O5A—Cl2A—O6A	103.1 (3)	N2—C1—N3	117.5 (2)
O5A—Cl2A—O7A	107.4 (3)	N3—C2—N4	117.3 (2)
O5A—Cl2A—O8A	114.1 (3)	N3—C2—N5	124.5 (2)
O6A—Cl2A—O7A	105.5 (3)	N4—C2—N5	118.1 (2)
O6A—Cl2A—O8A	115.1 (3)	N6—C3—N7	118.2 (2)
O7A—Cl2A—O8A	110.9 (3)	N6—C3—N8	124.8 (2)
O5B—Cl2B—O6B	112.1 (3)	N7—C3—N8	116.9 (2)
O5B—Cl2B—O7B	112.9 (3)	N8—C4—N9	117.6 (2)
O5B—Cl2B—O8B	105.6 (3)	N8—C4—N10	124.4 (2)
O6B—Cl2B—O7B	113.1 (3)	N9—C4—N10	117.9 (2)

Table 6. *Hydrogen-bonding geometry (Å, °) for (BIGH)(ClO₄)*

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
N1—H1···N8^{i}	0.95	2.2625	141.50
N1—H2···O3^{ii}	0.95	2.1417	162.68
N2—H3···O5*A*	0.95	2.0652	150.77
N2—H3···O5*B*	0.95	2.1877	157.64
N2—H4···O4^{ii}	0.95	2.0562	171.99
N4—H5···O4^{i}	0.95	2.1893	175.92
N4—H6···N3^{iii}	0.95	1.9802	176.95
N5—H7···O1^{i}	0.95	1.9894	161.96
N5—H8···O7*A*^{ii}	0.95	2.2240	129.83
N5—H8···O7*B*^{ii}	0.95	2.1728	138.40
N6—H9···O2	0.95	2.5337	150.00
N6—H9···O5*B*^{iv}	0.95	2.5061	102.76
N6—H10···O3^{iv}	0.95	2.3282	169.74
N7—H11···O6*B*^{v}	0.95	2.2010	160.57
N7—H11···O6*A*^{v}	0.95	2.1410	166.67
N7—H12···O1^{iv}	0.95	1.9873	168.42
N9—H13···O6*B*^{vi}	0.95	2.0675	144.61
N9—H13···O6*A*^{vi}	0.95	2.3080	139.06
N9—H14···O7*A*^{vii}	0.95	2.0913	168.67
N9—H14···O8*B*^{vii}	0.95	2.2183	139.99
N10—H15···O2^{viii}	0.95	2.4573	135.65
N10—H15···O6*B*^{vi}	0.95	2.3124	136.91
N10—H15···O6*A*^{vi}	0.95	2.3125	138.72
N10—H16···O8*B*^{viii}	0.95	2.4163	130.00
N10—H16···O8*A*^{viii}	0.95	2.3866	149.08

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, -y, 1-z$; (iii) $1-x, 1-y, 1-z$; (iv) $x-1, y, z$; (v) $x-1, 1+y, z$; (vi) $1-x, 1-y, 2-z$; (vii) $x, 1+y, z$; (viii) $-x, 1-y, 2-z$.

Preliminary examination and intensity data collection were carried out using an Enraf–Nonius CAD-4 diffractometer. Backgrounds were obtained from analysis of the scan profile (Blessing, Coppens & Becker, 1974). The crystal of the diperchlorate was lost before ψ scans were obtained, hence an absorption correction was applied using *DIFABS* (Walker & Stuart, 1983). All H atoms in the diperchlorate refined cleanly. This was not the case, however, for the monoperchlorate, for which all H atoms are reported in ideal positions. The computer programs used were taken from *MolEN* (Fair, 1990) and locally modified according to Blessing (1987). The molecular graphics were prepared with a CAChe workstation (CAChe Scientific, 1993).

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN PROCESS*; program(s) used to solve structures: *SIR* (Burla *et al.*, 1989); program(s) used to refine structures: *MolEN LSFM*; software used to prepare material for publication: *MolEN CIF VAX*.

