C6	0.2078 (4)	0.1000 (3)	−0.0153 (4)	0.065
C7	0.3617 (3)	0.1890 (3)	−0.0449 (3)	0.058
C8	0.4874 (3)	0.1672 (2)	0.0640 (3)	0.046
C9	0.4860 (4)	0.1915 (3)	0.4811 (4)	0.059
C10	0.6259 (3)	0.4103 (2)	0.1728 (3)	0.042
C11	0.4975 (4)	0.5269 (3)	0.2844 (4)	0.063
C12	0.7700 (3)	0.2950 (2)	0.0597 (3)	0.046
C13	1.0408 (4)	0.3854 (4)	0.0688 (4)	0.068
C14	0.8017 (4)	0.1189 (3)	0.4058 (3)	0.054
C15	0.9370 (3)	0.2341 (3)	0.5164 (3)	0.051
C16	0.8750 (4)	0.3354 (3)	0.5567 (3)	0.050
C17	0.9890 (5)	0.1969 (4)	0.6646 (4)	0.072
C18	1.0754 (4)	0.2863 (4)	0.4418 (4)	0.069

Table 3. *Selected geometric parameters* (Å, °) *for* (II)

O5—C2	1.426 (3)	C3—C9	1.323 (3)
O5—C14	1.434 (3)	C3—C4	1.502 (4)
O6—C2	1.396 (3)	C4—C5	1.534 (4)
O6—C16	1.449 (3)	C4—C8	1.555 (3)
C1—C10	1.526 (3)	C5—C6	1.517 (4)
C1—C12	1.528 (3)	C6—C7	1.524 (4)
C1—C2	1.561 (3)	C7—C8	1.542 (4)
C1—C8	1.568 (3)	C14—C15	1.516 (4)
C2—C3	1.528 (3)	C15—C16	1.520 (4)
C2—O5—C14	112.2 (2)	C9—C3—C2	127.3 (2)
C2—O6—C16	116.7 (2)	C4—C3—C2	106.6 (2)
C10—C1—C12	107.8 (2)	C3—C4—C5	118.4 (2)
C10—C1—C2	112.3 (2)	C3—C4—C8	106.7 (2)
C12—C1—C2	113.2 (2)	C5—C4—C8	104.4 (2)
C10—C1—C8	111.3 (2)	C6—C5—C4	104.0 (2)
C12—C1—C8	109.7 (2)	C5—C6—C7	103.0 (2)
C2—C1—C8	102.5 (2)	C6—C7—C8	103.7 (2)
O6—C2—O5	112.4 (2)	C7—C8—C4	106.6 (2)
O6—C2—C3	117.5 (2)	C7—C8—C1	119.7 (2)
O5—C2—C3	108.8 (2)	C4—C8—C1	106.4 (2)
O6—C2—C1	110.1 (2)	O5—C14—C15	111.0 (2)
O5—C2—C1	102.8 (2)	C14—C15—C16	106.5 (2)
C3—C2—C1	103.8 (2)	O6—C16—C15	112.7 (2)
C9—C3—C4	126.0 (2)		
C8—C1—C2—C3	−36.2 (2)	C6—C7—C8—C1	−140.7 (2)
C1—C2—C3—C4	35.6 (2)	C3—C4—C8—C7	−131.9 (2)
C2—C3—C4—C5	−137.2 (2)	C5—C4—C8—C7	−5.9 (3)
C2—C3—C4—C8	−20.1 (3)	C3—C4—C8—C1	−3.1 (3)
C3—C4—C5—C6	148.2 (2)	C5—C4—C8—C1	123.0 (2)
C8—C4—C5—C6	29.9 (3)	C2—C1—C8—C7	144.9 (2)
C4—C5—C6—C7	−43.0 (3)	C12—C1—C8—C4	144.8 (2)
C5—C6—C7—C8	38.7 (3)	C2—C1—C8—C4	24.2 (2)
C6—C7—C8—C4	−20.1 (3)		

For crystal (I), H atoms were refined as riding on their associated atoms. The distance C4B—C3 was constrained.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structures: *TEXSAN* for (I); *SHELXS*86 (Sheldrick, 1985) for (II). For both compounds, program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry for both structures have been deposited with the IUCr (Reference: AS1138). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,2-Diiod-1,2-bis(pentamethyl-cyclopentadienyl)diphosphan

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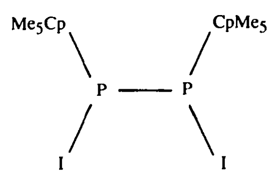
(*Eingegangen am* 14. *Oktober* 1994; *angenommen am* 16. *November* 1994)

Abstract

The title compound, 1,2-diiodo-1,2-bis(pentamethyl-cyclopentadienyl)diphosphane, $C_{20}H_{30}I_2P_2$, is obtained as the *d,l*-diastereomer with a P—P distance of 2.234 (4) Å and a small I—P—P—I torsion angle of 13.0 (2)°.

