Two Energetic Ionic Materials: the Biguanidium Perchlorates

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Abstract

The structures of two energetic biguanidium salts have been determined from low-temperature X-ray diffraction data collected at 100 K. Biguanidium perchlorate, $C_2H_8N_5^+.ClO_4^-$, and biguanidium diperchlorate, $C_2H_9N_5^{2+}.2ClO_4^-$, have structures characterized by twisted cations and extensive hydrogen bonding.

Comment

There is a great deal of current interest in the production of energetic materials (Borman, 1994). A newly discovered class of energetic materials is based on the salts of biguanide (Bottaro, Gilardi, Martin & Pinkerton, 1996). The present paper describes two other energetic biguanidium salts, the mono- and diperchlorate. Perchlorates have a long and sometimes checkered history in the field of energetic materials due to their unpredictable nature; nevertheless, they have an important role. Ammonium perchlorate, for example, is used in the solid-fuel booster rockets of the space shuttle and an unspecified biguanidium perchlorate was included in an explosive formulation in 1917 (Manuelli & Bernardini, 1917). The two nitrate salts of biguanide (Martin, Pinkerton & Schiemann, 1996) have densities that are higher than many other organic materials, although not much higher than predicted by empirical calculations (Chichra, Holden & Dickinson, 1980; Stine, 1981). These factors encouraged us to synthesize and structurally characterize the diprotonated biguanidium diperchlorate, $(BIGH_2)(ClO_4)_2$, and the monoprotonated biguanidium perchlorate, $(BIGH)(ClO_4)$.
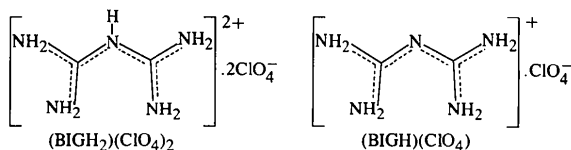
$(BIGH_2)(ClO_4)_2$. The structure of the diperchlorate consists of a biguanidium unit and two perchlorate anions linked by an extensive hydrogen-bond network (Fig. 1). The diprotonated biguanidium cation is fairly symmetric about the central N atom, as observed for the carbonate, sulfate and nitrate but not the free base (Pinkerton & Schwarzenbach, 1978; Martin, Pinkerton & Schiemann, 1996).

As expected, the biguanidium unit is not planar, but consists of two planar moieties twisted by 43.7 (1)° with respect to one another; this is comparable to 49.1° for the analogous sulfate. The other metric parameters are similar to those previously reported.

The bridging C—N bonds of the biguanidium unit [C1—N3 1.369 (3), C2—N3 1.367 (3) Å] are slightly shorter than in the analogous sulfate [room temperature data: C1—N3 1.383 (5), C2—N3 1.373 (5) Å]. The bond angle at the bridging N atom (C1—N3—C2) is 127.0 (2)°, which is comparable to the same angle in the sulfate [126.2 (3)°]. The terminal C—N bonds are significantly shorter than the bridging bonds and range from 1.308 (3) (N1—C1) to 1.313 (3) Å (N2—C1); the same range is found in the sulfate [1.308 (5)–1.315 (5) Å].

The two perchlorate anions are well behaved with unusually small displacement parameters and have the expected tetrahedral geometry. One anion accepts five hydrogen bonds from four different biguanidium cations using three O atoms (with O···H distances less than 2.5 Å). The hydrogen-bond angles vary from 114 (2) (O1···H7—N4) to 176 (3)° (O4···H2—N1), the latter also being the shortest of these hydrogen bonds [O4···H2 2.04 (3) Å]. The other anion accepts six hydrogen bonds from four different biguanidium cations using all four O atoms (with O···H distances less than 2.5 Å); the angles vary from 135 (3) (O6···H1—N1, O7···H4—N2) to 170 (3)° (O5···H9—N5). The shortest of these is N3—H5···O7 with an angle of 162 (3)° and an O···H distance of 2.05 (3) Å. The H atom on the bridging N atom (H5) is known to be the most acidic, and is also known to form a very short hydrogen bond in the analogous nitrate, but with an angle slightly closer to linearity [168 (3)°]. We note that the more linear the
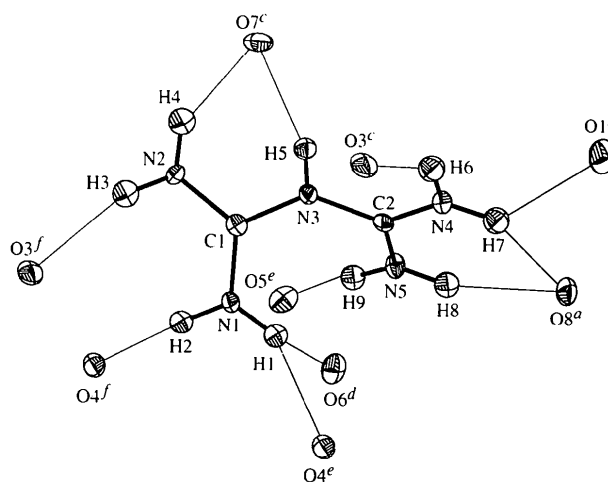

