

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 ⁱ)...N(1 ⁱ)	2.06 (5)	2.867 (5)	174 (1)
O(6 ⁱⁱ)—H(3 ⁱ)...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) Å². 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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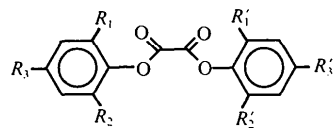
(Received 19 April 1993; accepted 2 November 1993)

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, C₃₂H₄₆O₆ (3), adopts an *s-trans* oxalate conformation due to steric constraints; such derivatives constitute conformationally well defined molecular structural units. Diphenyl ethanedioate, C₁₄H₁₀O₄ (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, C₂₆H₃₄O₄ (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) $R_n = R'_n = \text{H}$
 (2) $R_n = \text{'Bu}$; $R'_n = \text{H}$
 (3) $R_1 = R_2 = R'_1 = R'_2 = \text{'Bu}$; $R_3 = R'_3 = \text{MeO}$

In each of these structures the observed bond distances and angles are normal. Both (1) and (2) crystallize with a single molecule in the asymmetric unit while (3) has a half molecule in the asymmetric unit located such that a center of symmetry lies midway between the oxalate C atoms. In the general case, conformations in substituted oxalates differ and

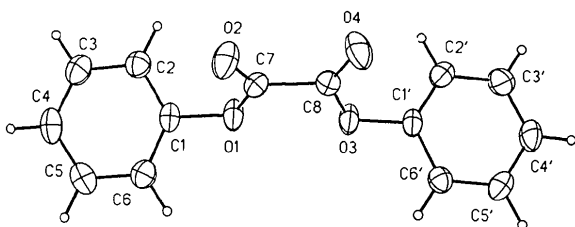


Fig. 1. A displacement ellipsoid plot of (1) with ellipsoids drawn at the 50% probability level.

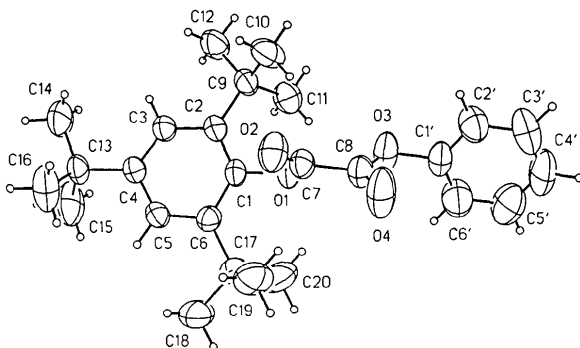


Fig. 2. A displacement ellipsoid plot of (2) with ellipsoids drawn at the 50% probability level.

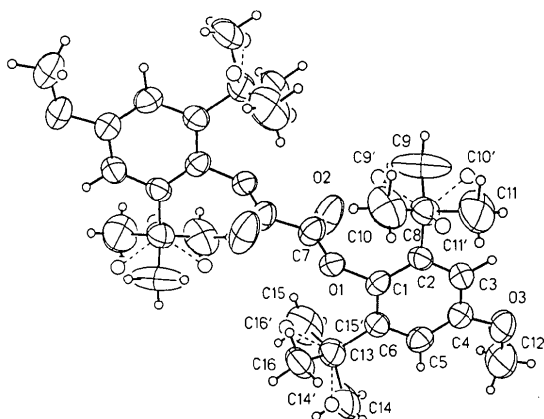


Fig. 3. A displacement ellipsoid plot of (3) with ellipsoids drawn at the 50% probability level. The dashed bonds to isotropic atoms represent the alternate position for the lower occupancy *tert*-butyl disorder. Lower occupancy *tert*-butyl H atoms are omitted.

are not predictable *a priori*. For example, hexapotassium μ -(2-oxalato)-bis(dioxalato-oxo-vanadium) (Zhou, Huang & Lu, 1983) and dimethyl oxalate (Adiwidjaja & Voss, 1976) have *cis* conformations. In earlier work (Modarelli, George & Lahti, 1991), some of us argued that compound (3) would have an *s-trans* conformation by analogy to the crystallographically determined geometries of bis-(2,4,6-tris-*tert*-butylphenyl) oxalate (4) and bis-(4-phenyl-2,6-di-*tert*-butylphenyl) oxalate (5). This assumption was important for the estimation of electron-spin-resonance triplet radical-pair zero-field splitting parameters. The present results confirm our earlier assumption of an *s-trans* geometry for molecule (3).

