Absorption correction:	$h = -7 \rightarrow 7$
ψ scan (North *et al.*, 1968)	$k = -8 \rightarrow 13$
$T_{min} = 0.358$, $T_{max} = 0.406$	$l = -25 \rightarrow 25$
3044 measured reflections	3 standard reflections
2778 independent reflections	every 150 reflections
1588 reflections with $I > 2\sigma(I)$	intensity decay: 3.14%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.016$
$R[F^2 > 2\sigma(F^2)] = 0.059$	$\Delta\rho_{max} = 0.438$ e Å^{-3}
$wR(F^2) = 0.190$	$\Delta\rho_{min} = -0.328$ e Å^{-3}
$S = 1.088$	Extinction correction: *SHELXL*93
2770 reflections	Extinction coefficient: 0.0249 (14)
167 parameters	Scattering factors from *International Tables for Crystallography* (Vol. C)
Only H-atom U's refined	
$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 2.8628P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected geometric parameters (Å, °)*

Cl16—C15	1.766 (6)	O6—C2	1.204 (6)
Cl17—C15	1.769 (5)	O8—C7	1.199 (6)
Cl18—C15	1.757 (6)	O9—C7	1.318 (7)
O1—C2	1.374 (6)	O9—C10	1.473 (7)
O1—C5	1.426 (6)		
C2—O1—C5	111.1 (4)	C12—C4—C3	62.3 (3)
O1—C2—C3	110.0 (4)	C3—C4—C5	105.6 (4)
C2—C3—C4	105.6 (4)	O1—C5—C4	106.9 (4)
C4—C3—C12	58.7 (3)	C4—C12—C3	59.0 (3)
O1—C2—C3—C12	−59.3 (6)	C7—O9—C10—C11	93.9 (7)
C12—C4—C5—O1	58.6 (6)	C2—C3—C12—C14	−18.5 (7)
C3—C4—C5—C15	110.8 (5)	C2—C3—C12—C13	−159.7 (5)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN*: *PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *TEXSAN*: *FINISH*.

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A Triclinic Modification of Triphenylphosphine

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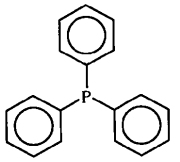
Abstract

A triclinic modification of triphenylphosphine, $C_{18}H_{15}P$, is reported. Two of the four unique molecules are in virtually the same conformation and are related by a local inversion centre; the other two molecules each have a different conformation. The structure contains a number of short C—H$\cdots\pi$ contacts.

Comment

The monoclinic modification of the title compound has been reported earlier by a number of authors (Daly, 1964; Dunne & Orpen, 1991; Chekhlov, 1993*a*,*b*; Bruckmann *et al.*, 1995).

In the triclinic modification reported here, the title compound, (I), crystallizes with four independent molecules in the asymmetric unit. As expected, the bond distances and angles of these four molecules display no significant differences from those observed in other determinations of the structure of triphenylphosphines, either in the monoclinic modification or cocrystallized with a variety of other molecules.



(I)

For the description of the conformation of a triphenylphosphine molecule, we follow the system introduced by Bye *et al.* (1982) in their study of triphenylphosphine oxides. The orientation of a phenyl ring is given by the torsion φ of the P—C bond. For triphenylphosphine, φ is defined to be zero when the phenyl group eclipses the lone-pair direction of the phosphorous atom and increases when the phenyl group is rotated clockwise viewed along the P—C bond. Three angles φ define the conformation of the molecule. Due to the internal symmetry of the phenyl ring, φ has a period of 180°. Bye *et al.* (1982) have described the allowed permutations of the three torsion angles φ in detail. In this paper a conformation will be described with the numeric values of the three φ angles, transformed and permutated so that the largest angle is taken positive and given first in the description. The standard uncertainty in each of the φ angles reported is 1°.

In 18 free triphenylphosphine molecules found in the Cambridge Structural Database [Allen & Kennard (1993): version of October 1997 containing 175093 entries], φ is in the range −60 to 60°. In triphenylphosphine moieties forming part of a larger molecule (7000 examples found in the CSD), the full range from −90 to 90° is observed, with a slight preference for values in the ranges −60 to −30° and 30 to 60°. Due to the flexibility of the molecule, no clearly preferred conformations can be discerned.

Molecules 1 and 2 display approximately the same orientation of the phenyl groups (φ angles are 54, 43, 43° for molecule 1 and 51, 48, 43° for the inverted molecule 2) and are related by a non-crystallographic inversion centre located at (0.255 0.251 0.492) [r.m.s. deviation of the quaternion-fit (Mackay, 1984) is 0.066 Å; maximum deviations are 0.134 Å for C125 and C225]. No other local symmetry relations were found between the independent molecules. The conformation adopted by molecules 1 and 2 has not been found in other neutral triphenylphosphine molecules reported in the literature (Allen & Kennard, 1993).

The conformations of molecules 3 (φ angles 38, 33, 30° for the inverted molecule) and 4 (φ angles 59, 43, 27°) are clearly different from the conformation shared by molecules 1 and 2. The conformations adopted by molecules 3 and 4 have been found in other non-bonded triphenylphosphine molecules [*e.g.* Fenske *et al.* (1984) and Fryzuk *et al.* (1991) for conformations 3 and 4, respectively]. The conformation found in the monoclinic modification of triphenylphosphine (φ angles 59, 27, 25°) is not present in the triclinic modification.