Fig. 1. The biguanidium cation in $(BIGH_2)(ClO_4)_2$ showing the hydrogen bonds. Displacement ellipsoids are shown at the 50% probability level [symmetry codes: (a) $-x$, $1 - y$, $-z$; (b) $1 - x$, $1 - y$, $-z$; (c) $1 + x$, y, z; (d) $1 + x$, $1 + y$, z; (e) x, $1 + y$, z; (f) $-x$, $1 - y$, $1 - z$].

hydrogen bond, the shorter it is, and that the H atom bonded to the central N atom has a significantly different character to the others.

Examination of the biguanidium cation (Fig. 1) shows that every H atom (of which there are nine) forms a hydrogen bond to an O atom resulting in bonds to a total of six different anions. Two O atoms bind to two H atoms from the same biguanidium unit (O7 to H4 and H5, O8 to H7 and H8). We note that there are two bifurcated hydrogen bonds, involving H1 and H7.

(BIGH)(ClO₄). The structure of the monoprotonated perchlorate is more complex. There are two biguanidium units and two perchlorate anions in the asymmetric unit, again connected by an extensive hydrogen-bond network (Figs. 2 and 3). One perchlorate ion is well behaved with small displacement parameters; the other is disordered. Attempts to refine the structure in space group $P1$ were unsuccessful, thus we report the disordered structure in $P\bar{1}$. The refinement of the H-atom positions was not well behaved as a result of the disorder; as these atoms are attached to planar sp^2-hybridized N atoms the discussion of the hydrogen bonding below is based on ideal H-atom positions (N—H 0.95 Å). (We believe this to be more meaningful than an alternative description based on O···N contact distances.) We have modeled the disorder using two equally occupied sites, A and B, for each atom in the anion; refinement of the occupancies showed no significant deviation from 0.5. The Cl atom and two of the O atoms were refined isotropically due to the proximity of the disordered partner atoms (<0.4 Å); O7 and O8, however, were refined anisotropically as their partners are further away (>0.8 Å). Although it is not unusual for a perchlorate ion to show disorder, this is usually prevented by strong hydrogen bonding. In the present case the opposite is true; the hydrogen bonding to both possible perchlorate-ion orientations is very similar, with the exception that H14 forms a strong hydrogen bond to O7A in orientation A and to O8B in orientation B. We believe that this choice of two possible hydrogen-bonding schemes is the origin of the observed disorder.

The second, ordered perchlorate ion accepts eight hydrogen bonds from five different biguanidium cations using all four O atoms. The hydrogen-bond distances involving the perchlorate anions range from 1.99 (O1···H7, O1···H12) to 2.53 Å (O2···H9) with angles ranging from 103 (O5B···H9—N6) to 176° (O4···H5—N4).

Again, the biguanidium units consist of two planar halves twisted with respect to each other. One has a 43.5 (1)° twist about N3; the other has 45.6 (1)° twist about N8. This is similar to the twist of 44.0° reported for the monoprotonated biguanidium sulfate, and not very different to that in the diprotonated cation (see above).

The bridging C—N bonds range from 1.334 (3) (N8—C4) to 1.341 (3) Å (N3—C2) and are slightly longer than

the terminal C—N bonds, which range from 1.326 (3) (N2—C1) to 1.339 (3) Å (N6—C3). The bond angles at the bridging N atoms are 121.2 (2) (C1—N3—C2) and 121.3 (2)° (C3—N8—C4), and are identical to that reported for the analogous sulfate [121.2 (2)°].

