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Unexpected crystallization of 1,3-bis(4-fluorophenyl)propan-2-one in paratone oil

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Unexpected crystallization of 1,3-bis(4-fluorophenyl)propan-2-one in paratone oil

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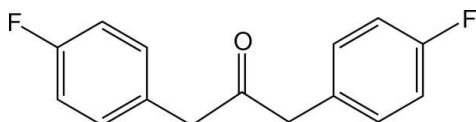
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.034; wR factor = 0.073; data-to-parameter ratio = 10.1.

The title compound, $\text{C}_{15}\text{H}_{12}\text{F}_2\text{O}$, crystallizes in paratone oil as a room-temperature decomposition product of the crystalline air- and moisture-sensitive lithium enolate of 1,3-di(*p*-fluorophenyl)acetone diethyl ether solvate. Such spontaneous crystallization in paratone oil is rare, yet in this case it yielded X-ray quality crystals. The title compound can be prepared directly by a modified procedure of Resendiz & Garibay [*Org. Lett.* (2005), **7**, 371–374]. The molecular features are typical: the endocyclic angles at the electron-withdrawing F substituent average 123.0 (2)°, while the endocyclic angles at the methylene C atom average 118.3 (3)°. These findings are in excellent agreement with the values of 122.3 and 118.5 ° computed for the theoretically (DFT, density functional theory) optimized geometry of the title compound.

Related literature

Resendiz & Garibay (2005) report a direct synthesis of the title compound. Kolonko *et al.* (2007) report the synthesis and characterization of a Li salt that, upon decomposition, yields the title compound. For details of the software used for the computational calculations, see Frisch *et al.* (2004).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{12}\text{F}_2\text{O}$	$V = 1206.9$ (2) Å ³
$M_r = 246.25$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 4.5204$ (5) Å	$\mu = 0.11$ mm ⁻¹
$b = 11.3606$ (14) Å	$T = 100$ (2) K
$c = 23.501$ (3) Å	$0.50 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	15238 measured reflections
Absorption correction: multi-scan SADABS (Bruker, 2007)	1643 independent reflections
$T_{\min} = 0.950$, $T_{\max} = 0.990$	1210 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.100$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	163 parameters
$wR(F^2) = 0.073$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{\text{max}} = 0.19$ e Å ⁻³
1643 reflections	$\Delta\rho_{\text{min}} = -0.17$ e Å ⁻³

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2007); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *publCIF* (Westrip, 2007) and *modiCIFer* (Guzei, 1995).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2068).

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supplementary materials

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Unexpected crystallization of 1,3-bis(4-fluorophenyl)propan-2-one in paratone oil

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Comment

This paper documents an unusual fact of spontaneous crystallization of the title compound in paratone oil. Crystals of the air- and moisture-sensitive lithium enolate of 1,3-di(*p*-fluorophenyl)acetone ether solvate (Fig.1) were examined under ambient conditions in paratone oil to select a crystal suitable for an X-ray single-crystal diffraction experiment (Kolonko *et al.*, 2007). During the 22-hour data acquisition on the lithium enolate the glass slide with the crystals was left under air. By the next day the crystals decomposed to yield crystals of the title compound propagating from them as thin needles (Fig. 2). Such spontaneous crystallization in paratone oil is rare, yet in this case it yielded X-ray quality crystals. The title compound, Fig. 3, can be prepared directly by a modified procedure of Resendiz & Garibay (2005). Its molecular features are typical: the endocyclic angles at the electron-withdrawing F substituent average 123.0 (2)° while the endocyclic angles at the methylene carbon atom average 118.3 (3)°. These findings are in excellent agreement with the values of 122.3 and 118.5° computed for the theoretically (DFT) optimized geometry of (I) at the b3lyp/6–31+G* level of theory (Frisch *et al.*, 2004).

