

Literatur

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2-Nitrophenyl Phenoxyformate, C₁₃H₉NO₅

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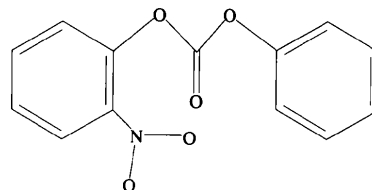
Abstract

The title mononitrodiphenyl carbonate constitutes the simplest congener in the arylnitrocarbonate family. The structure contains two independent molecules. The two O—C (ester) bond lengths average 1.340 (7) (phenyl) and 1.354 (6) Å (nitrophenyl). The average C=O (carbonyl) bond length is 1.180 (7) Å. In both molecules there is a close intramolecular interaction between an O atom of the nitro group and the carbonyl C atom. The configuration and the average C···O distance [2.672 (7) Å] are similar to those observed in other nitrophenyl carbonate structures.

Comment

The study of the structure of mono-*ortho*-nitrodiphenyl carbonate (I) is part of our continuing work in the area of aryl carbonate chemistry (King & Bryant, 1990, 1993; King & Codella, 1990). Nitro-substituted aryl carbonates show enhanced reactivity towards transesterification relative to the parent diphenyl carbonate (DPC) under basic conditions. Symmetrically substituted nitroaryl carbonates are known to have an O atom on each *ortho*-nitro group orientated towards the carbonyl moiety (King & Bryant, 1990); O_(nitro)···C_(carbonyl) interatomic distances average 2.75 (2) Å in 2,2'-dinitrodiphenyl carbonate (DNDPC) and 2.65 (6) Å in 2,2',4,4'-tetranitrodiphenyl carbonate (TNDPC). The present crystal structure work indicates that symmetrically substituted systems are not required for the observed nitro-group orientation. A single *ortho*-nitro

substituent is sufficient. The O_(nitro)···C_(carbonyl) distance [2.672 (7) Å] is similar to those reported earlier. The inherent polarity of each group is a probable source for this preferred orientation. The determined carbonyl bond length of 1.180 (7) Å is similar to that in TNDPC [1.178 (3) Å] but slightly shorter than in the parent DPC [1.191 (3)] and in DNDPC [1.188 (4) Å].



The two independent molecules have slightly different relative conformations. The unsubstituted phenyl rings in each structure have similar orientations relative to the carbonate plane, with C(1)—O(2)—C(2)—C(3) = -120.8 (5) and C(14)—O(7)—C(15)—C(20) = -112.6 (6)°. However, the *ortho*-nitro-substituted phenyl rings are orientated quite differently due to the two (possible) energy minima existing for the dipole–dipole interactions between the carbonyl and nitro group moieties. In the first molecule, the phenyl ring is almost perpendicular to the carbonate [C(1)—O(3)—C(8)—C(9) = -75.5 (6)°], the phenyl and nitro groups are close to coplanarity with each other [C(8)—C(9)—N(1)—O(5) = 10.9 (8)°], as are the carbonate and nitro groups [C(1)···O(5)—N(1)—C(9) = 11.1 (6)°]. In the second molecule, the *ortho*-nitro-substituted phenyl ring is canted 52.9 (7)° relative to the plane of the carbonate moiety [C(14)—O(8)—C(21)—C(22)] and the nitro group is twisted out of coplanarity with the phenyl ring [C(21)—C(22)—N(2)—O(10) = 31.8 (8)°]. The carbonate–nitro orientation is substantially twisted relative to that in the first structure [C(14)···O(10)—N(2)—C(22) = -56.0 (7)°].

The principal conformational difference between the two molecules results from the orientation of the group dipole–dipole interactions. In the first molecule, only an O atom [O(5)] of the nitro group is orientated towards the carbonyl C atom [C(1)···O(5) = 2.614 (7) Å] and there is no interaction between N(1) and O(1) [3.435 (7) Å]; this allows the nitro group to orientate

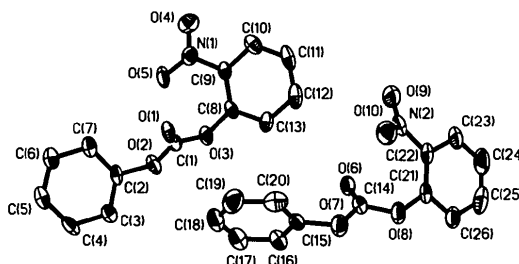


Fig. 1. Displacement ellipsoid (50% probability) plot.