Molecular-modeling studies indicate that the *s-trans* geometry with rings perpendicular to the carbonyls will be preferred for the bis(2,6-di-*tert*-butylphenyl) oxalates, since steric interactions are minimized in this conformer and since the oxalate group linking the two phenyl rings is of appropriate length to hold the rings in this manner without bond-stretching strain. A linking group shorter than oxalyl ($-\text{CO}-\text{CO}-$) would produce great steric strain between *tert*-butyl groups, as shown by our inability to make bis(2,6-di-*tert*-butylphenyl) carbonates (Modarelli, 1991). The bis(2,6-di-*tert*-butylphenyl) oxalates, therefore, represent a geometrically unambiguous structural unit for molecular-design considerations.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
(1)				
O(1)	0.7171 (1)	0.0429 (2)	0.6740 (1)	0.036 (1)
O(2)	0.5452 (1)	0.2144 (2)	0.6206 (1)	0.045 (1)
O(3)	0.7743 (1)	0.0434 (2)	0.5076 (1)	0.036 (1)
O(4)	0.5875 (1)	0.1741 (2)	0.4355 (1)	0.049 (1)
C(1)	0.6987 (2)	0.0368 (2)	0.7707 (1)	0.029 (1)
C(2)	0.5915 (2)	-0.0435 (2)	0.7891 (1)	0.035 (1)
C(3)	0.5832 (2)	-0.0579 (3)	0.8850 (1)	0.042 (1)
C(4)	0.6792 (2)	0.0078 (3)	0.9598 (1)	0.045 (1)
C(5)	0.7851 (2)	0.0885 (2)	0.9392 (1)	0.041 (1)
C(6)	0.7950 (2)	0.1038 (2)	0.8435 (1)	0.035 (1)
C(7)	0.6334 (2)	0.1321 (2)	0.6071 (1)	0.029 (1)
C(8)	0.6614 (2)	0.1195 (2)	0.5055 (1)	0.029 (1)
C(1')	0.8134 (2)	0.0269 (2)	0.4180 (1)	0.029 (1)
C(2')	0.7516 (2)	-0.0846 (2)	0.3479 (1)	0.039 (1)
C(3')	0.7979 (2)	-0.1024 (3)	0.2642 (1)	0.044 (1)
C(4')	0.9038 (2)	-0.0110 (2)	0.2529 (1)	0.040 (1)
C(5')	0.9663 (2)	0.0985 (2)	0.3256 (1)	0.036 (1)
C(6')	0.9208 (2)	0.1179 (2)	0.4093 (1)	0.032 (1)
(2)				
O(1)	0.4369 (2)	0.0461 (2)	0.2261 (1)	0.051 (1)
O(2)	0.2984 (2)	0.0609 (2)	0.3835 (2)	0.074 (1)
O(3)	0.2712 (2)	-0.1242 (2)	0.1670 (2)	0.077 (1)
O(4)	0.0999 (2)	0.0100 (3)	0.2460 (2)	0.104 (1)
C(1)	0.5397 (2)	0.1118 (2)	0.2693 (2)	0.045 (1)
C(2)	0.6417 (2)	0.0328 (2)	0.3148 (2)	0.046 (1)
C(3)	0.7337 (2)	0.1020 (2)	0.3636 (2)	0.048 (1)
C(4)	0.7267 (2)	0.2410 (2)	0.3644 (2)	0.047 (1)

