Table 2. *Bond distances* (Å), *angles* (°) *and hydrogen-bond geometry* (Å, °)

N(1)—C(2)	1.434 (3)	N(1)—C(6)	1.391 (3)
N(1)—C(11)	1.465 (3)	C(2)—N(3)	1.351 (3)
C(2)—O(21)	1.229 (3)	N(3)—C(4)	1.334 (3)
C(4)—C(5)	1.368 (3)	C(4)—N(9)	1.387 (3)
C(5)—C(6)	1.421 (3)	C(5)—N(7)	1.389 (3)
C(6)—O(61)	1.236 (3)	N(7)—C(8)	1.319 (3)
N(7)—C(71)	1.468 (3)	C(8)—N(9)	1.341 (3)
N(9)—C(91)	1.458 (3)		
C(2)—N(1)—C(6)	125.8 (2)	C(2)—N(1)—C(11)	116.8 (2)
C(6)—N(1)—C(11)	117.3 (2)	N(1)—C(2)—N(3)	119.7 (2)
N(1)—C(2)—O(21)	117.1 (2)	N(3)—C(2)—O(21)	123.2 (2)
C(2)—N(3)—C(4)	114.6 (2)	N(3)—C(4)—C(5)	128.4 (2)
N(3)—C(4)—N(9)	125.3 (2)	C(5)—C(4)—N(9)	106.3 (2)
C(4)—C(5)—C(6)	120.2 (2)	C(4)—C(5)—N(7)	107.7 (2)
C(6)—C(5)—N(7)	132.0 (2)	N(1)—C(6)—C(5)	111.3 (2)
N(1)—C(6)—O(61)	121.6 (2)	C(5)—C(6)—O(61)	127.2 (2)
C(5)—N(7)—C(8)	107.9 (2)	C(5)—N(7)—C(71)	127.2 (2)
C(8)—N(7)—C(71)	124.9 (2)	N(7)—C(8)—N(9)	110.0 (2)
C(4)—N(9)—C(8)	108.2 (2)	C(4)—N(9)—C(91)	126.1 (2)
C(8)—N(9)—C(91)	125.7 (2)		

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O(1*W*)—H···N(3)	2.05 (4)	2.896 (3)	174 (3)
O(1*W*)—H···O(61^{i})	2.06 (4)	2.918 (3)	173 (3)
C(8)—H···O(21^{ii})	2.06 (4)	3.009 (3)	156 (3)

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

Space group $P2_1/c$ was determined from systematic absences (0*k*0, *k* odd; *h*0*l*, *l* odd). Corrections for Lorentz–polarization effects were applied. The structure was solved by direct methods using *MULTAN*80 (Main *et al.*, 1980) and refined by full-matrix least-squares calculations. Non-H atoms were allowed to refine with anisotropic displacement parameters. H-atoms were allowed to refine with overall isotropic displacement parameters. Other computer programs used include *SHELX*76 (Sheldrick, 1976) and *XANADU* (Roberts & Sheldrick, 1975).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BR1053). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Fluorinated Barbituric Acid Derivatives

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Abstract

The structures of 5,5-difluorobarbituric acid, $C_4H_2F_2N_2O_3$ (1), and 5-fluoro-5-phenylbarbituric acid, $C_{10}H_7FN_2O_3$ (2), have been determined [barbituric acid is 2,4,6(1*H*,3*H*,5*H*)-pyrimidinetrione]. Both compounds have the expected keto structure. The C—C bonds in the heterocyclic ring [1.526 (8) Å for (1), 1.525 (6) and 1.537 (6) Å for (2)] are elongated relative to those of the parent compounds, consistent with the electron-withdrawing power of the F-atom substituent(s). There is extensive intermolecular hydrogen bonding in both compounds.

