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A second polymorph of bis(*o*-nitrophenyl) carbonate

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The title compound, $C_{13}H_8N_2O_7$, displays *s-cis–s-cis* conformation of the carbonate group. Bond lengths and angles (Å and °) involving this group are: C═O 1.1839 (13), C—O 1.3462 (13) and 1.3483 (13), O—C_{arom} 1.3947 (13) and 1.3994 (13); O═C—O 127.21 (10) and 127.02 (10), O—C—O 105.77 (9). The aromatic rings are perpendicular to the carbonate plane.

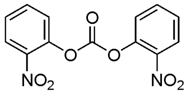
Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.002 Å
R factor = 0.034
wR factor = 0.097
Data-to-parameter ratio = 16.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

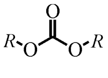
Comment

Bis(*o*-nitrophenyl) carbonate, (I), was synthesized some 50 years ago (Deutsch & Fernö, 1950), but has not been widely used in synthesis, in contrast to its *p*-isomer, which has been used for activating the carboxylate group in peptide synthesis (Glatthard & Matter, 1963) and as a carbonylation reagent (Nesnyov & Pel'kis, 1962; Izdebsky & Pawlok, 1989; Takata *et al.*, 1991; Enders *et al.*, 1999). Recently we noticed that the *o*-isomer is more reactive than the *p*-isomer in reactions with N-nucleophiles in organic solvents (Simon *et al.*, 2002), a property that might be extended to other reactions.

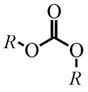


(I)

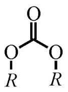
As part of our investigations of the structure and reactivity of organic carbonates, we have begun to study the solid state structures of some organic carbonates. Here we present the structure of (I). This had already been determined by King & Bryant (1990) in space group *Pc* (with *Z* = 2) after recrystallization from dichloromethane/hexane; our structure, recrystallized from benzene, represents a new polymorph.



s-cis-s-cis



s-cis-s-trans



s-trans-s-trans

In principle, the *s-cis–s-cis*, *s-cis–s-trans* or *s-trans–s-trans* conformations are all possible for organic carbonates; early studies of dimethyl and diphenyl carbonate by IR spectroscopy (Oki & Nakanishi, 1971) or by dipole moments and Molar Kerr constants (Chia *et al.*, 1981) showed that the probable conformations were *s-cis–s-cis* or *s-cis–s-trans*. However, molecular polarization measurements of various diaryl carbonates by Exner & Jehlicka (1981) established that all investigated organic carbonates adopted only the *s-cis–s-cis*

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conformation. Finally, X-ray investigations of diphenyl (King & Bryant, 1993), bis(*o*-nitrophenyl) and bis(2,4-dinitrophenyl) carbonates (King & Bryant, 1990) unambiguously demonstrated *s-cis-s-cis* conformations.

The molecule of (I) is shown in Fig. 1. The carbonate moiety displays the *s-cis–s-cis* conformation (*cf.* torsion angles in Table 1); atoms C11 and C21 lie 0.186 (2) and 0.155 (2) Å, respectively, on opposite sides of the plane defined by C1, O1, O2 and O3. The aromatic rings are perpendicular to this plane [interplanar angles 86.41 (3) and 86.86 (3)°]. In the previous modification (King & Bryant, 1990), only one aromatic ring was perpendicular to the carbonate group; corresponding angles were 89.9 and 54.6°.

Bond lengths and angles of the carbonate moiety (Table 1) may be considered normal. A search of the Cambridge Structural Database (Allen, 2002) for the diaryl carbonate moiety revealed 15 hits, with mean values of 105.7° for the O—C—O and 127.1° for the O═C—O angles, 1.175 Å for the C═O and 1.342 Å for the C—O bonds of 21 carbonate groups. Some of the structures involved cyclic carbonate oligomers (Nagahata *et al.*, 2000).

Short intramolecular contacts C1···O5, 2.7829 (14), and C1···O7, 2.7228 (13) Å, are observed, as are intermolecular contacts O2···C23, 2.9642 (14), and O3···N2, 3.0143 (13) Å (operator for second atoms: $x, \frac{1}{2} - y, \frac{1}{2} + z$). The molecular packing is further determined by four weak C—H···O hydrogen bonds (Table 2).

The structure of the corresponding *para* derivative is described in the following paper (Simon *et al.*, 2003).

Experimental

Triphosgene (bis(trichloromethyl) carbonate) was treated with six equivalents of *o*-nitrophenol and six equivalents of triethylamine in dichloromethane and the product was recrystallized from benzene (Simon *et al.*, 2001).