C(5)	0.6289 (2)	0.3126 (2)	0.3093 (2)	0.051 (1)	(2)			
C(6)	0.5333 (2)	0.2526 (2)	0.2583 (2)	0.048 (1)	O(1)—C(1)	1.428 (3)	O(1)—C(7)	1.344 (3)
C(7)	0.3219 (2)	0.0303 (3)	0.2921 (2)	0.054 (1)	O(2)—C(7)	1.185 (3)	O(3)—C(8)	1.321 (3)
C(8)	0.2173 (3)	-0.0276 (3)	0.2323 (2)	0.059 (1)	O(3)—C(1')	1.424 (4)	O(4)—C(8)	1.182 (3)
C(1')	0.1822 (3)	-0.1815 (3)	0.1033 (2)	0.064 (1)	C(1)—C(2)	1.388 (3)	C(1)—C(6)	1.408 (3)
C(2')	0.1079 (3)	-0.2814 (3)	0.1443 (3)	0.079 (1)	C(2)—C(3)	1.400 (3)	C(2)—C(9)	1.545 (3)
C(3')	0.0258 (4)	-0.3374 (4)	0.0801 (3)	0.100 (2)	C(3)—C(4)	1.387 (3)	C(4)—C(5)	1.386 (3)
C(4')	0.0204 (4)	-0.2900 (5)	-0.0235 (4)	0.107 (2)	C(4)—C(13)	1.538 (4)	C(5)—C(6)	1.392 (4)
C(5')	0.0968 (5)	-0.1918 (5)	-0.0630 (3)	0.111 (2)	C(6)—C(17)	1.542 (4)	C(7)—C(8)	1.514 (4)
C(6')	0.1789 (4)	-0.1342 (4)	0.0006 (3)	0.092 (1)	C(1')—C(2')	1.348 (4)	C(1')—C(6')	1.358 (5)
C(9)	0.6597 (3)	-0.1220 (2)	0.3111 (2)	0.054 (1)	C(2')—C(3')	1.375 (6)	C(3')—C(4')	1.370 (6)
C(10)	0.5444 (3)	-0.1859 (3)	0.3822 (3)	0.076 (1)	C(4')—C(5')	1.342 (6)	C(5')—C(6')	1.377 (6)
C(11)	0.6650 (4)	-0.1676 (3)	0.1944 (2)	0.080 (1)	C(9)—C(10)	1.537 (4)	C(9)—C(11)	1.538 (4)
C(12)	0.7937 (3)	-0.1771 (3)	0.3537 (3)	0.071 (1)	C(9)—C(12)	1.536 (4)	C(13)—C(14)	1.505 (5)
C(13)	0.8255 (2)	0.3168 (2)	0.4208 (2)	0.055 (1)	C(13)—C(15)	1.527 (4)	C(13)—C(16)	1.508 (4)
C(14)	0.9219 (4)	0.2245 (4)	0.4797 (4)	0.121 (2)	C(17)—C(18)	1.531 (4)	C(17)—C(19)	1.537 (4)
C(15)	0.9103 (4)	0.3977 (4)	0.3365 (3)	0.103 (2)	C(17)—C(20)	1.527 (4)		
C(16)	0.7465 (3)	0.4150 (4)	0.4987 (3)	0.101 (2)				
C(17)	0.4347 (3)	0.3375 (3)	0.1908 (2)	0.060 (1)	C(1)—O(1)—C(7)	116.6 (2)	C(2')—C(3')—C(4')	119.5 (4)
C(18)	0.4703 (4)	0.4832 (3)	0.1782 (3)	0.100 (2)	O(1)—C(1)—C(2)	118.1 (2)	C(4')—C(5')—C(6')	120.7 (4)
C(19)	0.2866 (3)	0.3434 (3)	0.2446 (3)	0.091 (1)	C(2)—C(1)—C(6)	124.6 (2)	C(2)—C(9)—C(10)	109.8 (2)
C(20)	0.4405 (4)	0.2811 (4)	0.0783 (3)	0.099 (2)	C(1)—C(2)—C(9)	124.0 (2)	C(10)—C(2)—C(11)	107.2 (2)
(3)					C(2)—C(3)—C(4)	122.6 (2)	C(10)—C(9)—C(12)	106.5 (2)
C(1)	0.0109 (4)	0.6208 (3)	0.6795 (3)	0.051 (1)	C(3)—C(4)—C(13)	122.5 (2)	C(4)—C(13)—C(14)	112.8 (2)
C(2)	0.1048 (4)	0.5710 (3)	0.7433 (3)	0.051 (1)	C(4)—C(5)—C(6)	123.5 (2)	C(14)—C(13)—C(15)	108.2 (3)
