

N1—C11	1,469 (4)	C33—C43	1,373 (4)
C11—C61	1,370 (4)	C43—C53	1,388 (4)
C11—C21	1,374 (4)	C53—C63	1,379 (4)
C21—C31	1,383 (4)		
O11—P1—O21	120,1 (1)	C11—C21—C31	119,0 (3)
O11—P1—O(L13)	108,9 (1)	C41—C31—C21	119,9 (3)
O21—P1—O(L13)	105,7 (1)	O1—C41—C31	122,3 (3)
O11—P1—O(L12)	108,2 (1)	O1—C41—C51	117,4 (3)
O21—P1—O(L12)	111,0 (1)	C31—C41—C51	120,3 (3)
O(L13)—P1—O(L12)	101,1 (1)	C41—C51—C61	119,9 (3)
O22—P2—O12	119,1 (1)	C11—C61—C51	118,9 (3)
O22—P2—O(L23)	111,0 (1)	C22—C12—C62	120,2 (3)
O12—P2—O(L23)	107,0 (1)	C22—C12—N2	120,0 (3)
O22—P2—O(L12 ⁱ)	106,6 (1)	C62—C12—N2	119,7 (3)
O12—P2—O(L12 ^j)	108,7 (1)	C12—C22—C32	120,1 (3)
O(L23)—P2—O(L12 ^k)	103,3 (1)	C42—C32—C22	119,9 (3)
O13—P3—O23	118,7 (1)	O2—C42—C32	122,9 (3)
O13—P3—O(L23)	106,5 (1)	O2—C42—C52	117,4 (3)
O23—P3—O(L23)	109,9 (1)	C32—C42—C52	119,7 (3)
O13—P3—O(L13)	110,5 (1)	C62—C52—C42	120,3 (3)
O23—P3—O(L13)	109,8 (1)	C52—C62—C12	119,8 (3)
O(L23)—P3—O(L13)	106,6 (1)	C63—C13—C23	120,5 (3)
P2 ⁱ —O(L12)—P1	135,1 (1)	C63—C13—N3	120,1 (3)
P1—O(L13)—P3	127,5 (1)	C23—C13—N3	119,3 (3)
P2—O(L23)—P3	136,5 (1)	C13—C23—C33	119,8 (3)
P3—P1—P2 ⁱ	109,30 (4)	C43—C33—C23	120,1 (3)
P3—P2—P1 ⁱ	91,91 (3)	O3—C43—C33	122,6 (3)
P1—P3—P2	108,62 (3)	O3—C43—C53	117,7 (3)
C61—C11—C21	122,0 (3)	C33—C43—C53	119,7 (3)
C61—C11—N1	118,5 (3)	C63—C53—C43	120,2 (3)
C21—C11—N1	119,5 (3)	C13—C63—C53	119,7 (3)

Code de symétrie: (i) $1 - x, -y, 1 - z$.

Tableau 3. Distances et liaisons hydrogène (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H(O1)...O11 ⁱ	0,87 (4)	1,76 (4)	2,619 (3)	166 (4)
O2—H(O2)...O12 ⁱⁱ	0,81 (4)	1,92 (4)	2,716 (3)	168 (4)
O3—H(O3)...O22 ⁱⁱⁱ	0,82 (5)	1,92 (5)	2,735 (3)	169 (5)
O(W1)—H1W1...O1 ⁱⁱⁱ	0,89 (5)	1,94 (5)	2,815 (4)	165 (4)
O(W1)—H2W1...O1 ^{iv}	0,75 (6)	2,54 (6)	3,056 (4)	128 (5)
O(W2)—H1W2...O23	0,82 (5)	1,97 (5)	2,783 (3)	177 (5)
O(W2)—H2W2...O(W1 ^v)	0,87 (5)	1,96 (5)	2,815 (4)	165 (5)
O(W3)—H1W3...O(W4 ^v)	0,96 (5)	1,77 (6)	2,721 (4)	171 (4)
O(W3)—H2W3...O2 ^v	0,86 (6)	2,14 (6)	2,964 (4)	158 (5)
O(W4)—H1W4...O3 ⁱ	0,74 (5)	2,14 (5)	2,871 (4)	169 (6)
O(W4)—H2W4...O11	0,84 (6)	2,15 (6)	2,994 (4)	173 (6)
N1—H1N1...O13 ^{vi}	0,88 (3)	1,79 (4)	2,671 (3)	176 (3)
N1—H2N1...O22	0,95 (4)	1,85 (4)	2,796 (3)	173 (3)
N1—H3N1...O21	0,96 (4)	1,92 (4)	2,828 (4)	157 (3)
N2—H1N2...O21 ^{iv}	0,94 (4)	1,88 (4)	2,806 (3)	170 (3)
N2—H2N2...O(W2 ^{vii})	0,89 (4)	1,88 (4)	2,774 (4)	177 (3)
N2—H3N2...O(W3 ⁱ)	0,96 (5)	1,86 (5)	2,795 (4)	164 (4)
N3—H1N3...O12 ^{viii}	0,99 (4)	1,82 (4)	2,784 (3)	164 (3)
N3—H2N3...O(W1)	0,89 (4)	2,14 (4)	3,029 (4)	175 (3)
N3—H3N3...O23	0,93 (4)	1,91 (4)	2,824 (4)	167 (3)