There is more hydrogen bonding to describe here than for the diperchlorate because of the larger asymmetric unit. All the H atoms form at least one hydrogen bond (<2.5 Å). One interesting feature is that one of the biguanidium units is hydrogen bonded to its symmetry-related partner through a center of inversion (Fig. 2). This 'dimer' is held together by two short hydrogen bonds between H6 and N3. This is the shortest hydrogen bond in the structure (1.98 Å) and, with an N4—H6···N3 angle of 177°, it is essentially linear. Fig. 2 also shows the eight O atoms (counting all atoms, disordered or not, equally) and one additional N atom that have hydrogen-bond distances less than 2.5 Å to one biguanidium cation. Removing the disorder would reduce this to six O atoms from four different perchlorate ions. The hydrogen-bond angles involving O atoms range from 130 (O7A···H8—N5) to 176° (O4···H5—N4).

The other biguanidium unit is shown in Fig. 3, and forms hydrogen bonds to 13 O atoms (removing the disorder would reduce this to nine O atoms). The hydrogen-bond angles range from 103 (O5B···H9—N6) to 170° (O3···H10—N6). We note that H9 and H15 form bifurcated hydrogen bonds.

Clearly, the geometries of the cations in these salts are very similar to those observed previously. The increased
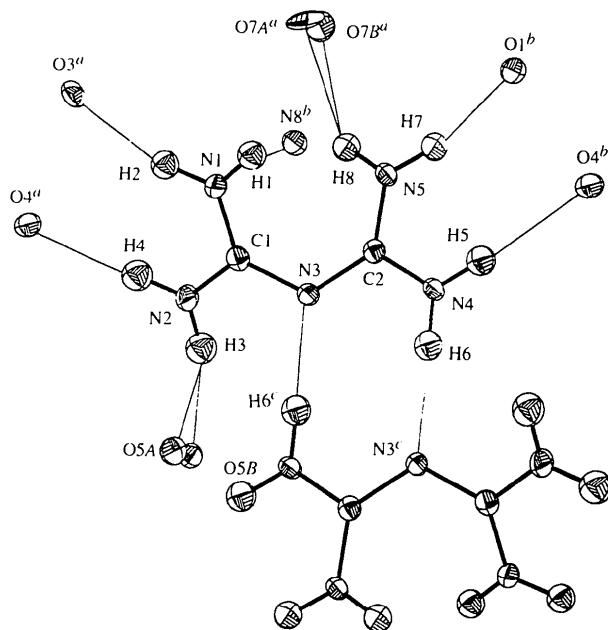

Fig. 2. The biguanidium cation 'dimer' in (BIGH)(ClO₄) showing the hydrogen bonds. Displacement ellipsoids are shown at the 50% probability level [symmetry codes: (a) $-x$, $-y$, $1-z$; (b) $-x$, $1-y$, $1-z$; (c) $1-x$, $1-y$, $1-z$].
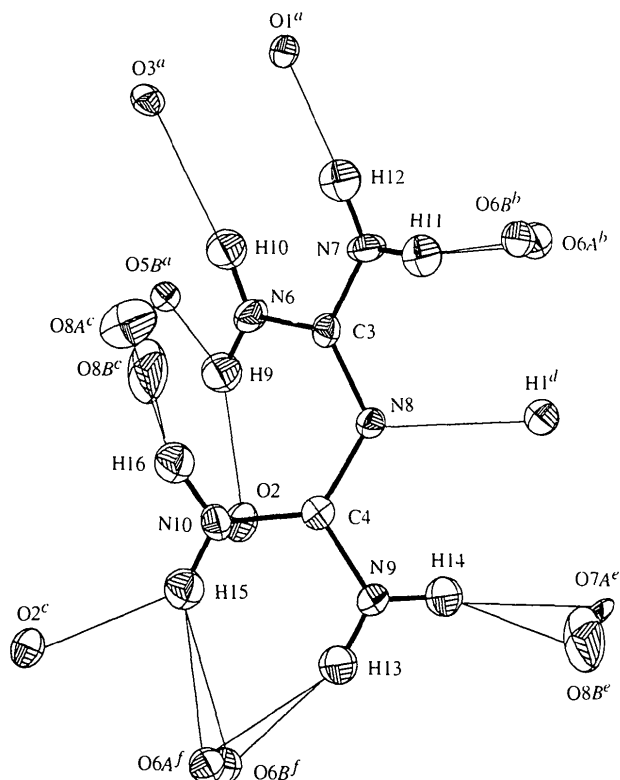
Fig. 3. The second biguanidium cation in $(BIGH)(ClO_4)$ showing the hydrogen bonds. Displacement ellipsoids are shown at the 50% probability level [symmetry codes: (a) $x - 1, y, z$; (b) $x - 1, y + 1, z$; (c) $-x, 1 - y, 2 - z$; (d) $-x, 1 - y, 1 - z$; (e) $x, 1 + y, z$; (f) $1 - x, 1 - y, 2 - z$].