Kommentar

Bei der Synthese der Titelverbindung aus dem Cyclotriphosphan $[(Me_5Cp)P]_3$ (Jutzi, Kroos, Müller, Bögge & Penk, 1991) und elementarem Iod entstehen zwei Diastereomere, wobei sich die *meso*-Form innerhalb von ein bis zwei Stunden bei Raumtemperatur durch Inversion am Phosphor in die *d-l*-Form umwandelt. Wie Fig. 1 zeigt, hüllen die Pentamethylcyclopentadienyl (Pcp)-Liganden die Phosphoratome vollständig ein; das Diphosphan zeigt eine nahezu ekliptische Konformation mit einem Torsionswinkel I(1)—P(1)—P(2)—I(2) von 13,0 (2)°. Diese sterische Belastung führt zu einer Aufweitung der P—P—I-Winkel auf 109,9 (1) an P(1) bzw. 109,4 (1)° an P(2), verringert aber offenbar die erheblichen sterischen Wechselwirkungen zwischen den Iodatomen und den Pcp-Liganden, die bei einer gestaffelten Konformation aufträten.



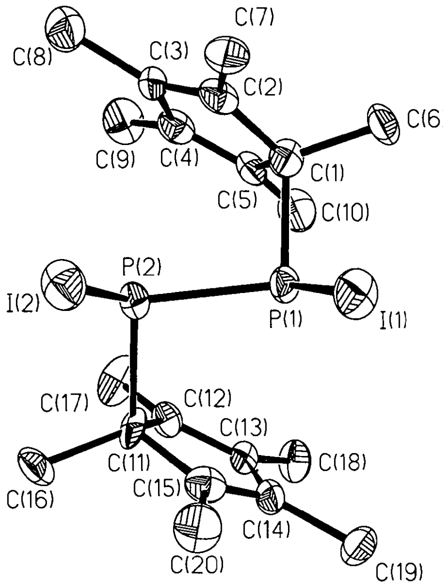


Fig. 1. Die Schwingungsellipsoide entsprechen einer Aufenthaltswahrscheinlichkeit von 50%. H-atome wurden der Übersichtlichkeit wegen weggelassen.

Experimentelles

Zu einer Lösung von 2,5 g (5,01 mmol) $[PC_5(CH_3)_5]_3$ in 25 ml thf tropft man bei 195 K eine Lösung von 1,91 g (7,52 mmol) Iod in thf. Die Lösung färbt sich dabei tiefrot. Man rührt noch 30 min und läßt die Lösung langsam auf Raumtemperatur erwärmen. Das thf wird im Vakuum weitgehend abgezogen. Kristallisation bei 253 K liefert 3,1 g (70%) roter Prismen.

Kristalldaten

$C_{20}H_{30}I_2P_2$
$M_r = 586{,}18$
Monoklin
$P2_1/n$
$a = 8{,}336$ (2) Å
$b = 18{,}259$ (5) Å
$c = 15{,}183$ (4) Å
$\beta = 91{,}58$ (2)°
$V = 2310{,}1$ (10) Å^3
$Z = 4$
$D_x = 1{,}685$ Mg m^{-3}

Mo $K\alpha$ Strahlung
$\lambda = 0{,}71073$ Å
Gitterparameter aus 31 Reflexen
$\theta = 2–13°$
$\mu = 2{,}862$ mm^{-1}
$T = 173$ (2) K
Prism
0,4 × 0,25 × 0,15 mm
Rot

Datensammlung

Siemens $P2_1$ Diffraktometer
ω-Abtastung
Absorptionskorrektur: keine
4828 gemessene Reflexe
4530 unabhängige Reflexe
3181 beobachtete Reflexe $[I > 2\sigma(I)]$
$R_{int} = 0{,}0466$

$\theta_{max} = 30{,}0°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 25$
$l = 0 \rightarrow 21$
3 Kontrollreflexe gemessen nach je 100 Reflexen
Intensitätsschwankung: ±4%

Verfeinerung

Verfeinerung auf F^2
$R[F^2 > 2\sigma(F^2)] = 0{,}0703$
$wR(F^2) = 0{,}1456$
$S = 1{,}554$
4524 Reflexe
218 Parameter
$w = 1/[\sigma^2(F_o^2) + (0{,}05P)^2]$ mit $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 2{,}464$ e Å^{-3}
$\Delta\rho_{min} = -2{,}157$ e Å^{-3}

Extinktionskorrektur: *SHELXL*93 (Sheldrick, 1993)
Extinktionskoeffizient: 0,0011 (2)
Atomformfaktoren aus *International Tables for Crystallography* (1992, Bd. C, Tabelle 4.2.6.8 und 6.1.1.4)