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essentially perpendicular to the carbonate plane and coplanar with the aromatic ring. In the second molecule, both the carbonyl atoms, C(14) and O(6), interact with N(2) and O(10) of the nitro group [C(14)···O(10) = 2.729 (7), O(6)···N(2) = 2.843 (7) Å].

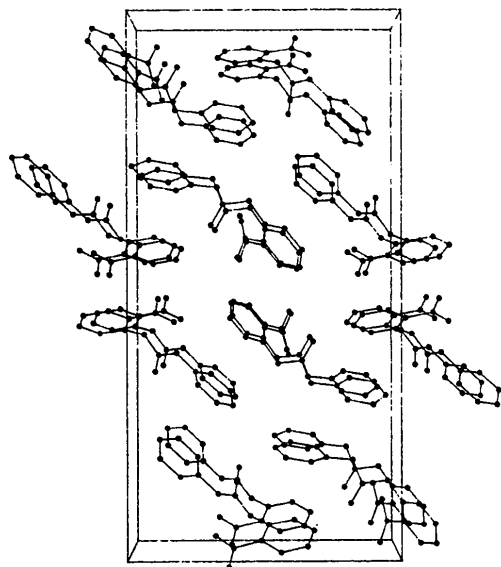


Fig. 2. Projected packing plot viewed down the *b* axis.

Experimental

The title compound was obtained by the reaction of 2-nitrophenol with phenyl chloroformate in acetonitrile, and recrystallized from methylene chloride/pentane at 298 K. The crystal was sealed in a glass capillary under dry nitrogen because of its moisture sensitivity.

Crystal data

C₁₃H₉NO₅
M_r = 259.2
 Monoclinic
*P*2₁/*n*
a = 14.445 (3) Å
b = 5.767 (1) Å
c = 28.603 (5) Å
 β = 90.27 (2)°
V = 2382.8 (8) Å³
Z = 8
D_x = 1.445 Mg m⁻³

Cu *K*α radiation
 λ = 1.54178 Å
 Cell parameters from 21 reflections
 θ = 3.13–20.545°
 μ = 0.917 mm⁻¹
T = 213.9 K
 Needle
 0.36 × 0.16 × 0.08 mm
 Colourless

Data collection

Siemens *R3mV* upgrade of
 Nicolet *P3F* diffractometer

Wycoff scans

Absorption correction:
 none

3181 measured reflections
 2693 independent reflections
 2025 observed reflections
 $[F > 2\sigma(F)]$

*R*_{int} = 0.021
 θ_{\max} = 52.5°
h = -2 → 14
k = -5 → 5
l = -29 → 29
 3 standard reflections
 monitored every 47 reflections
 intensity decay: 6, 7, 6%

Refinement

Refinement on *F*
R = 0.066
wR = 0.087
S = 0.91
 2025 reflections
 343 parameters
 $w = 1/\sigma^2(F)$
 $(\Delta/\sigma)_{\max} = 0.016$