densities result from the more efficient packing of the perchlorate compared, for example, to the sulfate. This is most evident in the diperchlorate (D_x = 1.95 Mg m^{-3} at 100 K). The hydrogen bonding is important and extensive in both salts.

$(BIGH)(ClO_4)$ has been shown to explode with a green flash on heating. An analysis of the mechanism of the thermal decomposition of $(BIGH)(ClO_4)$ based on thermogravimetric analysis, mass spectroscopy and time-resolved visible spectroscopy will be published elsewhere (Dollimore, Martin & Pinkerton, 1996).

Experimental

$(BIGH)(ClO_4)$ is easily prepared from biguanidium sulfate and barium perchlorate. $(BIGH_2)(ClO_4)_2$ can be prepared by dissolving $(BIGH)(ClO_4)$ in perchloric acid. Good crystals of $(BIGH)(ClO_4)$ were obtained from ethyl acetate and those of $(BIGH_2)(ClO_4)_2$ were obtained by slow evaporation of the perchloric acid solution.

$(BIGH_2)(ClO_4)_2$

Crystal data

$C_2H_9N_5^{2+} \cdot 2ClO_4^-$
$M_r = 302.03$
Triclinic
$P\bar{1}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections

$a = 7.409\,(1)$ Å
$b = 7.619\,(1)$ Å
$c = 9.843\,(1)$ Å
$\alpha = 82.02\,(1)°$
$\beta = 83.20\,(1)°$
$\gamma = 69.92\,(1)°$
$V = 515.3\,(2)$ Å^3
$Z = 2$
$D_x = 1.95$ Mg m^{-3}

$\theta = 8–17°$
$\mu = 0.673$ mm^{-1}
$T = 100$ K
Parallelepiped
$0.30 \times 0.28 \times 0.18$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.855$, $T_{max} = 1.000$
2188 measured reflections
2020 independent reflections

1803 observed reflections
$[I > 3.0\sigma(I)]$
$R_{int} = 0.022$
$\theta_{max} = 25.97°$
$h = 0 \rightarrow 9$
$k = -8 \rightarrow 9$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 50 min
intensity decay: 3.20%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.035$
$S = 3.205$
1803 reflections
191 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = {<}0.001$

$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.18×10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2) *for* $(BIGH_2)(ClO_4)_2$

U_{iso} for H atoms. $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$ for all other atoms.

	x	y	z	U_{eq}/U_{iso}
Cl1	0.03513 (8)	0.29809 (8)	0.20887 (6)	0.0113 (1)
Cl2	−0.34878 (8)	−0.00828 (8)	0.26851 (6)	0.0096 (1)
O1	0.1937 (3)	0.3628 (3)	0.1649 (2)	0.0255 (5)
O2	−0.0076 (3)	0.2133 (2)	0.1022 (2)	0.0210 (5)
O3	−0.1328 (3)	0.4559 (2)	0.2452 (2)	0.0193 (5)
O4	0.0799 (2)	0.1667 (2)	0.3311 (2)	0.0165 (5)
O5	−0.1571 (2)	−0.1295 (2)	0.2936 (2)	0.0198 (5)
O6	−0.4835 (2)	−0.0935 (2)	0.3376 (2)	0.0180 (5)
O7	−0.3822 (2)	0.1686 (2)	0.3209 (2)	0.0190 (5)
O8	−0.3726 (3)	0.0235 (2)	0.1231 (2)	0.0203 (5)
N1	0.2037 (3)	0.7550 (3)	0.4354 (2)	0.0123 (5)
N2	0.2784 (3)	0.4354 (3)	0.4772 (2)	0.0163 (6)
N3	0.4085 (3)	0.5585 (3)	0.2801 (2)	0.0113 (5)
N4	0.5480 (3)	0.6551 (3)	0.0783 (2)	0.0143 (6)
N5	0.2291 (3)	0.8132 (3)	0.1367 (2)	0.0141 (6)
C1	0.2922 (3)	0.5856 (3)	0.3995 (2)	0.0109 (6)
C2	0.3929 (3)	0.6809 (3)	0.1631 (2)	0.0108 (6)
H1	0.234 (4)	0.843 (4)	0.391 (3)	0.021 (8)
H2	0.120 (4)	0.773 (4)	0.506 (3)	0.023 (8)
H3	0.227 (3)	0.443 (3)	0.552 (3)	0.011 (7)
H4	0.326 (4)	0.331 (4)	0.454 (3)	0.04 (1)
H5	0.482 (3)	0.451 (3)	0.275 (3)	0.012 (7)
H6	0.649 (3)	0.596 (3)	0.108 (3)	0.013 (7)
H7	0.540 (4)	0.736 (4)	−0.004 (3)	0.033 (9)
H8	0.236 (4)	0.881 (4)	0.059 (3)	0.021 (8)
H9	0.131 (4)	0.816 (4)	0.183 (3)	0.015 (7)