Codes de symétrie: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, 1 + y, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iv) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (v) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (vi) $1 - x, -y, 1 - z$; (vii) $-x, 1 - y, 1 - z$; (viii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

La largeur de balayage est (0,67 + 1,01tgθ)°. Les intensités ont été corrigées des facteurs de Lorentz et de polarisation. La structure a été résolue par les méthodes directes puis affinée par la méthode des moindres carrés.

Collection des données: CAD-4 EXPRESS (Duisenberg, 1992; Macicek & Yordanov, 1992). Affinement des paramètres de la maille: CAD-4 EXPRESS. Réduction des données: MolEN (Fair, 1990). Programme pour la solution de la structure: SHELXS86 (Sheldrick, 1985). Programme pour l'affinement de la structure: SHELXL93 (Sheldrick, 1993). Les dessins ont été obtenus à l'aide de ORTEPII (Johnson, 1976). Programme pour la préparation du manuscrit: SHELXL93.

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène et des distances et angles ont été déposées au dépôt d'archives de l'UITC (Référence: DU1139). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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Dimethyl 2,2,6,6-Tetramethyl-3,5-dioxo-4-oxaheptanedioate

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Abstract

The title compound, C₁₂H₁₈O₇, crystallizes with the anhydride moiety non-planar and in the *trans,trans* conformation. The stability of this compound suggests that quaternary C atoms attached to carbonyl C atoms have a stabilizing influence on acyclic anhydride compounds.

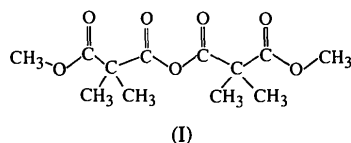
Comment

While the Cambridge Structural Database (1994) contains more than 200 examples of structures of molecules

containing an anhydride group, more than 80% of them are cyclic anhydrides in which the anhydride group is incorporated in a five-membered ring. A smaller number show the anhydride group incorporated in a six-membered ring. For these cyclic anhydride compounds, the torsion angles $C-C_{\text{carbonyl}}-O_{\text{bridging}}-C_{\text{carbonyl}}$ are close to 0° and the anhydride conformation is referred to as *cis,cis* (Valle, Toniolo & Jung, 1986). Carbonyl groups are constrained to near coplanarity when the anhydride group is incorporated in a five-membered ring.

Many examples of open-chain anhydride structures have at least one of the carbonyl groups attached to a phenyl ring or to an unsaturated C atom. A further group of structures, smaller in number, have the bonding of at least one carbonyl C atom to a quaternary C atom in common. There are no acyclic anhydride structures which do not fall into one of these categories. Thus, it appears that the presence of the quaternary C atom stabilizes the anhydride moiety in some way.

For acyclic anhydride compounds, the $C_{\text{carbonyl}}-O_{\text{bridging}}-C_{\text{carbonyl}}-C$ torsion angles are *transoid* and the conformation is referred to as *trans,trans*. Furthermore, the carbonyl groups may deviate significantly from coplanarity as quantified by the interplanar angle between the two $C(=O)-O$ planes. An interplanar angle of 37.4° is observed in α -(phthalimido)isobutyric anhydride (Valle, Toniolo & Jung, 1986) and this angle is 48.8° in benzyloxycarbonyl-1-aminocyclohexane-1-carboxylic anhydride (Valle, Crisma, Toniolo, Sen, Sukumar & Balaram, 1988).



The title compound, (I), shows a *trans,trans* conformation of the anhydride group, with an interplanar angle of 6.5° . The $C(4)-O(4)-C(5)$ angle is opened to $124.8(3)^\circ$. Atoms $C(9)$, $C(3)$, $C(4)$, $O(3)$, $O(4)$, $C(5)$,

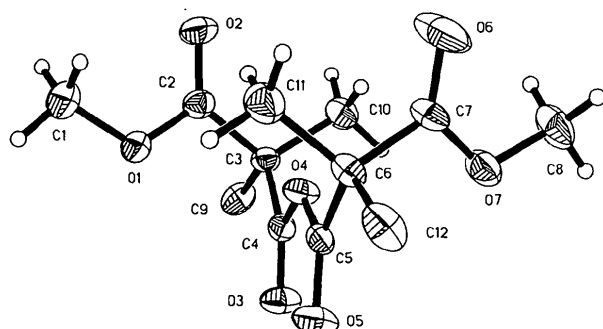


Fig. 1. Projection view of the title compound with displacement ellipsoids shown at the 50% probability level for non-H atoms. H atoms are represented as spheres of arbitrary radii except for those bonded to $C(9)$ and $C(12)$, which have been omitted for clarity.