C(3)	0.0673 (4)	0.5876 (3)	0.8321 (3)	0.059 (2)	C(1)—C(6)—C(17)	124.2 (2)	C(14)—C(13)—C(16)	109.2 (3)
C(4)	-0.0516 (5)	0.6518 (4)	0.8553 (3)	0.063 (2)	O(1)—C(7)—O(2)	127.1 (2)	C(6)—C(17)—C(18)	111.4 (2)
C(5)	-0.1346 (4)	0.7068 (4)	0.7904 (3)	0.062 (2)	O(2)—C(7)—C(8)	122.3 (2)	C(18)—C(17)—C(19)	105.9 (2)
C(6)	-0.1062 (4)	0.6930 (4)	0.6992 (3)	0.055 (2)	O(3)—C(8)—C(7)	112.8 (2)	C(18)—C(17)—C(20)	107.9 (3)
O(1)	0.0363 (3)	0.6000 (2)	0.5855 (2)	0.0521	C(8)—O(3)—C(1')	117.3 (2)	O(3)—C(1')—C(6')	117.5 (3)
C(7)	-0.0175 (5)	0.5027 (5)	0.5502 (3)	0.065 (2)	O(1)—C(1)—C(6)	117.2 (2)	C(1')—C(2')—C(3')	119.0 (3)
O(2)	-0.0832 (4)	0.4282 (3)	0.5882 (2)	0.104 (2)	C(1)—C(2)—C(3)	115.9 (2)	C(3')—C(4')—C(5')	120.4 (4)
C(8)	0.2441 (4)	0.5011 (4)	0.7239 (3)	0.066 (2)	C(3)—C(2)—C(9)	120.1 (2)	C(1')—C(6')—C(5')	118.1 (3)
C(9)	0.2105 (7)	0.3730 (5)	0.7204 (7)	0.147 (4)	C(3)—C(4)—C(5)	117.9 (2)	C(2)—C(9)—C(11)	110.1 (2)
C(10)	0.3204 (5)	0.5392 (6)	0.6399 (4)	0.102 (3)	C(5)—C(4)—C(13)	119.6 (2)	C(2)—C(9)—C(12)	110.8 (2)
C(11)	0.3581 (7)	0.5259 (8)	0.7981 (5)	0.130 (3)	C(1)—C(6)—C(5)	114.9 (2)	C(11)—C(9)—C(12)	107.7 (2)
C(9')	† 0.2592 (56)	0.4367 (43)	0.6329 (19)	0.111 (13)	C(5)—C(6)—C(17)	120.8 (2)	C(4)—C(13)—C(15)	109.0 (2)
C(10')	† 0.2793 (60)	0.4087 (39)	0.7988 (26)	0.111 (13)	O(1)—C(7)—C(8)	110.6 (2)	C(4)—C(13)—C(16)	110.2 (2)
C(11')	† 0.3797 (41)	0.5832 (38)	0.7306 (38)	0.111 (13)	O(3)—C(8)—O(4)	125.0 (3)	C(15)—C(13)—C(16)	107.4 (3)
O(3)	-0.0777 (4)	0.6557 (3)	0.9457 (2)	0.093 (1)	O(4)—C(8)—C(7)	122.2 (3)	C(6)—C(17)—C(19)	111.8 (2)
C(12)	-0.2041 (8)	0.7071 (6)	0.9730 (3)	0.137 (3)	O(3)—C(1')—C(2')	120.3 (3)	C(6)—C(17)—C(20)	110.8 (2)
C(13)	-0.2028 (5)	0.7553 (4)	0.6288 (3)	0.067 (2)	C(2')—C(1')—C(6')	122.2 (3)	C(19)—C(17)—C(20)	108.8 (3)
C(14)	-0.2980 (7)	0.8487 (6)	0.6715 (4)	0.123 (3)				
C(15)	-0.3035 (6)	0.6659 (6)	0.5827 (5)	0.112 (3)	(3)			
C(16)	-0.1163 (5)	0.8183 (5)	0.5568 (3)	0.079 (2)	C(1)—C(2)	1.394 (5)	C(1)—C(6)	1.395 (5)
C(14')	† -0.1982 (139)	0.8898 (18)	0.6238 (89)	0.325 (42)	C(1)—O(1)	1.442 (5)	C(2)—C(3)	1.385 (6)
C(15')	† -0.3567 (55)	0.7174 (109)	0.6520 (80)	0.325 (42)	C(2)—C(8)	1.546 (6)	C(3)—C(4)	1.370 (6)
C(16')	† -0.1680 (132)	0.7081 (107)	0.5350 (39)	0.325 (42)	C(4)—C(5)	1.372 (6)	C(4)—O(3)	1.372 (5)