Table 2. *Selected geometric parameters* ($\mathring{A}$, $°$) *for* $(BIGH_2)(ClO_4)_2$

Cl1—O1	1.424 (2)	Cl2—O8	1.439 (2)
Cl1—O2	1.424 (2)	N1—C1	1.308 (3)
Cl1—O3	1.452 (2)	N2—C1	1.313 (3)
Cl1—O4	1.446 (2)	N3—C1	1.369 (3)
Cl2—O5	1.431 (2)	N3—C2	1.367 (3)
Cl2—O6	1.429 (2)	N4—C2	1.311 (3)
Cl2—O7	1.441 (2)	N5—C2	1.311 (3)
O1—Cl1—O2	110.6 (1)	O6—Cl2—O8	109.7 (1)
O1—Cl1—O3	109.3 (1)	O7—Cl2—O8	109.4 (1)
O1—Cl1—O4	109.3 (1)	C1—N3—C2	127.0 (2)
O2—Cl1—O3	109.2 (1)	N1—C1—N2	122.0 (2)
O2—Cl1—O4	110.9 (1)	N1—C1—N3	120.6 (2)
O3—Cl1—O4	107.6 (1)	N2—C1—N3	117.3 (2)
O5—Cl2—O6	109.2 (1)	N3—C2—N4	116.5 (2)
O5—Cl2—O7	109.0 (1)	N3—C2—N5	121.1 (2)
O5—Cl2—O8	110.1 (1)	N4—C2—N5	122.4 (2)
O6—Cl2—O7	109.4 (1)		

Table 3. *Hydrogen-bonding geometry* ($\mathring{A}$, $°$) *for* $(BIGH_2)(ClO_4)_2$

D—H$\cdots A$	D—H	H$\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O4$^{\text{i}}$	0.83 (3)	2.36 (3)	137 (3)
N1—H1$\cdots$O6$^{\text{ii}}$	0.83 (3)	2.30 (3)	135 (3)
N1—H2$\cdots$O4$^{\text{iii}}$	0.87 (3)	2.04 (3)	176 (3)
N2—H3$\cdots$O3$^{\text{iiii}}$	0.79 (2)	2.19 (3)	159 (3)
N2—H4$\cdots$O7$^{\text{iv}}$	0.80 (3)	2.42 (4)	135 (3)
N3—H5$\cdots$O7$^{\text{iv}}$	0.82 (2)	2.05 (3)	162 (3)
N4—H6$\cdots$O3$^{\text{iv}}$	0.80 (2)	2.12 (3)	163 (3)
N4—H7$\cdots$O1$^{\text{v}}$	0.94 (3)	2.35 (3)	114 (2)
N4—H7$\cdots$O8$^{\text{vi}}$	0.94 (3)	2.11 (4)	147 (3)
N5—H8$\cdots$O8$^{\text{vi}}$	0.87 (3)	2.12 (3)	156 (3)
N5—H9$\cdots$O5$^{\text{i}}$	0.81 (3)	2.21 (3)	170 (3)

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

(BIGH)(ClO₄)