$O(5)$, $C(6)$ and $C(12)$ are coplanar, with an average standard deviation of 0.0591 \AA . Bond distances, however, reveal no electron delocalization involving atoms $C(9)$ and $C(12)$. The ester groups are *trans* relative to the plane of the anhydride moiety, as are the $C(10)$ and $C(11)$ methyl groups.

Experimental

Dimethyl 2,2,6,6-tetramethyl-3,5-dioxo-4-oxaheptanedioate was prepared by mixing dimethylmalonic acid monomethyl ester (50 mmol) with thionyl chloride (50 mmol) in 150 ml of benzene followed by stirring (2 h). The methyl 2,2-dimethylmalonyl chloride formed reacted further with excess dimethylmalonic acid monomethyl ester present to form the anhydride as a side product. This crystallized as clear rhombic crystals from the oily reaction residue.

Crystal data

$C_{12}H_{18}O_7$
 $M_r = 274.3$
 Triclinic
 $P\bar{1}$
 $a = 8.052(2) \text{ \AA}$
 $b = 9.627(3) \text{ \AA}$
 $c = 10.017(3) \text{ \AA}$
 $\alpha = 72.38(2)^\circ$
 $\beta = 73.20(2)^\circ$
 $\gamma = 88.54(2)^\circ$
 $V = 706.9(4) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.289 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 53 reflections
 $\theta = 3.5-20.0^\circ$
 $\mu = 0.107 \text{ mm}^{-1}$
 $T = 301 \text{ K}$
 Rhombic
 $0.25 \times 0.25 \times 0.25 \text{ mm}$
 Colorless

Data collection

Siemens P4 four-circle diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 1667 measured reflections
 1292 independent reflections
 962 observed reflections
 $[F > 4.0\sigma(F)]$

$R_{\text{int}} = 0.0477$
 $\theta_{\text{max}} = 20^\circ$
 $h = -7 \rightarrow 7$
 $k = -8 \rightarrow 8$
 $l = 0 \rightarrow 9$
 3 standard reflections monitored every 97 reflections
 intensity decay: 7.71%

Refinement

Refinement on F
 $R = 0.0406$
 $wR = 0.0516$
 $S = 1.15$
 962 reflections
 173 parameters
 $w = 1/[\sigma^2(F) + 0.008F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.21 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$
 Atomic scattering factors from Ibers & Hamilton (1984)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^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}
C(1)	0.1098 (6)	0.3802 (5)	0.1252 (5)	0.065 (2)
O(1)	0.2404 (3)	0.2961 (3)	0.1777 (3)	0.050 (1)
C(2)	0.3593 (5)	0.3648 (5)	0.2075 (4)	0.042 (2)

O(2)	0.3696 (4)	0.4947 (3)	0.1837 (3)	0.072 (2)
C(3)	0.4802 (4)	0.2601 (4)	0.2691 (4)	0.037 (2)
C(4)	0.3708 (5)	0.1255 (5)	0.3820 (4)	0.038 (2)
O(3)	0.3885 (3)	0.0024 (3)	0.3853 (3)	0.056 (1)
O(4)	0.2464 (3)	0.1700 (3)	0.4842 (3)	0.042 (1)
C(5)	0.1204 (5)	0.0775 (5)	0.6018 (4)	0.037 (2)
O(5)	0.1006 (4)	-0.0487 (3)	0.6217 (3)	0.058 (1)
C(6)	0.0181 (4)	0.1668 (4)	0.6939 (4)	0.039 (2)
C(7)	0.1433 (5)	0.2418 (5)	0.7424 (4)	0.046 (2)
O(6)	0.1319 (5)	0.3611 (4)	0.7525 (5)	0.104 (2)
O(7)	0.2646 (4)	0.1569 (3)	0.7753 (3)	0.056 (1)
C(8)	0.3968 (6)	0.2144 (5)	0.8183 (5)	0.069 (2)
C(9)	0.6046 (5)	0.2123 (4)	0.1460 (4)	0.055 (2)
C(10)	0.5795 (5)	0.3286 (4)	0.3448 (5)	0.059 (2)
C(11)	-0.0773 (6)	0.2795 (5)	0.6041 (5)	0.063 (2)
C(12)	-0.1100 (5)	0.0641 (5)	0.8310 (4)	0.062 (2)