Comment

Selective fluorination of biologically active compounds often induces useful pharmacological proper-

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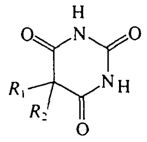
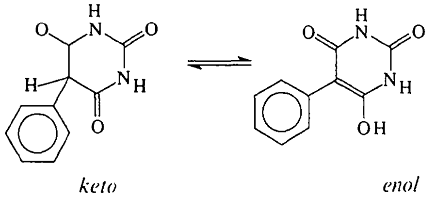
ties or enhances the therapeutic effectiveness of the product (Welch, 1987; Resnati, 1990*a*,*b*). Recently we synthesized several 5-fluorobarbituric acids (Resnati & DesMarteau, 1992). The presence of F may alter the acidity and hydrophilic/lipophilic nature of these compounds. A comparison of the mass spectrometric behavior of these fluorinated derivatives with that of their parent compounds has revealed major differences in the fragmentation process (DesMarteau, Resnati, Favretto & Traldi, 1992). The parent compounds yielded fragments consistent with cleavage of a ketoimidic bond. This ring-opening process is similar to that which occurs in basic media to yield a β-keto acid derivative (Harvey, 1985). The fluorinated derivatives, however, gave fragments which originated from a structure resulting from the rupture of a C—C (F_2C—CO) bond. This alternative cleavage was believed to be due to the electron-withdrawing power of the F atom. Structure determinations of 5,5-difluorobarbituric acid (1) and 5-fluoro-5-phenylbarbituric acid (2) were undertaken to support this conclusion (see Fig. 1).



(1) $R_1 = R_2 =$ F
(2) R_1 = F; $R_2 = C_6H_5$



The influence of the F atoms in (1) is evident by comparison to barbituric acid (Bolton, 1963). The C—C bonds in (1) are considerably longer than those in the parent compound [1.526 (8) Å *versus* 1.471 (7) and 1.490 (7) Å]. The C—C bonds in (2) [1.525 (6) and 1.537 (6) Å] are similar to those of (1), and are also considerably longer than those observed in the parent compound, 5-phenylbarbituric acid [1.363 (3) and 1.422 (3) Å (de Meester, Jovanovic, Chu & Biehl, 1986)]. However, the differences between this compound and compound (2) are due primarily to the fact that 5-phenylbarbituric acid was found to have an unusual enol structure, while (2) has the more typical keto structure.

Crystal packing in both compounds is dominated by extensive intermolecular hydrogen bonding. In (1), strong interactions between molecules related by a 2_1 screw operation parallel to the *a* axis [N(3)—H(3)···O(2)] and between molecules related by a 2_1 screw operation parallel to the *b* axis [N(1)—H(1)···O(6)] result in a three-dimensional network of hydrogen bonds. In (2), molecules related by a 2_1 screw operation parallel to the *a* axis are joined through two interactions [N(1)—H(1)···O(4) and O(6)···H(3)—N(3)] to form an infinite chain structure. Geometric details of these interactions are given in Table 2.

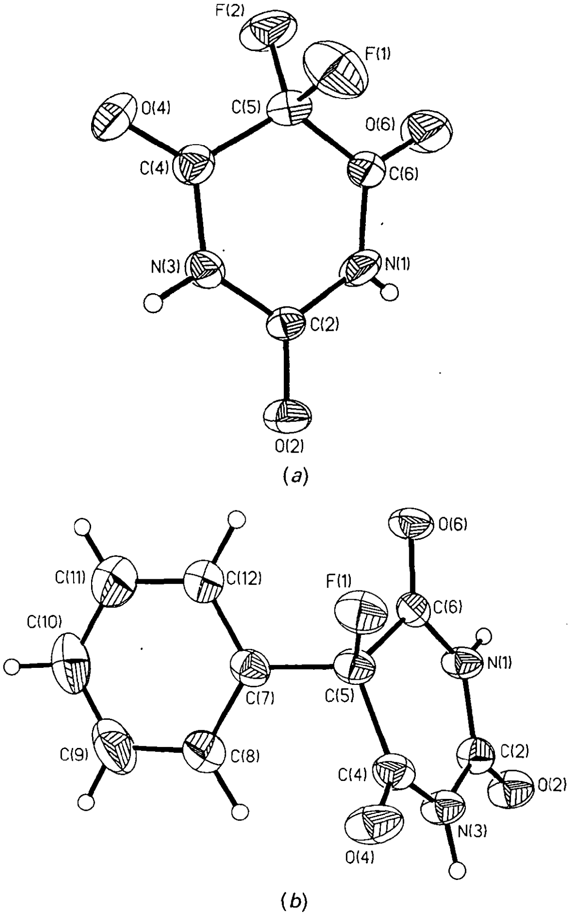


Fig. 1. Views showing the labeling of non-H atoms. Displacement ellipsoids are shown at 50% probability levels. (*a*) Compound (1); (*b*) compound (2).