Crystal data

$C_2H_8N_5^+.ClO_4^-$
$M_r = 201.57$
Triclinic
$P\bar{1}$
$a = 7.7421$ (9) $\mathring{A}$
$b = 9.874$ (2) $\mathring{A}$
$c = 12.267$ (2) $\mathring{A}$
$\alpha = 112.75$ (1)$°$
$\beta = 91.89$ (1)$°$
$\gamma = 111.91$ (1)$°$
$V = 784.9$ (6) $\mathring{A}^3$
$Z = 4$
$D_x = 1.71$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ $\mathring{A}$
Cell parameters from 25 reflections
$\theta = 9-15°$
$\mu = 0.472$ mm^{-1}
$T = 100$ K
Parallelepiped
$0.37 \times 0.31 \times 0.11$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$3\theta/2\theta$ scans
Absorption correction:
  ψ scans (North, Phillips & Mathews, 1968)
  $T_{min} = 0.9312$, $T_{max} = 0.9982$
3322 measured reflections
3069 independent reflections

2680 observed reflections
  $[I > 3.0\sigma(I)]$
$R_{int} = 0.027$
$\theta_{max} = 25.99°$
$h = 0 \rightarrow 9$
$k = -12 \rightarrow 11$
$l = -15 \rightarrow 15$
3 standard reflections
  frequency: 50 min
  intensity decay: 2.27%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.047$
$S = 2.677$
2680 reflections
233 parameters
H atoms placed in ideal positions (N—H 0.95 $\mathring{A}$)
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max} = <0.001$

$\Delta\rho_{max} = 0.35$ e $\mathring{A}^{-3}$
$\Delta\rho_{min} = -0.12$ e $\mathring{A}^{-3}$
Extinction correction:
  isotropic (Zachariasen, 1963)
Extinction coefficient:
  0.15×10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 4. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* ($\mathring{A}^2$) *for* $(BIGH)(ClO_4)$

U_{iso} for Cl2, O5 and O6, $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all other atoms.

	x	y	z	U_{eq}/U_{iso}
Cl1	0.04296 (6)	0.38504 (5)	0.73141 (4)	0.0147 (1)
Cl2A†	0.4842 (1)	0.12244 (9)	0.80259 (7)	0.0121 (2)
Cl2B†	0.4697 (1)	0.0957 (1)	0.77591 (8)	0.0182 (2)
O1	0.1661 (2)	0.5207 (1)	0.7109 (1)	0.0197 (4)
O2	−0.0401 (2)	0.4397 (2)	0.8326 (1)	0.0234 (4)
O3	0.1550 (2)	0.3067 (1)	0.7545 (1)	0.0209 (4)
O4	−0.1032 (2)	0.2734 (2)	0.6245 (1)	0.0206 (4)
O5A†	0.5098 (4)	0.1876 (3)	0.7122 (2)	0.0221 (6)
O5B†	0.5062 (4)	0.2206 (3)	0.7376 (2)	0.0173 (6)
O6B†	0.6440 (4)	0.1125 (3)	0.8429 (2)	0.0203 (6)
O6A†	0.6560 (4)	0.0993 (3)	0.8174 (2)	0.0205 (6)
O7A†	0.3302 (4)	−0.0397 (3)	0.7457 (2)	0.0239 (9)
O7B†	0.3681 (5)	−0.0590 (4)	0.6821 (4)	0.052 (1)
O8B†	0.3547 (5)	0.1233 (5)	0.8660 (3)	0.059 (1)
O8A†	0.4475 (5)	0.2178 (5)	0.9087 (3)	0.042 (1)
N1	0.0788 (2)	0.0536 (2)	0.3172 (1)	0.0168 (4)
N2	0.2518 (2)	0.0883 (2)	0.4883 (1)	0.0215 (5)
N3	0.2834 (2)	0.3142 (2)	0.4654 (1)	0.0156 (4)
N4	0.3032 (2)	0.5429 (2)	0.4509 (1)	0.0185 (5)
N5	0.0078 (2)	0.3365 (2)	0.4005 (1)	0.0165 (4)
N6	−0.3967 (2)	0.5610 (2)	0.8366 (2)	0.0219 (5)
N7	−0.4395 (2)	0.7622 (2)	0.8061 (2)	0.0226 (5)
N8	−0.1359 (2)	0.8050 (2)	0.8683 (1)	0.0166 (4)
N9	0.1672 (2)	0.8462 (2)	0.9315 (1)	0.0194 (5)
N10	−0.0605 (2)	0.7448 (2)	1.0272 (1)	0.0213 (5)
C1	0.2015 (3)	0.1528 (2)	0.4230 (2)	0.0155 (5)
C2	0.1956 (3)	0.3936 (2)	0.4364 (2)	0.0150 (5)
C3	−0.3221 (3)	0.7090 (2)	0.8398 (2)	0.0174 (5)
C4	−0.0143 (3)	0.7949 (2)	0.9412 (2)	0.0164 (5)

† Site occupancy = 0.5.