Experimental

1,3-Di(*p*-fluorophenyl)acetone (prepared using a modified procedure from Resendiz & Garibay (2005)): 4-Fluorophenylacetic acid (4.14 g, 26.8 mmol), 4-(dimethylamino)pyridine (3.53 g, 28.8 mmol), *N*-ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI·HCl) (5.00 g, 26.0 mmol) and 80 ml of dichloromethane were added to a 250 ml round bottom flask. The solution was stirred for four days at room temperature, after which 100 ml of 10% HCl solution was added. The organic layer was separated, washed with 10% HCl twice, saturated NaHCO₃ once, dried over MgSO₄ and the solvent was removed by vacuum. The resulting solid was recrystallized from aqueous ethanol to yield 2.35 g (73.5%) of the title compound. Melting Point 335–337 K. ¹H NMR (300 MHz, CDCl₃), δ 3.69 (s, 4H), 6.99 (m, 4H), 7.09 (m, 4H). ¹³C NMR (75.4 MHz, CDCl₃), δ 48.4 (s), 115.8 (d, J=21.5 Hz), 129.7 (d, J=3.2 Hz), 131.2 (d, J=7.8 Hz), 162.2 (d, J=246.6 Hz), 205.3 (s). ¹⁹F NMR (282 MHz, CDCl₃) δ –116 (tt, J=5.5, 8.8 Hz). HRMS (EI) (m/z): calcd. for C₁₅H₁₂OF₂ (M⁺) 246.0856; found 246.0860.

Lithium enolate of 1,3-di(*p*-fluorophenyl)acetone ether solvate: 1,3-di(*p*-fluorophenyl)acetone (0.29 g, 1.19 mmol) was placed in a 15 ml conical vial, dissolved in 1 ml of diethylether and cooled to 273 K. Diisopropylamine (0.2 ml, 1.41 mmol) and 2 ml of diethyl ether were placed in to a flame dried and argon purged 5 ml round bottom flask and cooled to 195 K. *n*BuLi (0.53 ml, 1.32 mmol) was added and the solution was warmed to 273 K for 5 minutes. The freshly prepared lithium diisopropylamide (LDA) was added to the conical vial *via* cannula at 273 K and the flask was shaken to mix the reactants. The solution was allowed to warm to room temperature for 30 minutes and then cooled to 253 K. Upon sitting overnight crystals formed.

The crystal of the title compound chosen for the X-ray structural characterization was selected from the paratone oil 24 h after crystals of the lithium enolate were immersed in it. Thus, the title compound is a decomposition product of the lithium enolate under ambient conditions in paratone oil.

supplementary materials

Refinement

All H-atoms were placed in idealized locations and refined as riding with appropriate thermal displacement coefficients $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 times $U_{\text{eq}}(\text{bearing atom})$.

Figures

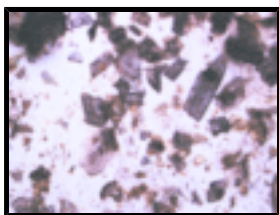


Fig. 1. Crystals of the lithium enolate of 1,3-di(*p*-fluorophenyl)acetone ether solvate freshly isolated from mother liquor.

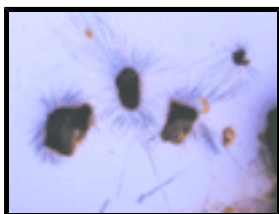


Fig. 2. Crystals of the title compound are the clear needles growing from the decomposed crystals of the lithium enolate.

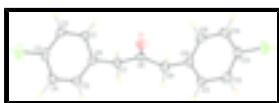


Fig. 3. Molecular drawing with 50% probability ellipsoids.

1,3-bis(4-fluorophenyl)propan-2-one

Crystal data

$\text{C}_{15}\text{H}_{12}\text{F}_2\text{O}$

$M_r = 246.25$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 4.5204$ (5) Å

$b = 11.3606$ (14) Å

$c = 23.501$ (3) Å

$V = 1206.9$ (2) Å³

$Z = 4$

$F_{000} = 512$

$D_x = 1.355$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 2606 reflections

$\theta = 2.5$ – 22.9°

$\mu = 0.11$ mm⁻¹

$T = 100$ (2) K

Needle, colourless

$0.50 \times 0.10 \times 0.10$ mm

Data collection

Bruker CCD-1000 area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100$ (2) K

1643 independent reflections

1210 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.100$

$\theta_{\text{max}} = 27.5^\circ$

0.30° ω and 0.4° φ scans $\theta_{\min} = 1.7^\circ$
 Absorption correction: multi-scan $h = -5 \rightarrow 5$
 SADABS (Bruker, 2007)
 $T_{\min} = 0.950, T_{\max} = 0.990$ $k = -14 \rightarrow 14$
 15238 measured reflections $l = -30 \rightarrow 30$