Experimental

Compounds (1) and (2) were recrystallized from methyl cyanide/2-propanol (Resnati & DesMarteau, 1992).

Compound (1)

Crystal data

$C_4H_2F_2N_2O_3$
M_r = 164.08
Orthorhombic
$P2_12_12_1$
a = 6.603 (4) Å
b = 7.718 (4) Å
c = 11.260 (6) Å

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 44 reflections
θ = 8.6–16.2°
μ = 0.20 mm^{-1}
T = 294 (1) K

$V = 573.8$ (5) Å^3
$Z = 4$
$D_x = 1.90$ Mg m^{-3}

Parallelepiped
$0.35 \times 0.25 \times 0.24$ mm
Colorless

Data collection

Nicolet *R*3*m*/*V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.93$, $T_{\max} = 1.00$
557 measured reflections
557 independent reflections
520 observed reflections
$[I > 3\sigma(I)]$

$\theta_{\max} = 24.0°$
$h = -7 \rightarrow 0$
$k = -8 \rightarrow 0$
$l = 0 \rightarrow 12$
3 standard reflections
monitored every 97 reflections
intensity variation: ±2%

Refinement

Refinement on *F*
$R = 0.0536$
$wR = 0.0736$
$S = 2.96$
520 reflections
102 parameters
$w = 1/[\sigma^2(F) + 0.00025F^2]$
$(\Delta/\sigma)_{\max} = 0.0008$
$\Delta\rho_{\max} = 0.273$ e Å^{-3}
$\Delta\rho_{\min} = -0.304$ e Å^{-3}

Extinction correction: Larson (1970)
Extinction coefficient: 0.015 (4)
Atomic scattering factors from Cromer & Waber (1974)

Compound (2)

Crystal data

$C_{10}H_7FN_2O_3$
$M_r = 222.18$
Orthorhombic
Pbca
$a = 12.072$ (3) Å
$b = 8.349$ (2) Å
$c = 18.819$ (7) Å
$V = 1896.7$ (7) Å^3
$Z = 8$
$D_x = 1.55$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 49 reflections
$\theta = 12.1\text{–}22.9°$
$\mu = 0.12$ mm^{-1}
$T = 294$ (1) K
Parallelepiped
$0.32 \times 0.31 \times 0.19$ mm
Colorless

Data collection

Nicolet *R*3*m*/*V* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.84$, $T_{\max} = 1.00$
1740 measured reflections
1740 independent reflections
919 observed reflections
$[I > 3\sigma(I)]$

$\theta_{\max} = 24.0°$
$h = -14 \rightarrow 0$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 22$
3 standard reflections
monitored every 97 reflections
intensity variation: ±2%

Refinement

Refinement on *F*
$R = 0.0523$
$wR = 0.0646$
$S = 1.63$
919 reflections
173 parameters
$w = 1/[\sigma^2(F) + 0.00025F^2]$

$(\Delta/\sigma)_{\max} = 0.0006$
$\Delta\rho_{\max} = 0.231$ e Å^{-3}
$\Delta\rho_{\min} = -0.366$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Cromer & Waber (1974)