Table 5. *Selected geometric parameters* ($\mathring{A}$, $°$) *for* $(BIGH)(ClO_4)$

Cl1—O1	1.445 (2)	N1—C1	1.337 (3)
Cl1—O2	1.428 (2)	N2—C1	1.326 (3)
Cl1—O3	1.444 (2)	N3—C1	1.340 (3)
Cl1—O4	1.438 (2)	N3—C2	1.341 (3)
Cl2A—O5A	1.467 (5)	N4—C2	1.331 (3)
Cl2A—O6A	1.448 (5)	N5—C2	1.334 (3)
Cl2A—O7A	1.459 (4)	N6—C3	1.339 (3)
Cl2A—O8A	1.392 (5)	N7—C3	1.332 (3)
Cl2B—O5B	1.421 (4)	N8—C3	1.338 (3)
Cl2B—O6B	1.475 (5)	N8—C4	1.334 (3)
Cl2B—O7B	1.400 (5)	N9—C4	1.331 (3)
Cl2B—O8B	1.450 (5)	N10—C4	1.335 (3)
O1—Cl1—O2	110.0 (1)	O6B—Cl2B—O8B	103.9 (3)
O1—Cl1—O3	108.5 (1)	O7B—Cl2B—O8B	108.5 (4)
O1—Cl1—O4	108.64 (9)	C1—N3—C2	121.2 (2)
O2—Cl1—O3	109.9 (1)	C3—N8—C4	121.3 (2)
O2—Cl1—O4	110.2 (1)	N1—C1—N2	118.4 (2)
O3—Cl1—O4	109.5 (1)	N1—C1—N3	124.0 (2)

O5A—C12A—O6A	103.1 (3)	N2—C1—N3	117.5 (2)
O5A—C12A—O7A	107.4 (3)	N3—C2—N4	117.3 (2)
O5A—C12A—O8A	114.1 (3)	N3—C2—N5	124.5 (2)
O6A—C12A—O7A	105.5 (3)	N4—C2—N5	118.1 (2)
O6A—C12A—O8A	115.1 (3)	N6—C3—N7	118.2 (2)
O7A—C12A—O8A	110.9 (3)	N6—C3—N8	124.8 (2)
O5B—C12B—O6B	112.1 (3)	N7—C3—N8	116.9 (2)
O5B—C12B—O7B	112.9 (3)	N8—C4—N9	117.6 (2)
O5B—C12B—O8B	105.6 (3)	N8—C4—N10	124.4 (2)
O6B—C12B—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···O5A	0.95	2.0652	150.77
N2—H3···O5B	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···O7A^{ii}	0.95	2.2240	129.83
N5—H8···O7B^{ii}	0.95	2.1728	138.40
N6—H9···O2	0.95	2.5337	150.00
N6—H9···O5B^{iv}	0.95	2.5061	102.76
N6—H10···O3^{iv}	0.95	2.3282	169.74
N7—H11···O6B^v	0.95	2.2010	160.57
N7—H11···O6A^v	0.95	2.1410	166.67
N7—H12···O1^{iv}	0.95	1.9873	168.42
N9—H13···O6B^{vi}	0.95	2.0675	144.61
N9—H13···O6A^{vi}	0.95	2.3080	139.06
N9—H14···O7A^{vii}	0.95	2.0913	168.67
N9—H14···O8B^{vii}	0.95	2.2183	139.99
N10—H15···O2^{viii}	0.95	2.4573	135.65
N10—H15···O6B^{vi}	0.95	2.3124	136.91
N10—H15···O6A^{vi}	0.95	2.3125	138.72
N10—H16···O8B^{viii}	0.95	2.4163	130.00
N10—H16···O8A^{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*.

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

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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