We thank the College of Arts and Sciences of the University of Toledo for generous financial support of the X-ray diffraction facility and thank the Office of Naval Research for funding this work (contract No. N000149310597).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK1092). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1052–1054

8-(3-Methylphenoxy)-16*H*-dinaphtho[2,1-*d*;1′,2′-*g*][1,3,2]dioxaphosphocine 8-Oxide

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(*Received 20 January 1994; accepted 9 October 1995*)

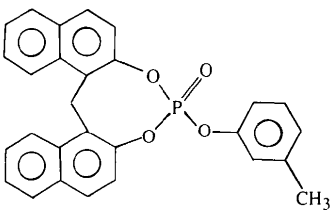
Abstract

In the title compound, $C_{28}H_{21}O_4P$, the eight-membered heterocyclic dioxaphosphocine ring has a distorted boat conformation, with the phosphoryl O atom axial and

the phenoxy group equatorial. The P═O distance is 1.451 (1) Å and the average length of the three P—O bonds is 1.573 (1) Å. The phenyl ring is nearly perpendicular to both naphthalene planes, making dihedral angles of 91.30 (3) and 97.65 (5)° with them. The angle between the two naphthalene planes is 67.73 (3)°. The crystal structure is stabilized by van der Waals interactions.

Comment

The dioxaphosphocine ring in the title compound, (I), is an eight-membered ring containing P, O and C atoms. Crystallographic reports of such structures are very rare in the literature. The present report is part of a program of study of substituted 3,2-dioxaphosphocine derivatives (Mani Naidu, Krishnaiah & Sivakumar, 1992).



(I)

The bond lengths in the two P—O—C—C—CH_2 fragments of the eight-membered ring are equal within the limits of error. The mean P—O single-bond length of 1.573 Å and the average P═O bond length of 1.451 (1) Å are comparable to those observed in *cis*- and *trans*-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocine derivatives (Goddard, Payne, Cook & Luss, 1988). The least-squares plane calculations for atoms O(2), C(1), C(12) and C(21) show that the bonds C(1)—O(2) and C(12)—C(21) cross the plane in opposite directions. The remaining atoms of the heterocyclic ring are above this plane at unequal heights, resulting in a distorted boat conformation for the dioxaphosphocine ring. The steric repulsion between the non-bonded O(1) and C(1) atoms [3.051 (2) Å] may be the reason for the distortion from a regular boat conformation. The C_{sp^2}—C_{sp^2} bond lengths in the two naphthalene ring systems are in the range 1.351 (2)–1.442 (2) Å, with a mean value of 1.401 (2) Å.

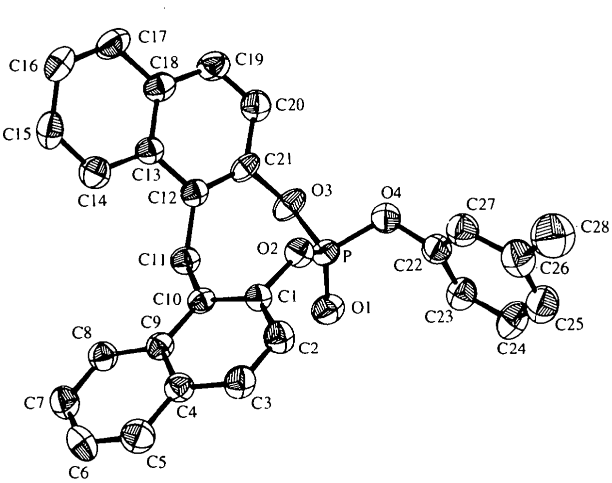


Fig. 1. An *ORTEP*II view (Johnson, 1976) of the title compound with displacement ellipsoids plotted at the 50% probability level. H atoms have been omitted for clarity.