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

$U_{\rm iso}$ for H atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
(1)				
F(1)	0.0504 (7)	0.6731 (6)	0.7811 (3)	0.058 (1)
F(2)	0.2045 (6)	0.8684 (4)	0.6796 (4)	0.053 (1)
O(2)	0.1883 (6)	0.2414 (5)	0.5068 (4)	0.034 (1)
O(4)	−0.1196 (7)	0.7653 (6)	0.5480 (4)	0.052 (2)
O(6)	0.4881 (10)	0.6347 (6)	0.7472 (5)	0.058 (2)
N(1)	0.3309 (7)	0.4350 (6)	0.6307 (4)	0.033 (1)
N(3)	0.0286 (7)	0.4968 (5)	0.5326 (4)	0.029 (1)
C(2)	0.1844 (9)	0.3823 (6)	0.5538 (5)	0.025 (2)
C(4)	0.0084 (10)	0.6613 (7)	0.5781 (5)	0.032 (2)
C(5)	0.1549 (9)	0.7023 (7)	0.6790 (5)	0.032 (2)
C(6)	0.3449 (10)	0.5906 (8)	0.6881 (5)	0.033 (2)
H(1)	0.4339	0.3590	0.6367	0.078 (20)
H(3)	−0.0680	0.4661	0.4802	0.078 (20)
(2)				
F(1)	0.1264 (2)	−0.0261 (3)	0.1016 (1)	0.036 (1)
O(2)	0.1341 (2)	0.4508 (4)	−0.0782 (2)	0.042 (1)
O(4)	−0.0646 (2)	0.1099 (4)	0.0589 (2)	0.041 (1)
O(6)	0.3222 (2)	0.1124 (3)	0.0655 (2)	0.035 (1)
N(1)	0.2263 (3)	0.2817 (5)	−0.0055 (2)	0.031 (1)
N(3)	0.0327 (3)	0.2886 (5)	−0.0063 (2)	0.033 (1)
C(2)	0.1315 (3)	0.3489 (5)	−0.0333 (2)	0.031 (1)
C(4)	0.0234 (3)	0.1746 (5)	0.0450 (2)	0.030 (1)
C(5)	0.1268 (3)	0.1380 (4)	0.0884 (2)	0.028 (1)
C(6)	0.2349 (3)	0.1742 (5)	0.0486 (2)	0.026 (1)
C(7)	0.1267 (3)	0.2259 (5)	0.1591 (2)	0.031 (1)
C(8)	0.0461 (4)	0.3377 (6)	0.1768 (3)	0.043 (2)
C(9)	0.0468 (5)	0.4075 (7)	0.2437 (3)	0.061 (2)
C(10)	0.1276 (5)	0.3706 (7)	0.2918 (3)	0.060 (2)
C(11)	0.2087 (5)	0.2638 (8)	0.2734 (3)	0.061 (2)
C(12)	0.2087 (4)	0.1912 (6)	0.2078 (3)	0.044 (2)
H(1)	0.2839 (36)	0.3105 (50)	−0.0234 (22)	0.028 (13)
H(3)	−0.0260 (52)	0.3391 (76)	−0.0288 (33)	0.094 (23)
H(8)	−0.0087 (41)	0.3684 (62)	0.1395 (27)	0.057 (15)
H(9)	−0.0081 (48)	0.4866 (71)	0.2550 (30)	0.076 (19)
H(10)	0.1193 (51)	0.4155 (80)	0.3371 (40)	0.108 (25)
H(11)	0.2612 (42)	0.2397 (61)	0.3075 (27)	0.061 (16)
H(12)	0.2642 (47)	0.1080 (66)	0.1953 (30)	0.079 (18)

Table 2. *Selected geometric parameters* (Å, °) *for compounds* (1) *and* (2)

(1)			
F(1)—C(5)	1.359 (7)	F(2)—C(5)	1.324 (6)
O(2)—C(2)	1.209 (6)	O(4)—C(4)	1.213 (8)
O(6)—C(6)	1.205 (9)	N(1)—C(2)	1.361 (7)
N(1)—C(6)	1.367 (7)	N(3)—C(2)	1.377 (7)
N(3)—C(4)	1.376 (7)	C(4)—C(5)	1.526 (8)
C(5)—C(6)	1.526 (8)		
C(2)—N(1)—C(6)	127.7 (5)	C(2)—N(3)—C(4)	126.9 (5)
O(2)—C(2)—N(1)	122.1 (5)	O(2)—C(2)—N(3)	121.2 (5)
N(1)—C(2)—N(3)	116.7 (4)	O(4)—C(4)—N(3)	125.0 (6)
O(4)—C(4)—C(5)	120.8 (5)	N(3)—C(4)—C(5)	114.0 (5)
F(1)—C(5)—F(2)	106.4 (5)	F(1)—C(5)—C(4)	105.9 (5)
F(2)—C(5)—C(4)	111.2 (5)	F(1)—C(5)—C(6)	105.5 (4)
F(2)—C(5)—C(6)	110.1 (5)	C(4)—C(5)—C(6)	117.0 (5)
O(6)—C(6)—N(1)	124.2 (6)	O(6)—C(6)—C(5)	121.5 (5)
N(1)—C(6)—C(5)	114.2 (5)		
O(2)···N(3$^{\rm i}$)	2.937 (7)	O(6)···N(1$^{\rm ii}$)	2.948 (7)