† Lower occupancy C atoms of the disordered *tert*-butyl groups; refined isotropically.

Table 2. Selected geometric parameters (Å, °)

(1)								
O(1)—C(1)	1.422 (2)	O(1)—C(7)	1.331 (2)					
O(2)—C(7)	1.189 (2)	O(3)—C(8)	1.333 (2)					
O(3)—C(1')	1.425 (2)	O(4)—C(8)	1.187 (2)					
C(1)—C(2)	1.377 (3)	C(1)—C(6)	1.370 (2)					
C(2)—C(3)	1.379 (3)	C(3)—C(4)	1.381 (2)					
C(4)—C(5)	1.380 (3)	C(5)—C(6)	1.383 (3)					
C(7)—C(8)	1.533 (3)	C(1')—C(2')	1.365 (2)					
C(1')—C(6')	1.374 (2)	C(2')—C(3')	1.388 (3)					
C(3')—C(4')	1.373 (3)	C(4')—C(5')	1.380 (2)					
C(5')—C(6')	1.383 (3)							
C(1)—O(1)—C(7)	118.4 (1)	C(8)—O(3)—C(1')	118.0 (1)					
O(1)—C(1)—C(2)	120.1 (1)	O(1)—C(1)—C(6)	117.2 (2)					
C(2)—C(1)—C(6)	122.6 (2)	C(1)—C(2)—C(3)	117.9 (2)					
C(2)—C(3)—C(4)	120.7 (2)	C(3)—C(4)—C(5)	120.2 (2)					
C(4)—C(5)—C(6)	119.8 (2)	C(1)—C(6)—C(5)	118.8 (2)					
O(1)—C(7)—O(2)	126.3 (2)	O(1)—C(7)—C(8)	112.5 (1)					
O(2)—C(7)—C(8)	121.2 (1)	O(3)—C(8)—O(4)	126.6 (2)					
O(3)—C(8)—C(7)	112.3 (1)	O(4)—C(8)—C(7)	121.1 (2)					
O(3)—C(1')—C(2')	120.5 (2)	O(3)—C(1')—C(6')	116.9 (1)					
C(2')—C(1')—C(6')	122.4 (2)	C(1')—C(2')—C(3')	118.2 (2)					
C(2')—C(3')—C(4')	120.6 (2)	C(3')—C(4')—C(5')	120.2 (2)					
C(4')—C(5')—C(6')	119.8 (2)	C(1')—C(6')—C(5')	118.8 (2)					
C(2)—C(1)—C(6)	124.9 (4)	C(2)—C(1)—O(1)	118.8 (3)					
C(6)—C(1)—O(1)	116.2 (3)	C(1)—C(2)—C(3)	115.5 (3)					
C(1)—C(2)—C(8)	126.3 (4)	C(3)—C(2)—C(8)	118.2 (3)					
C(2)—C(3)—C(4)	121.9 (4)	C(3)—C(4)—C(5)	120.5 (4)					
C(3)—C(4)—O(3)	114.9 (4)	C(5)—C(4)—O(3)	124.6 (4)					
C(4)—C(5)—C(6)	121.3 (4)	C(1)—C(6)—C(5)	115.6 (3)					
C(1)—C(6)—C(13)	124.9 (3)	C(5)—C(6)—C(13)	119.5 (3)					
C(1)—O(1)—C(7)	117.2 (3)	O(1)—C(7)—O(2)	126.9 (4)					
O(1)—C(7)—C(7A)	109.6 (5)	O(2)—C(7)—C(7A)	123.5 (5)					
C(2)—C(8)—C(9)	109.7 (4)	C(2)—C(8)—C(10)	114.2 (4)					
C(9)—C(8)—C(10)	110.6 (5)	C(2)—C(8)—C(11)	109.5 (4)					
C(9)—C(8)—C(11)	110.1 (5)	C(10)—C(8)—C(11)	102.6 (4)					
C(2)—C(8)—C(9')	119.8 (19)	C(2)—C(8)—C(10')	112.1 (19)					
C(2)—C(8)—C(11')	110.4 (16)	C(4)—O(3)—C(12)	118.1 (4)					
C(6)—C(13)—C(14)	111.7 (4)	C(6)—C(13)—C(15)	109.7 (4)					
C(14)—C(13)—C(15)	107.4 (4)	C(6)—C(13)—C(16)	112.9 (3)					
C(14)—C(13)—C(16)	106.1 (4)	C(15)—C(13)—C(16)	108.7 (4)					
C(6)—C(13)—C(14')	118.5 (47)	C(6)—C(13)—C(15')	104.2 (43)					
C(6)—C(13)—C(16')	109.2 (42)	C(14')—C(13)—C(15')	108.9 (67)					
C(14')—C(13)—C(16')	108.6 (66)	C(15')—C(13)—C(16')	108.5 (65)					