Refinement

Refinement on F^2 H-atom parameters constrained
 Least-squares matrix: full $w = 1/[\sigma^2(F_o^2) + (0.0301P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $R[F^2 > 2\sigma(F^2)] = 0.034$ $(\Delta/\sigma)_{\max} = 0.001$
 $wR(F^2) = 0.073$ $\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$
 $S = 1.00$ $\Delta\rho_{\min} = -0.17 \text{ e } \text{\AA}^{-3}$
 1643 reflections Extinction correction: none
 163 parameters
 Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
F1	-0.1730 (3)	0.96475 (11)	0.68798 (5)	0.0339 (4)
F2	0.0973 (4)	0.40877 (12)	1.10857 (5)	0.0467 (5)
O1	0.2673 (4)	0.71247 (12)	0.89696 (6)	0.0238 (4)
C1	0.3178 (5)	0.88445 (17)	0.80243 (8)	0.0206 (5)
H1	0.3875	0.9158	0.8374	0.025*
C2	0.1182 (5)	0.94850 (18)	0.77045 (9)	0.0224 (5)
H2	0.0472	1.0225	0.7834	0.027*
C3	0.0252 (5)	0.90235 (19)	0.71955 (9)	0.0239 (5)
C4	0.1244 (5)	0.79668 (18)	0.69894 (9)	0.0243 (6)
H4	0.0597	0.7677	0.6631	0.029*
C5	0.3225 (5)	0.73345 (18)	0.73208 (8)	0.0216 (5)

supplementary materials

H5	0.3939	0.6599	0.7186	0.026*
C6	0.4188 (5)	0.77487 (18)	0.78442 (8)	0.0189 (5)
C7	0.6201 (5)	0.70229 (18)	0.82110 (8)	0.0214 (5)
H7A	0.8014	0.7483	0.8291	0.026*
H7B	0.6796	0.6311	0.7997	0.026*
C8	0.4829 (5)	0.66449 (19)	0.87723 (9)	0.0195 (5)
C9	0.6399 (5)	0.56467 (18)	0.90711 (8)	0.0251 (6)
H9A	0.6545	0.4973	0.8805	0.030*
H9B	0.8438	0.5902	0.9163	0.030*
C10	0.4930 (5)	0.52336 (18)	0.96098 (8)	0.0206 (5)
C11	0.3181 (5)	0.42347 (18)	0.96131 (9)	0.0236 (5)
H11	0.2909	0.3806	0.9270	0.028*
C12	0.1816 (6)	0.38470 (19)	1.01073 (9)	0.0288 (6)
H12	0.0600	0.3165	1.0108	0.035*
C13	0.2279 (6)	0.4481 (2)	1.05949 (9)	0.0293 (6)
C14	0.3959 (6)	0.54752 (19)	1.06119 (9)	0.0306 (6)
H14	0.4210	0.5898	1.0957	0.037*
C15	0.5291 (5)	0.58556 (19)	1.01147 (9)	0.0264 (6)
H15	0.6465	0.6549	1.0118	0.032*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0310 (9)	0.0389 (7)	0.0318 (7)	0.0070 (7)	-0.0021 (7)	0.0133 (6)
F2	0.0688 (12)	0.0433 (9)	0.0280 (8)	0.0117 (9)	0.0180 (8)	0.0118 (6)
O1	0.0235 (10)	0.0256 (8)	0.0222 (8)	0.0052 (8)	0.0033 (7)	0.0004 (6)
C1	0.0229 (14)	0.0192 (10)	0.0198 (11)	-0.0047 (10)	0.0013 (10)	-0.0009 (9)
C2	0.0229 (14)	0.0176 (11)	0.0266 (12)	-0.0004 (10)	0.0067 (10)	0.0032 (9)
C3	0.0186 (13)	0.0284 (12)	0.0246 (12)	0.0000 (11)	0.0003 (10)	0.0117 (10)
C4	0.0263 (15)	0.0282 (12)	0.0183 (11)	-0.0044 (11)	0.0006 (10)	0.0025 (9)
C5	0.0229 (14)	0.0207 (11)	0.0213 (11)	-0.0026 (11)	0.0050 (10)	-0.0003 (9)
C6	0.0168 (13)	0.0203 (11)	0.0196 (10)	-0.0028 (10)	0.0044 (9)	0.0039 (9)
C7	0.0216 (14)	0.0222 (11)	0.0204 (11)	-0.0004 (10)	0.0019 (10)	-0.0008 (9)
C8	0.0173 (15)	0.0203 (11)	0.0207 (11)	-0.0027 (10)	-0.0015 (11)	-0.0021 (9)
C9	0.0221 (15)	0.0268 (12)	0.0264 (12)	0.0044 (11)	0.0024 (10)	0.0052 (10)
C10	0.0194 (14)	0.0211 (11)	0.0214 (11)	0.0050 (10)	0.0006 (11)	0.0028 (9)
C11	0.0298 (15)	0.0219 (11)	0.0191 (10)	0.0034 (11)	-0.0008 (10)	-0.0015 (9)
C12	0.0337 (17)	0.0211 (11)	0.0318 (13)	-0.0033 (12)	0.0026 (12)	0.0037 (10)
C13	0.0388 (17)	0.0302 (13)	0.0188 (11)	0.0115 (12)	0.0054 (11)	0.0072 (10)
C14	0.0421 (18)	0.0300 (13)	0.0197 (11)	0.0049 (12)	-0.0059 (11)	-0.0045 (10)
C15	0.0296 (16)	0.0204 (12)	0.0291 (12)	0.0004 (11)	-0.0044 (11)	-0.0006 (10)