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

(2)		C(5)—C(7)	1.519 (6)
F(1)—C(5)	1.392 (4)	O(2)—C(2)	1.199 (5)
O(4)—C(4)	1.221 (5)	O(6)—C(6)	1.217 (5)
N(1)—C(2)	1.380 (6)	N(1)—C(6)	1.362 (6)
N(3)—C(4)	1.360 (6)	N(3)—C(2)	1.393 (6)
C(4)—C(5)	1.525 (6)	C(5)—C(6)	1.537 (6)

C(2)—N(1)—C(6)	128.0 (4)	C(2)—N(3)—C(4)	125.7 (4)
O(2)—C(2)—N(1)	122.3 (4)	O(2)—C(2)—N(3)	122.5 (4)
N(1)—C(2)—N(3)	115.2 (4)	O(4)—C(4)—N(3)	122.3 (4)
O(4)—C(4)—C(5)	120.6 (4)	N(3)—C(4)—C(5)	117.0 (3)
F(1)—C(5)—C(4)	106.8 (3)	F(1)—C(5)—C(6)	106.4 (3)
C(4)—C(5)—C(6)	113.3 (3)	F(1)—C(5)—C(7)	108.7 (3)
C(4)—C(5)—C(7)	111.9 (3)	C(6)—C(5)—C(7)	109.5 (3)
O(6)—C(6)—N(1)	122.8 (4)	O(6)—C(6)—C(5)	121.7 (4)
N(1)—C(6)—C(5)	115.5 (3)		

D—H···*A*	*D*···H	*D*···*A*	*D*—H···*A*
O(4^i)—H(1)···N(1^i)	2.06 (5)	2.867 (5)	174 (1)
O(6^{ii})—H(3)···N(3^{ii})	2.00 (5)	2.899 (5)	162 (1)

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

The structures were solved by direct methods and refined by full-matrix least squares. The non-H atoms were refined anisotropically; H atoms were located by standard techniques and were refined isotropically [for (2)], or were placed in optimized positions (C—H = 0.96 Å) as a riding model contribution to the structure-factor calculations [for (1); group isotropic displacement parameter = 0.08 (2) Å^2]. Corrections were applied for Lorentz and polarization effects, and real and imaginary anomalous dispersion (Cromer, 1974). Structure solution, refinement and the calculation of derived results were performed using *SHELXTL* (Sheldrick, 1986).

Lists of structure factors and anisotropic displacement parameters for (1) and (2), complete geometry for (2) and packing diagrams for (1) and (2) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71818 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1077]

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Substituted Diphenyl Oxalates

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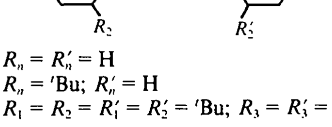
Abstract

The ethanedioic acid (oxalic acid) diphenyl ester derivative with bis(2,6-*tert*-butyl) substitution, bis(2,6-di-*tert*-butyl-4-methoxyphenyl) ethanedioate, $C_{32}H_{46}O_6$ (3), adopts an *s-trans* oxalate conformation due to steric constraints; such derivatives constitute conformationally well defined molecular structural units. Diphenyl ethanedioate, $C_{14}H_{10}O_4$ (1), has approximate *s-cis* geometry and diphenyl ethanedioate with *tert*-butylation on only one ring, 1-(2,4,6-tris-*tert*-butylphenyl) 2-phenyl ethanedioate, $C_{26}H_{34}O_4$ (2), has a *gauche* conformation.

Comment

During studies of radical pairs photochemically generated in neat solid diphenyl ethanedioates (more commonly called oxalates, a usage we retain in this work), some of us (Modarelli, George & Lahti, 1991) wished to study the crystallography of these compounds as a function of different substitution patterns. We found that triplet radical-pair electron-spin-resonance (ESR) spectra could be most readily detected in diphenyl oxalates with 2,6-di-*tert*-butylated phenyl rings. More extensive ESR studies of such radical pairs in oriented crystalline arrays required definitive structural information. In this report, we describe the crystal structures and variation in solid-state molecular conformation of the following substituted oxalates: diphenyl oxalate (1), phenyl 2,4,6-tris-*tert*-butylphenyl oxalate (2) and bis(2,6-di-*tert*-butyl-4-methoxyphenyl) oxalate (3).



(1) $R_n = R'_n = $ H
(2) $R_n = {}^t$Bu; $R'_n = $ H
(3) $R_1 = R_2 = R'_1 = R'_2 = {}^t$Bu; $R_3 = R'_3 = $ MeO

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