Experimental

The title compound was synthesized by Dr C. D. Reddy and his co-workers, Department of Chemistry, S. V. University, Tirupati. 3-Methylphenylphosphoric acid dichloride in dry benzene was added dropwise to a stirred solution of bis(2-hydroxy-1-naphthyl)methane and triethylamine in benzene. The temperature was raised gradually to 323–333 K and the solution was stirred for 10 h. The triethylamine hydrochloride salt was removed by filtration and evaporation of the solvent under reduced pressure gave the title compound. Crystals of the title compound were grown in 1-butanol and the density D_m of the crystals was measured by flotation in KI solution.

Crystal data

$C_{28}H_{21}O_4P$
M_r = 452.45
Monoclinic
$P2_1/n$
a = 11.721 (1) Å
b = 13.156 (1) Å
c = 14.278 (1) Å
β = 95.10 (1)°
V = 2193.0 (2) Å^3
Z = 4
D_x = 1.370 Mg m^{-3}
D_m = 1.40 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.153 mm^{-1}
T = 293 K
Needle
0.4 × 0.3 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3808 measured reflections
3447 independent reflections
2990 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int}$ = 0.0196
$\theta_{\rm max}$ = 25°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections monitored every 100 reflections
intensity decay: <3%

Refinement

Refinement on F
R = 0.040
wR = 0.048
S = 1.23
2990 reflections
297 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.28 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.40 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELX*76 (Sheldrick, 1976) and *SHELXS*86 (Sheldrick, 1985)

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

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
P	0.0576 (1)	0.2056 (1)	0.4991 (1)	2.90 (1)
O(1)	0.0423 (1)	0.1593 (1)	0.4066 (1)	3.76 (3)
O(2)	0.0276 (1)	0.3217 (1)	0.5044 (1)	3.01 (3)
O(3)	0.1833 (1)	0.1946 (1)	0.5471 (1)	3.79 (3)
O(4)	−0.0136 (1)	0.1584 (1)	0.5768 (1)	3.55 (3)
C(1)	0.0325 (1)	0.3898 (1)	0.4283 (1)	2.76 (4)
C(2)	−0.0729 (1)	0.4317 (1)	0.3947 (1)	3.31 (4)
C(3)	−0.0762 (1)	0.5011 (1)	0.3243 (1)	3.58 (5)
C(4)	0.0249 (1)	0.5299 (1)	0.2844 (1)	3.20 (5)
C(5)	0.0216 (2)	0.6007 (1)	0.2089 (1)	4.14 (6)
C(6)	0.1177 (2)	0.6251 (2)	0.1677 (1)	4.56 (6)
C(7)	0.2228 (2)	0.5818 (2)	0.2002 (1)	4.36 (6)
C(8)	0.2302 (1)	0.5147 (1)	0.2733 (1)	3.53 (5)
C(9)	0.1320 (1)	0.4859 (1)	0.3186 (1)	2.87 (4)
C(10)	0.1346 (1)	0.4136 (1)	0.3947 (1)	2.71 (4)
C(11)	0.2443 (1)	0.3596 (1)	0.4307 (1)	3.01 (4)
C(12)	0.2743 (1)	0.3574 (1)	0.5367 (1)	2.87 (4)
C(13)	0.3368 (1)	0.4385 (1)	0.5845 (1)	2.90 (4)
C(14)	0.3626 (1)	0.5307 (1)	0.5386 (1)	3.46 (5)
C(15)	0.4199 (2)	0.6073 (1)	0.5878 (1)	4.16 (5)
C(16)	0.4560 (2)	0.5961 (2)	0.6834 (2)	4.39 (5)
C(17)	0.4338 (2)	0.5094 (2)	0.7291 (1)	3.96 (5)
C(18)	0.3721 (1)	0.4290 (1)	0.6821 (1)	3.18 (5)
C(19)	0.3432 (2)	0.3397 (1)	0.7310 (1)	3.67 (4)
C(20)	0.2799 (2)	0.2656 (1)	0.6860 (1)	3.62 (5)
C(21)	0.2463 (1)	0.2762 (1)	0.5897 (1)	3.12 (4)
C(22)	−0.1336 (1)	0.1422 (1)	0.5580 (1)	3.24 (4)
C(23)	−0.1720 (2)	0.0680 (1)	0.4953 (1)	3.96 (5)
C(24)	−0.2886 (2)	0.0512 (2)	0.4816 (2)	4.72 (5)
C(25)	−0.3639 (2)	0.1068 (2)	0.5306 (2)	4.79 (6)
C(26)	−0.3243 (2)	0.1804 (1)	0.5946 (1)	4.18 (6)
C(27)	−0.2063 (2)	0.1984 (1)	0.6074 (1)	3.84 (5)
C(28)	−0.4054 (2)	0.2383 (2)	0.6501 (2)	6.05 (8)