Crystal data

$C_{13}H_8N_2O_7$
$M_r = 304.21$
Monoclinic, $P2_1/c$
$a = 11.9789$ (12) Å
$b = 11.9076$ (12) Å
$c = 9.1495$ (11) Å
$\beta = 92.128$ (3)°
$V = 1304.2$ (2) Å^3
$Z = 4$
$D_x = 1.549$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4316 reflections
$\theta = 2.4$–27.0°
$\mu = 0.13$ mm^{-1}
$T = 133$ (2) K
Prism, colourless
0.55 × 0.27 × 0.17 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: none
9339 measured reflections
3286 independent reflections
2594 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$
$\theta_{\rm max} = 28.5°$
$h = -16 \rightarrow 15$
$k = -11 \rightarrow 15$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.097$
$S = 1.06$
3286 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 0.1183P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}

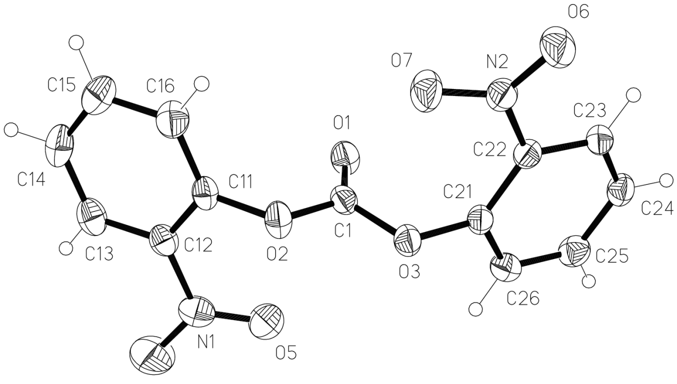

Figure 1
The molecule of the title compound in the crystal. Ellipsoids are drawn at the 50% probability level and H-atom radii are arbitrary.

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.1839 (13)	O3—C1	1.3483 (13)
O2—C1	1.3462 (13)	O3—C21	1.3994 (13)
O2—C11	1.3947 (13)		
C1—O2—C11	115.40 (8)	O1—C1—O3	127.02 (10)
C1—O3—C21	114.06 (8)	O2—C1—O3	105.77 (9)
O1—C1—O2	127.21 (10)		
C11—O2—C1—O1	8.87 (16)	C21—O3—C1—O2	−172.96 (8)
C11—O2—C1—O3	−171.56 (8)	C1—O2—C11—C12	91.49 (13)
C21—O3—C1—O1	6.62 (15)	C1—O3—C21—C22	85.88 (12)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13···O1$^{\rm i}$	0.95	2.43	3.1060 (14)	128.3
C26—H26···O1$^{\rm ii}$	0.95	2.57	3.3782 (15)	142.9
C16—H16···O6$^{\rm iii}$	0.95	2.44	3.1756 (15)	134.6
C24—H24···O6$^{\rm iv}$	0.95	2.62	3.5351 (15)	162.8

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

H atoms were included using a riding model, with fixed C—H bond lengths of 0.95 Å; $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$ of the parent atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bruker (1998). *SMART* (Version 5.0) and *SAINT* (Version 4.0). Bruker AXS Inc., Madison, Wisconsin, USA.

Chia, L. H. L., Kwan, K. J. & Huang, H. H. (1981). *Austr. J. Chem.* **34**, 349–351.

Deutsch, A. & Fernö, O. (1950). Swed. Patent 128,292; *Chem. Abstr.* 44, 9477c.

Enders, D., Wortmann, L., Dücker, B. & Raabe, G. (1999). *Helv. Chim. Acta*, **82**, 1195–1201.

Exner, O. & Jehlicka, V. (1981). *Collect. Czech. Chem. Commun.* **46**, 856–860.

Glatthard, R. & Matter, M. (1963). *Helv. Chim. Acta*, **46**, 795–798.

Izdebsky, I. & Pawlok, D. (1989). *Synthesis*, pp. 423–425.

King, J. A. Jr. & Bryant, G. L. Jr. (1990). *Acta Cryst.* C**46**, 1330–1332.

King, J. A. Jr. & Bryant, G. L. Jr. (1993). *Acta Cryst.* C**49**, 550–551.

Nagahata, R., Sugiyama, J., Goyal, M., Goto, M., Asai, M., Ueda, M. & Takeuchi, K. (2000). *Polym. Adv. Technol.* **11**, 294–300.

Nesnyov, E. P. & Pel'kis, P. S. (1962). *J. Gen. Chem. USSR*, **32**, 3929–3931.

Oki, M. & Nakanishi, H. (1971). *Bull. Chem. Soc. Jpn*, **44**, 3419–3422.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments, Madison, Wisconsin, USA.

Simon, M., Csunderlik, C., Jones, P. G., Neda, I. & Fischer, A. K. (2003). *Acta Cryst.* E**59**, o691–o692.

Simon, M., Csunderlik, C., Medeleanu, M. & Dinache, A. (2002). *Rev. Chim.* **53**, 535–539.

Simon, M., Csunderlik, C. & Tirnaveanu, A. (2001). *Rev. Chim.* **52**, 371–376.

Takata, T., Matsuoka, H. & Endo, T. (1991). *Chem. Lett.* pp. 2091–2094.