Tabelle 1. *Atomkoordinaten und isotrope äquivalente Verschiebungsparameter* (Å^2)

$$U_{äq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{äq}$
I(1)	0,59151 (10)	0,24400 (4)	0,30394 (5)	0,0393 (2)
I(2)	0,17515 (9)	0,22628 (4)	0,17682 (6)	0,0409 (2)
P(1)	0,6272 (3)	0,2551 (2)	0,1429 (2)	0,0260 (6)
P(2)	0,3971 (3)	0,22873 (15)	0,0709 (2)	0,0264 (6)
C(1)	0,6261 (13)	0,3576 (6)	0,1209 (6)	0,030 (2)
C(2)	0,4659 (14)	0,3940 (6)	0,1296 (7)	0,030 (2)
C(3)	0,4055 (12)	0,4067 (6)	0,0473 (7)	0,028 (2)
C(4)	0,5206 (14)	0,3852 (6)	−0,0170 (7)	0,033 (3)
C(5)	0,6550 (12)	0,3571 (6)	0,0231 (7)	0,027 (2)
C(6)	0,7627 (14)	0,3922 (6)	0,1761 (7)	0,036 (3)
C(7)	0,3920 (14)	0,4117 (6)	0,2151 (7)	0,038 (3)
C(8)	0,2410 (14)	0,4393 (7)	0,0234 (9)	0,051 (4)
C(9)	0,4923 (16)	0,3955 (7)	−0,1164 (8)	0,048 (3)
C(10)	0,8076 (14)	0,3338 (7)	−0,0165 (8)	0,045 (3)
C(11)	0,4421 (11)	0,1278 (6)	0,0490 (7)	0,027 (2)
C(12)	0,5708 (13)	0,1380 (6)	−0,0174 (7)	0,029 (2)
C(13)	0,7129 (12)	0,1133 (5)	0,0170 (6)	0,022 (2)
C(14)	0,6843 (12)	0,0848 (6)	0,1056 (7)	0,029 (2)
C(15)	0,5296 (14)	0,0903 (6)	0,1243 (7)	0,031 (2)
C(16)	0,2907 (14)	0,0888 (6)	0,0139 (8)	0,040 (3)
C(17)	0,5380 (14)	0,1674 (7)	−0,1089 (7)	0,045 (3)
C(18)	0,8729 (12)	0,1143 (6)	−0,0250 (7)	0,034 (3)
C(19)	0,8192 (14)	0,0538 (6)	0,1628 (8)	0,039 (3)
C(20)	0,4451 (15)	0,0604 (7)	0,2042 (8)	0,044 (3)

Tabelle 2. *Ausgewählte Geometrische Parameter* (Å, °)

I(1)—P(1)	2,480 (3)	P(1)—P(2)	2,234 (4)
I(2)—P(2)	2,485 (3)	P(2)—C(11)	1,911 (11)
P(1)—C(1)	1,902 (11)		
C(1)—P(1)—P(2)	97,2 (3)	C(11)—P(2)—P(1)	97,0 (3)
C(1)—P(1)—I(1)	104,7 (3)	C(11)—P(2)—I(2)	104,4 (3)
P(2)—P(1)—I(1)	109,89 (13)	P(1)—P(2)—I(2)	109,38 (13)

Sechs Reflexe mit stark negativen $|F_o|^2$ oder vermuteten systematischen Fehlern wurden ausgeschieden. Die H-Atome besetzen berechnete Positionen, $U(H) = 1{,}5 \times U_{äq}$ des entsprechenden C-Atome.

Datensammlung und Gitterkonstanten: *P*3 (Siemens, 1990). Datenreduktion und Strukturbestimmung: *SHELXS*86 (Sheldrick, 1985). Strukturverfeinerung: *SHELXL*93 (Sheldrick, 1993).

Die Listen der Strukturfaktoren, anisotropen Verschiebungsparameter, H-Atom Koordinaten und vollständigen geometrischen Daten sind bei der IUCr (Aktenzeichen: SH1103) hinterlegt. Kopien sind erhältlich durch: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Nitrophenyl Phenoxyformate, $C_{13}H_9NO_5$

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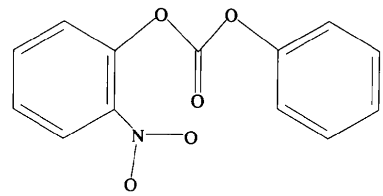
Abstract

The title mononitrodiphenyl carbonate consitutes 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); $O_{(nitro)}\cdots C_{(carbonyl)}$ 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 $O_{(nitro)}\cdots C_{(carbonyl)}$ 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

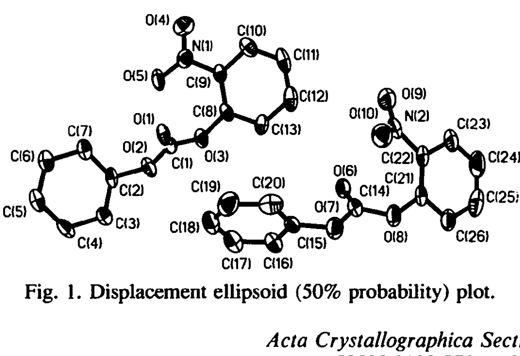


Fig. 1. Displacement ellipsoid (50% probability) plot.

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