
C10	0.7883 (4)	0.2354 (8)	−0.0014 (4)	0.051 (2)
O2	0.8234 (3)	0.3604 (6)	−0.0156 (3)	0.076 (2)
C11	0.8414 (5)	0.1038 (8)	0.0446 (4)	0.048 (2)
C12	0.8056 (5)	−0.0456 (8)	0.0512 (4)	0.061 (2)
C13	0.8587 (5)	−0.1662 (8)	0.0922 (5)	0.071 (2)
C14	0.9486 (5)	−0.1398 (10)	0.1302 (5)	0.071 (2)
C17	1.0080 (10)	−0.2742 (18)	0.1773 (10)	0.130 (5)
C15	0.9835 (5)	0.0077 (11)	0.1263 (5)	0.077 (2)
C16	0.9315 (5)	0.1260 (9)	0.0843 (4)	0.066 (2)
F	0.6426 (2)	0.1512 (4)	0.0334 (3)	0.0679 (12)

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

C1—C2	1.493 (11)	C18—O3	1.200 (7)
C2—C7	1.364 (8)	C18—O4	1.322 (8)
C5—C8	1.479 (8)	O4—C19	1.451 (7)
C8—O1	1.201 (7)	C19—C20	1.400 (15)
C8—C9	1.545 (8)	C10—O2	1.220 (6)
C9—F	1.382 (6)	C10—C11	1.471 (8)
C9—C18	1.529 (9)	C14—C17	1.540 (13)
C9—C10	1.531 (8)		
C6—C5—C8	124.8 (7)	O3—C18—O4	127.5 (8)
C4—C5—C8	117.9 (7)	O3—C18—C9	123.4 (7)
O1—C8—C5	121.9 (7)	O4—C18—C9	109.1 (7)
O1—C8—C9	118.4 (7)	C18—O4—C19	116.9 (6)
C5—C8—C9	119.8 (6)	C20—C19—O4	112.8 (8)
F—C9—C18	107.2 (6)	O2—C10—C11	122.4 (6)
F—C9—C10	110.6 (5)	O2—C10—C9	117.0 (6)
C18—C9—C10	110.4 (6)	C11—C10—C9	120.6 (6)
F—C9—C8	108.6 (5)	C16—C11—C10	119.7 (7)
C18—C9—C8	107.9 (6)	C12—C11—C10	123.5 (6)
C10—C9—C8	111.9 (6)		

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Refinement was carried out by least-squares methods using *SHELXL*93 (Sheldrick, 1993). Non-H atoms were refined anisotropically. H atoms were added in calculated positions where possible. For the three methyl groups, C1, C17 and C20, a single H atom was located from a difference map and the remaining H atoms were added in calculated positions. An isotropic thermal parameter for all H atoms was included in the refinement but H-atom positional parameters were not refined. Geometric calculations on the crystal and molecular structure were performed using *GEOM* (Shin, 1978). All computations were performed using SUN SPARC station IPC and PC486 computers.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Kim, D. Y., Rhie, D. Y. & Oh, D. Y. (1996). *Tetrahedron Lett.* **37**, 653–654.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Shin, W. (1978). *GEOM*. Seoul National University, Korea.