$\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.46 \text{ e \AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV, Table
 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
C(14)	0.1441 (3)	0.0329 (10)	0.1409 (2)	0.034 (2)
O(6)	0.1856 (2)	0.0156 (7)	0.1056 (1)	0.039 (1)
O(7)	0.1776 (2)	0.0521 (7)	0.1847 (1)	0.046 (1)
C(15)	0.2754 (3)	0.0423 (10)	0.1897 (2)	0.036 (2)
C(16)	0.3276 (4)	0.2245 (10)	0.1763 (2)	0.041 (2)
C(17)	0.4225 (4)	0.2214 (12)	0.1843 (2)	0.050 (2)
C(18)	0.4605 (4)	0.0339 (12)	0.2071 (2)	0.052 (2)
C(19)	0.4067 (4)	-0.1467 (13)	0.2212 (2)	0.056 (2)
C(20)	0.3119 (4)	-0.1463 (11)	0.2123 (2)	0.047 (2)
O(8)	0.0516 (2)	0.0466 (7)	0.1462 (1)	0.045 (1)
C(21)	-0.0039 (3)	0.0116 (10)	0.1064 (2)	0.039 (2)
C(22)	0.0018 (3)	-0.1756 (11)	0.0777 (2)	0.043 (2)
C(23)	-0.0593 (4)	-0.1980 (13)	0.0394 (2)	0.057 (2)
C(24)	-0.1252 (4)	-0.0323 (15)	0.0320 (3)	0.067 (3)
C(25)	-0.1313 (4)	0.1536 (14)	0.0616 (3)	0.063 (3)
C(26)	-0.0700 (4)	0.1831 (11)	0.0984 (2)	0.049 (2)
N(2)	0.0679 (3)	-0.3673 (10)	0.0855 (2)	0.050 (2)
O(9)	0.0979 (3)	-0.4704 (9)	0.0513 (2)	0.072 (2)
O(10)	0.0881 (3)	-0.4132 (8)	0.1260 (2)	0.061 (2)
C(1)	0.6069 (3)	-0.2304 (10)	0.1277 (2)	0.032 (2)
O(1)	0.5987 (2)	-0.3756 (7)	0.1563 (1)	0.036 (1)
O(2)	0.6687 (2)	-0.0588 (6)	0.1256 (1)	0.041 (1)
C(2)	0.7402 (3)	-0.0612 (10)	0.1605 (2)	0.034 (2)
C(3)	0.7454 (3)	0.1296 (10)	0.1886 (2)	0.037 (2)
C(4)	0.8176 (4)	0.1367 (11)	0.2220 (2)	0.045 (2)
C(5)	0.8803 (4)	-0.0439 (11)	0.2239 (2)	0.043 (2)
C(6)	0.8734 (3)	-0.2313 (11)	0.1944 (2)	0.041 (2)
C(7)	0.8014 (3)	-0.2421 (11)	0.1618 (2)	0.040 (2)
O(3)	0.5508 (2)	-0.1954 (6)	0.0900 (1)	0.036 (1)
C(8)	0.4868 (3)	-0.3661 (10)	0.0796 (2)	0.031 (2)
C(9)	0.5115 (3)	-0.5763 (10)	0.0586 (2)	0.031 (2)
C(10)	0.4440 (4)	-0.7325 (10)	0.0444 (2)	0.038 (2)
C(11)	0.3518 (4)	-0.6792 (12)	0.0525 (2)	0.045 (2)
C(12)	0.3268 (4)	-0.4733 (12)	0.0727 (2)	0.044 (2)
C(13)	0.3942 (3)	-0.3196 (11)	0.0871 (2)	0.038 (2)
N(1)	0.6080 (3)	-0.6387 (9)	0.0486 (2)	0.038 (2)
O(4)	0.6226 (3)	-0.8037 (8)	0.0229 (1)	0.051 (2)
O(5)	0.6710 (3)	-0.5191 (8)	0.0652 (1)	0.057 (2)

Table 2. Selected geometric parameters (Å, °)

C(14)—O(6)	1.183 (6)	C(1)—O(1)	1.176 (7)
C(14)—O(7)	1.345 (6)	C(1)—O(2)	1.335 (7)
C(14)—O(8)	1.347 (6)	C(1)—O(3)	1.360 (6)
O(7)—C(15)	1.420 (6)	O(2)—C(2)	1.434 (6)
O(8)—C(21)	1.403 (6)	O(3)—C(8)	1.383 (6)
C(22)—N(2)	1.477 (8)	C(9)—N(1)	1.468 (6)
N(2)—O(9)	1.227 (8)	N(1)—O(4)	1.222 (6)
N(2)—O(10)	1.223 (8)	N(1)—O(5)	1.235 (6)
O(7)—C(14)—O(8)	104.1 (4)	C(22)—N(2)—O(9)	118.1 (5)
O(6)—C(14)—O(8)	127.4 (5)	C(1)—O(3)—C(8)	117.4 (4)
C(14)—O(8)—C(21)	117.6 (4)	C(9)—N(1)—O(5)	119.1 (5)
C(22)—N(2)—O(10)	117.3 (5)	C(9)—N(1)—O(4)	118.3 (4)
C(14)—O(7)—C(15)—C(20)	-112.6 (6)	C(1)—O(3)—C(8)—C(9)	-75.5 (6)
C(14)—O(8)—C(21)—C(22)	52.9 (7)	C(8)—C(9)—N(1)—O(5)	10.9 (8)
C(1)—O(2)—C(2)—C(3)	-120.8 (5)		

The structure was solved by direct methods and refined on F using the *SHELXTL-Plus* (MicroVAX II) program package (Sheldrick, 1987). H atoms were placed in idealized positions, and constrained to have $C-H = 0.96 \text{ \AA}$ and isotropic displacement parameters $U = 0.08 \text{ \AA}^2$. All non-H atoms were treated as anisotropic.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1151). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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S-Benzylisothiuronium Hydrogen 2-Oxopentanedioate, $C_8H_{11}N_2S^+ \cdot C_5H_5O_5^-$