Table 2. *Selected geometric parameters (Å, °)*

P—O(1)	1.451 (1)	P—O(2)	1.571 (1)
P—O(3)	1.575 (1)	P—O(4)	1.574 (1)
O(2)—C(1)	1.413 (2)	O(3)—C(21)	1.410 (2)
O(4)—C(22)	1.424 (2)	C(11)—C(12)	1.523 (2)
C(1)—C(10)	1.365 (2)	C(12)—C(21)	1.366 (2)
C(10)—C(11)	1.518 (2)		
O(3)—P—O(4)	101.0 (1)	O(2)—P—O(4)	102.4 (1)
O(2)—P—O(3)	105.9 (1)	O(1)—P—O(4)	116.4 (1)
O(1)—P—O(3)	113.1 (1)	O(1)—P—O(2)	116.2 (1)
P—O(2)—C(1)	123.7 (1)	P—O(3)—C(21)	123.5 (1)
P—O(4)—C(22)	120.2 (1)	O(2)—C(1)—C(10)	120.8 (1)
O(2)—C(1)—C(2)	114.8 (1)	C(2)—C(1)—C(10)	124.4 (1)
C(1)—C(10)—C(9)	117.1 (1)	C(9)—C(10)—C(11)	121.6 (1)
C(1)—C(10)—C(11)	121.1 (1)	C(10)—C(11)—C(12)	117.3 (1)
C(11)—C(12)—C(21)	121.3 (1)	C(11)—C(12)—C(13)	121.5 (1)
O(3)—C(21)—C(20)	116.0 (1)	O(3)—C(21)—C(12)	119.9 (1)
O(4)—C(22)—C(27)	118.1 (1)	O(4)—C(22)—C(23)	119.4 (1)

O(2)—P—O(3)—C(21)	3.6 (1)
O(3)—P—O(2)—C(1)	100.1 (1)
P—O(2)—C(1)—C(10)	−66.5 (2)
P—O(3)—C(21)—C(12)	−63.2 (2)
O(2)—C(1)—C(10)—C(11)	6.6 (2)
C(1)—C(10)—C(11)—C(12)	−52.9 (2)
C(10)—C(11)—C(12)—C(21)	95.8 (2)
C(11)—C(12)—C(21)—O(3)	−3.3 (2)

The preliminary cell parameters and the space group were obtained from oscillation and Weissenberg photographs. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985) and refined by a full-matrix least-squares method using *SHELX76* (Sheldrick, 1976). The H-atom positions were located from a difference Fourier map. The positional parameters of the non-H atoms were refined anisotropically. The U_{iso} values of the H atoms were obtained from those of their attached C atoms and the positional and U_{iso} parameters were not refined. Other geometrical calculations were carried out using *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including least-squares-planes data, torsion angles and intermolecular contact distances less than 3.75 Å, have been deposited with the IUCr (Reference: HA1100). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1054–1056

2,4-Pentanedione Bis(2,4-dinitrophenylhydrazone)

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(*Received 20 January 1994; accepted 9 October 1995*)

Abstract

The title molecule, $C_{17}H_{16}N_8O_8$, has approximate non-crystallographic twofold symmetry. The bond lengths in the chain of atoms connecting the two dinitrophenyl groups are consistent with some delocalization of the double bonds in the chain. The molecule adopts an *E,E* conformation, which favours intramolecular N—H···O hydrogen bonding. The dihedral angle between the planes of the phenyl rings is 69.6 (1)°.

Comment

The bond lengths and angles in the two chemically equivalent halves of the title molecule, (I), are similar,