Geometric parameters (\AA , $^\circ$)

F1—C3	1.362 (2)	C7—H7B	0.9900
F2—C13	1.371 (2)	C8—C9	1.511 (3)
O1—C8	1.209 (3)	C9—C10	1.505 (3)
C1—C2	1.381 (3)	C9—H9A	0.9900
C1—C6	1.392 (3)	C9—H9B	0.9900

supplementary materials

C1—H1	0.9500	C10—C11	1.383 (3)
C2—C3	1.372 (3)	C10—C15	1.391 (3)
C2—H2	0.9500	C11—C12	1.387 (3)
C3—C4	1.370 (3)	C11—H11	0.9500
C4—C5	1.387 (3)	C12—C13	1.370 (3)
C4—H4	0.9500	C12—H12	0.9500
C5—C6	1.387 (3)	C13—C14	1.361 (3)
C5—H5	0.9500	C14—C15	1.384 (3)
C6—C7	1.500 (3)	C14—H14	0.9500
C7—C8	1.520 (3)	C15—H15	0.9500
C7—H7A	0.9900		
C2—C1—C6	121.3 (2)	C9—C8—C7	115.1 (2)
C2—C1—H1	119.3	C10—C9—C8	114.70 (19)
C6—C1—H1	119.3	C10—C9—H9A	108.6
C3—C2—C1	118.24 (19)	C8—C9—H9A	108.6
C3—C2—H2	120.9	C10—C9—H9B	108.6
C1—C2—H2	120.9	C8—C9—H9B	108.6
F1—C3—C4	118.6 (2)	H9A—C9—H9B	107.6
F1—C3—C2	118.52 (19)	C11—C10—C15	118.64 (19)
C4—C3—C2	122.9 (2)	C11—C10—C9	120.86 (18)
C3—C4—C5	117.8 (2)	C15—C10—C9	120.5 (2)
C3—C4—H4	121.1	C10—C11—C12	121.31 (19)
C5—C4—H4	121.1	C10—C11—H11	119.3
C4—C5—C6	121.7 (2)	C12—C11—H11	119.3
C4—C5—H5	119.2	C13—C12—C11	117.7 (2)
C6—C5—H5	119.2	C13—C12—H12	121.1
C5—C6—C1	118.0 (2)	C11—C12—H12	121.1
C5—C6—C7	120.90 (19)	C14—C13—C12	123.1 (2)
C1—C6—C7	121.05 (19)	C14—C13—F2	119.09 (19)
C6—C7—C8	114.0 (2)	C12—C13—F2	117.8 (2)
C6—C7—H7A	108.8	C13—C14—C15	118.5 (2)
C8—C7—H7A	108.8	C13—C14—H14	120.8
C6—C7—H7B	108.8	C15—C14—H14	120.8
C8—C7—H7B	108.8	C14—C15—C10	120.7 (2)
H7A—C7—H7B	107.7	C14—C15—H15	119.6
O1—C8—C9	122.59 (19)	C10—C15—H15	119.6
O1—C8—C7	122.3 (2)		
C6—C1—C2—C3	-1.2 (3)	O1—C8—C9—C10	4.6 (3)
C1—C2—C3—F1	179.59 (19)	C7—C8—C9—C10	-176.77 (19)
C1—C2—C3—C4	-0.8 (3)	C8—C9—C10—C11	100.0 (2)
F1—C3—C4—C5	-178.96 (19)	C8—C9—C10—C15	-79.6 (3)
C2—C3—C4—C5	1.5 (3)	C15—C10—C11—C12	-0.4 (3)
C3—C4—C5—C6	0.0 (3)	C9—C10—C11—C12	-180.0 (2)
C4—C5—C6—C1	-1.9 (3)	C10—C11—C12—C13	-0.6 (4)
C4—C5—C6—C7	176.6 (2)	C11—C12—C13—C14	1.2 (4)
C2—C1—C6—C5	2.6 (3)	C11—C12—C13—F2	-178.9 (2)
C2—C1—C6—C7	-176.0 (2)	C12—C13—C14—C15	-0.8 (4)
C5—C6—C7—C8	-115.5 (2)	F2—C13—C14—C15	179.3 (2)