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Abstract

The 5-carboxylic acid end of the 2-oxopentanedioate group of *S*-benzylisothiuronium hydrogen 2-oxopentanedioate is linked by a hydrogen bond [$O \cdots O = 2.653(9) \text{ \AA}$] across a centre of inversion to give rise to a dianionic species. At the free carboxyl end, the two carboxyl O atoms form hydrogen bonds to the amino groups belonging to four adjacent cations [$O \cdots N = 2.757(9), 2.889(9), 2.785(8), 2.844(7) \text{ \AA}$].

Comment

The compound, (I), was synthesized for use in a condensation reaction with triphenyltin hydroxide to yield the $[(C_6H_5)_3SnO_2CCH_2CH_2COCO_2]^-$ anion, following the structural characterization of the $[(C_6H_5)_3SnO_2CCH_2CH_2CO_2]^-$ (Ng, Kumar Das, Xiao, van der Helm, Holecek & Lycka, 1991) and $[(C_6H_5)_3SnO_2CCO_2]^-$ (Ng & Kumar Das, 1993) stannate ions.

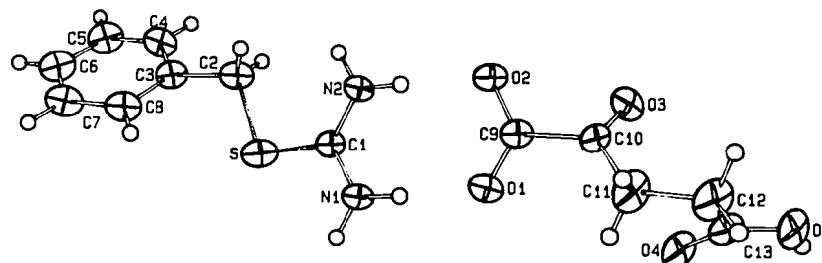
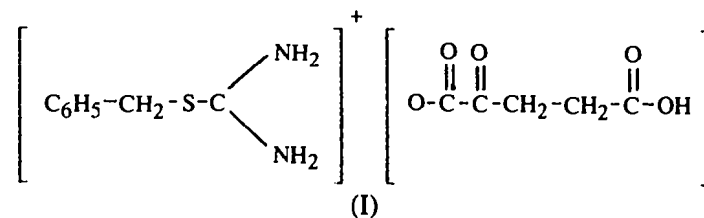


Fig. 1. ORTEP (Johnson, 1976) plot of the title compound showing the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The compound was synthesized from monosodium 2-oxoglutarate and *S*-benzylisothiuronium hydrochloride in water (Furniss, Hannaford, Smith & Tatchell, 1989), and transparent crystals were grown from an ethanol solution of the compound.

Crystal data

$C_8H_{11}N_2S^+ \cdot C_5H_5O_5^-$
 $M_r = 312.35$
 Monoclinic
 $P2_1/n$
 $a = 16.380(3) \text{ \AA}$
 $b = 5.5227(5) \text{ \AA}$
 $c = 17.355(3) \text{ \AA}$
 $\beta = 108.78(8)^\circ$
 $V = 1486.3(4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.396 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 6-10^\circ$

$\mu = 0.229 \text{ mm}^{-1}$

$T = 300 \text{ K}$

Platelet

$0.25 \times 0.25 \times 0.07 \text{ mm}$

Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scan (North, Phillips & Mathews, 1968)

$T_{\min} = 0.9173$, $T_{\max} = 0.9999$

3035 measured reflections

2723 independent reflections

1186 observed reflections [$I > 3\sigma(I)$]

$R_{\text{int}} = 0.025$

$\theta_{\max} = 25^\circ$

$h = 0 \rightarrow 19$

$k = 0 \rightarrow 6$

$l = -20 \rightarrow 19$

3 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on F

$R = 0.060$

$wR = 0.069$

$S = 0.465$

1186 reflections

190 parameters

H-atom parameters not refined

$w = 1/[\sigma^2(F) + 0.0004|F|^2 + 1]$

$(\Delta/\sigma)_{\max} = 0.01$

$\Delta\rho_{\max} = 0.28(4) \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.19(4) \text{ e \AA}^{-3}$

Extinction correction: none

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