Table 2. Selected geometric parameters (Å, °)

O(7)—C(7)	1.308 (5)	C(3)—C(4)	1.526 (5)
O(7)—C(8)	1.436 (7)	C(3)—C(9)	1.530 (6)
O(1)—C(2)	1.326 (6)	C(3)—C(10)	1.526 (7)
O(1)—C(1)	1.434 (6)	C(6)—C(5)	1.508 (6)
O(4)—C(5)	1.389 (4)	C(6)—C(7)	1.519 (7)
O(3)—C(4)	1.182 (6)	C(6)—C(12)	1.529 (5)
C(4)—O(4)	1.373 (5)	C(6)—C(11)	1.530 (6)
O(5)—C(5)	1.178 (6)	C(2)—O(2)	1.200 (6)
C(3)—C(2)	1.505 (6)	C(7)—O(6)	1.183 (7)
C(7)—O(7)—C(8)	118.4 (4)	C(12)—C(6)—C(11)	111.1 (3)
C(2)—O(1)—C(1)	118.1 (3)	O(1)—C(2)—C(3)	111.4 (4)
C(5)—O(4)—C(4)	124.8 (3)	O(1)—C(2)—O(2)	123.3 (4)
C(2)—C(3)—C(4)	108.0 (3)	C(3)—C(2)—O(2)	125.3 (4)
C(2)—C(3)—C(9)	109.4 (3)	O(4)—C(5)—O(5)	124.0 (4)
C(4)—C(3)—C(9)	108.4 (3)	O(4)—C(5)—C(6)	108.4 (3)
C(2)—C(3)—C(10)	111.1 (3)	O(5)—C(5)—C(6)	127.6 (3)
C(4)—C(3)—C(10)	108.6 (3)	O(4)—C(4)—O(3)	124.3 (3)
C(9)—C(3)—C(10)	111.3 (3)	O(4)—C(4)—C(3)	108.6 (3)
C(5)—C(6)—C(7)	108.5 (3)	O(3)—C(4)—C(3)	127.1 (3)
C(5)—C(6)—C(12)	108.8 (3)	O(7)—C(7)—C(6)	111.8 (4)
C(7)—C(6)—C(12)	108.1 (3)	O(7)—C(7)—O(6)	123.5 (5)
C(5)—C(6)—C(11)	109.6 (4)	C(6)—C(7)—O(6)	124.7 (4)
C(7)—C(6)—C(11)	110.7 (4)		

A variable scan rate, with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 40°, was used. Refinement was completed using full-matrix least-squares methods. H atoms were included in fixed positions with isotropic U values determined by assuming that they were riding on the methyl C atoms.

Data collection: XSCANS (Siemens, 1991). Cell refinement: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXS86. Molecular graphics: XP (Siemens, 1990). Software used to prepare material for publication: XP.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1201). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-(4-Bromophenyl)-5,6-dichloro-nicotinamide and 6-Chloro-5-fluoro-N-(3-pyridyl)nicotinamide

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Abstract

The title compounds, *N*-(4-bromophenyl)-5,6-dichloro-nicotinamide, C₁₂H₇BrCl₂N₂O, and 6-chloro-5-fluoro-*N*-(3-pyridyl)nicotinamide, C₁₁H₇ClFN₃O, crystallize as almost planar molecules held together by intermolecular hydrogen bonding. The dichloro compound shows C—Cl distances of 1.69 (2) and 1.725 (15) Å at C6 and C5, respectively. These compounds are representatives of a class of compounds biologically important as herbicidal, pesticidal or fungicidal agents.

Comment

Substituted nicotinamides (Heaney, Shephard, Crowley & Shearing, 1988), 2,5- and 5,6-disubstituted nicotinic acids (Setliff & Huie, 1981), and benzamidopyridine derivatives (Setliff & Palmer, 1987) have shown fungicidal and herbicidal activities towards barnyard grasses and wheat leaf rust. It has been observed that halogenated derivatives show increased activity. One compound, a halogenated benzamidopyridine derivative (Setliff & Rankin, 1988), effected a 70% growth reduction of giant foxtail weed. Substituted 5-bromo-6-chloronicotinic acid derivatives (Setliff & Caldwell, 1991) have proven to show activity towards the apple scab fungus and fall army worm. Based on the promise of these earlier studies, a series of halonicotinamide derivatives (Setliff & Soman, 1992; Soman, 1992) were synthesized to allow evaluation of their potential as active fungicides and herbicides, among them, *N*-