Table 3. Selected torsion angles ($^{\circ}$)

	O _C is a carbonyl O atom.				
	(1)	(2)	(3)	(4)	(5)
O _C —C—C—O _C	-9.1 (3)	37.6 (4)	180	180	180
O—C—C—O	-9.4 (2)	41.9 (3)	180	180	180
C(7)—O(1)—C(1)—C(2)	66.0 (2)	93.7 (2)	85.1 (6)	97.5 (6)	97.3 (4)
C(8)—O(3)—C(1')—C(2')	-71.2 (2)	-84.7 (3)	-85.1 (6) ⁱ	-97.5 (6) ⁱⁱ	-97.3 (4) ⁱⁱⁱ

Symmetry related to C7—O1—C1—C2: (i) $-x, 1-y, 1-z$; (ii) $1-x, 2-y, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, 1-z$.

The relative oxalate conformations may be quantified by the torsion angles given in Table 3 for (1)–(3) and the closely related compounds (4) and (5). It may be seen that the lesser degree of *tert*-butyl substitution in (1) and (2) allows more flexibility in conformation. Diphenyl oxalate has a nearly *s-cis* oxalate conformation with a torsion angle between the carbonyl groups of -9.1 (3) $^{\circ}$. In (2) the same torsion angle is 37.6 (4) $^{\circ}$, while in compound (3) it is 180° as required by the $\bar{1}$ molecular symmetry of that compound. Compounds (4) and (5) also possess $\bar{1}$ molecular symmetry and also have the same conformational preference as (3). These results show that 2,6-di-substitution on both phenyl rings is necessary and sufficient to control the conformation of diphenyl oxalates in a dependable fashion.

Experimental

The syntheses of compounds (1)–(3) are described elsewhere (Modarelli, 1991; Lahti, Modarelli, Rossitto, Inceli, Ichimura & Ivatury, 1993). All had satisfactory elemental analyses and exhibited sharp melting points upon slow crystallization from ethanol.

Compound (1)

Crystal data

C₁₄H₁₀O₄
 $M_r = 242.2$
 Monoclinic
 $P2_1/n$
 $a = 10.622$ (2) Å
 $b = 7.836$ (1) Å
 $c = 14.084$ (2) Å
 $\beta = 103.62$ (1) $^{\circ}$
 $V = 1139.3$ (3) Å³
 $Z = 4$
 $D_x = 1.412$ Mg m⁻³

Data collection

Siemens R3m/V diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 1781 measured reflections
 1494 independent reflections
 1354 observed reflections
 $[F_o > 3\sigma(F_o)]$

Cu K α radiation
 $\lambda = 1.5418$ Å
 Cell parameters from 25 reflections
 $\theta = 21$ – 33°
 $\mu = 0.83$ mm⁻¹
 $T = 233$ K
 Rod
 $0.35 \times 0.15 \times 0.10$ mm
 Clear

$R_{int} = 0.014$
 $\theta_{max} = 56^{\circ}$
 $h = -11 \rightarrow 0$
 $k = 0 \rightarrow 8$
 $l = -14 \rightarrow 15$
 3 standard reflections monitored every 97 reflections
 intensity variation: 1.9%

Refinement

Refinement on F

$R = 0.034$
 $wR = 0.041$
 $S = 1.61$
 1354 reflections
 164 parameters
 $w = 1/[\sigma^2(|F_o|) + 0.00023(F_o)^2]$
 $\Delta\rho_{max} = 0.12$ e Å⁻³
 $\Delta\rho_{min} = -0.17$ e Å⁻³

Compound (2)

Crystal data

C₂₆H₃₄O₄
 $M_r = 410.5$
 Triclinic
 $P\bar{1}$
 $a = 9.902$ (1) Å
 $b = 10.012$ (1) Å
 $c = 12.512$ (2) Å
 $\alpha = 88.05$ (2) $^{\circ}$
 $\beta = 83.27$ (2) $^{\circ}$
 $\gamma = 84.69$ (2) $^{\circ}$
 $V = 1226.2$ (3) Å³
 $Z = 2$
 $D_x = 1.112$ Mg m⁻³