supplementary materials

C1—C6—C7—C8	63.1 (3)	C13—C14—C15—C10	-0.2 (4)
C6—C7—C8—O1	-18.2 (3)	C11—C10—C15—C14	0.8 (3)
C6—C7—C8—C9	163.18 (18)	C9—C10—C15—C14	-179.6 (2)

Fig. 1

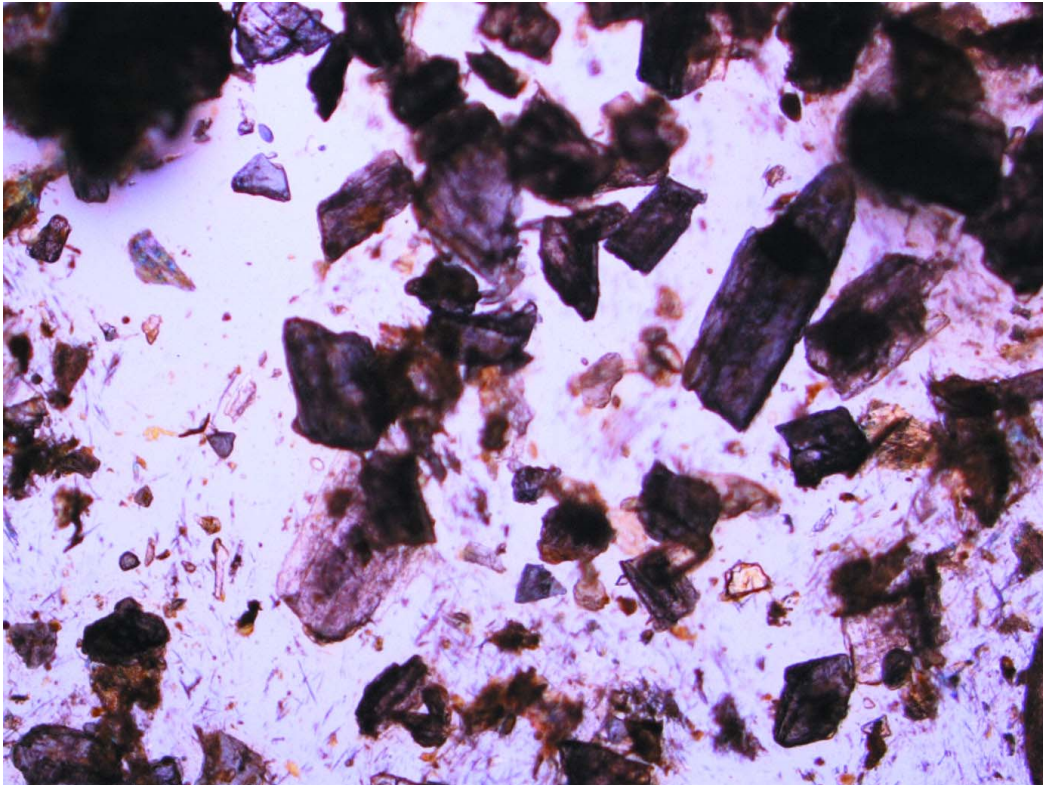


Fig. 2



Fig. 3