Data collection

Siemens R3m/V diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 3997 measured reflections
 3640 independent reflections
 3241 observed reflections
 $[F_o > 3\sigma(F_o)]$

Refinement

Refinement on F

$R = 0.066$
 $wR = 0.088$
 $S = 2.31$
 3241 reflections
 272 parameters
 $w = 1/[\sigma^2(|F_o|) + 0.00023(F_o)^2]$
 $\Delta\rho_{max} = 0.35$ e Å⁻³
 $\Delta\rho_{min} = -0.24$ e Å⁻³

Extinction correction:

$$F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$$

Extinction coefficient:

$$\chi = 0.035$$
 (2)

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Cu K α radiation

$\lambda = 1.5418$ Å
 Cell parameters from 25 reflections
 $\theta = 22$ – 32.5°
 $\mu = 0.55$ mm⁻¹
 $T = 293$ K
 Plate
 $0.52 \times 0.35 \times 0.15$ mm
 Clear

$R_{int} = 0.011$

$\theta_{max} = 56^{\circ}$

$h = -11 \rightarrow 11$

$k = 0 \rightarrow 11$

$l = -14 \rightarrow 14$

3 standard reflections

monitored every 97

reflections

intensity variation: 4.6%

Extinction correction:

$$F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$$

Extinction coefficient:

$$\chi = 0.014$$
 (2)

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (3)*Crystal data*C₃₂H₄₆O₆ $M_r = 526.7$

Monoclinic

 $P2_1/n$ $a = 9.241 (2) \text{ \AA}$ $b = 11.402 (3) \text{ \AA}$ $c = 14.877 (2) \text{ \AA}$ $\beta = 91.13^\circ$ $V = 1567.2 (5) \text{ \AA}^3$ $Z = 2$ $D_x = 1.116 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation $\lambda = 0.7107 \text{ \AA}$

Cell parameters from 25 reflections

 $\theta = 11\text{--}18^\circ$ $\mu = 0.08 \text{ mm}^{-1}$ $T = 293 \text{ K}$

Plate

 $0.40 \times 0.40 \times 0.10 \text{ mm}$

Clear

Data collection

Siemens R3m/V diffractometer

 $\theta/2\theta$ scans

Absorption correction: none

2421 measured reflections

2061 independent reflections

1335 observed reflections

 $[F_o > 3\sigma(F_o)]$ $R_{\text{int}} = 0.019$ $\theta_{\text{max}} = 22.5^\circ$ $h = 0 \rightarrow 9$ $k = 0 \rightarrow 12$ $l = -15 \rightarrow 16$

3 standard reflections

monitored every 97

reflections

intensity variation: 4.4%

*Refinement*Refinement on F $R = 0.064$ $wR = 0.065$ $S = 1.66$

1335 reflections

194 parameters

 $w = 1/[\sigma^2(|F_o|)$ $+ 0.00023(F_o)^2]$ $\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.20 \text{ e \AA}^{-3}$

Extinction correction:

 $F^* = F[1 + (0.002\chi$
 $\times F^2/\sin 2\theta)]^{-1/4}$

Extinction coefficient:

 $\chi = 0.0029 (5)$

Atomic scattering factors

from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71758 (38 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1075]

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Acta Cryst. (1994). **C50**, 1312–1314**3-[5-(3-Nitrophenyl)furfurylidene]-2,4-pentanedione, C₁₆H₁₃NO₅**

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Data were collected using a variable scan speed, with the ω -scan rate a function of count rate, and were corrected for Lorentz and polarization effects. The structure solution, by direct methods, and the full-matrix least-squares refinement used programs in *SHELXTL-Plus* (Sheldrick 1991). Atomic coordinates and anisotropic displacement parameters were refined for all non-H atoms. H atoms were included using a riding model (coordinate shifts of C applied to attached H atoms, C—H distance set to 0.96 Å, H angles idealized), and $U_{\text{iso}}(\text{H})$ were set to fixed values. The disordered *tert*-butyl groups in (3) were refined with bond distance and bond angle constraints, and the lower occupancy *tert*-butyl C atoms were refined isotropically. The occupancy ratio was 9:1.

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Abstract

The crystal structure consists of monomeric non-centrosymmetric nearly planar molecules. The shortest intermolecular distance [C(15)⋯O(2)′