The packing of the triclinic modification involves a number of C—H$\cdots\pi$ interactions [see Hunter (1994) for a review on interactions of π systems]. The most interesting of these is C225—H225$\cdots$C21*g* (1 − *x*, 1 − *y*, 1 − *z*), where C21*g* denotes the centre of

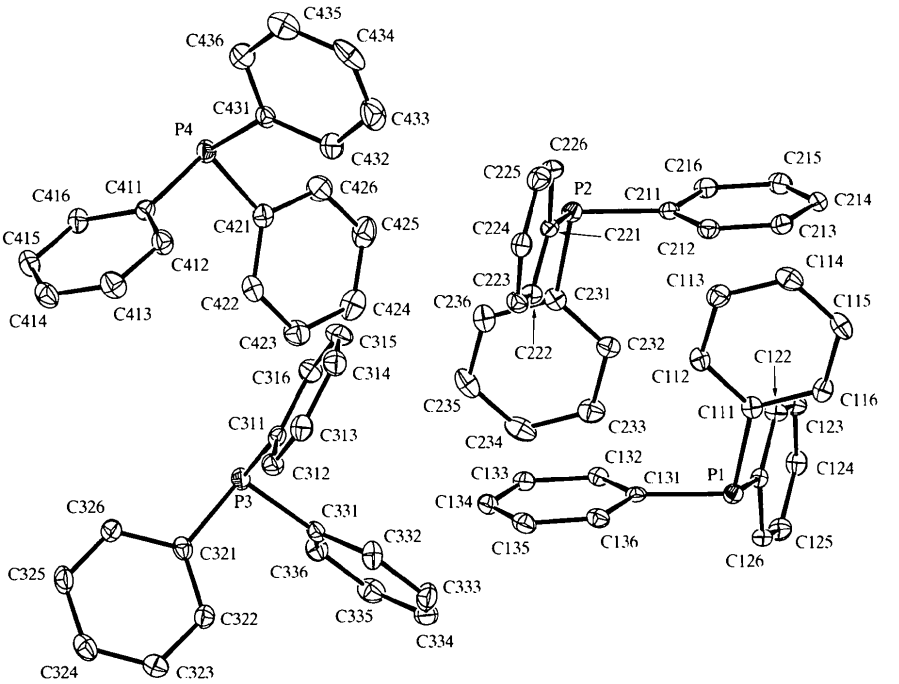


Fig. 1. Displacement ellipsoid plot of the four independent molecules of triphenylphosphine in the triclinic modification, drawn at the 50% probability level.

gravity of the atoms C211 through C216. For this contact a C···C*g* distance of 3.506 (3) Å is found, H···C*g* amounts to 2.60 Å and C—H···C*g* is 159°. The monoclinic modification does not display such short distances and approximately linear angles.

Experimental

The title compound was used as a reagent during the synthesis of a rhenium compound. During the crystallization from 1-propanol, pale green crystals of the title compound were formed together with crystals of the rhenium complex.

Crystal data

$C_{18}H_{15}P$
M_r = 262.29
Triclinic
$P\bar{1}$
a = 10.935 (1) Å
b = 15.064 (1) Å
c = 17.577 (1) Å
α = 84.467 (6)°
β = 80.458 (7)°
γ = 86.175 (7)°
V = 2838.3 (4) Å^3
Z = 8
D_x = 1.228 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 9.83–13.86°
μ = 0.18 mm^{-1}
T = 150 K
Plate-shaped
0.3 × 0.3 × 0.1 mm
Pale green

Data collection

Enraf–Nonius CAD-4-T on rotating-anode diffractometer
ω scans
Absorption correction: none
11747 measured reflections
9982 independent reflections
6421 reflections with $I > 2\sigma(I)$
R_{int} = 0.062

θ_{max} = 25°
$h = -9 \rightarrow 13$
$k = -17 \rightarrow 17$
$l = -20 \rightarrow 20$
3 standard reflections
frequency: 60 min
intensity decay: 20%

Refinement

Refinement on F^2
$R(F)$ = 0.053
$wR(F^2)$ = 0.135
S = 1.017
9982 reflections
685 parameters
H-atom treatment: see text
$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.8403P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.83 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C121—P1—C111—C112	107.9 (3)	C311—P3—C331—C332	24.1 (3)
C131—P1—C121—C122	96.4 (3)	C331—P3—C321—C322	19.6 (3)
C111—P1—C131—C132	97.7 (3)	C321—P3—C311—C312	13.9 (3)
C231—P2—C221—C222	5.0 (3)	C431—P4—C411—C412	−24.9 (3)
C211—P2—C231—C232	0.1 (3)	C411—P4—C431—C432	96.7 (3)
C221—P2—C211—C212	8.3 (3)	C431—P4—C421—C422	113.1 (3)

Table 2. *C—H ··· π interactions (Å, °)*

Label C*nng* indicates the centre of gravity of atoms C*nn*1 through C*nn*6.

D—H···C*g*	H···C*g*	*D*—H···C*g*	*D*···C*g*
C123—H123···C21*g*	3.24	127	3.893 (3)
C124—H124···C23*g*^{i}	2.75	147	3.588 (3)
C125—H125···C13*g*^{ii}	2.62	158	3.521 (3)
C133—H133···C23*g*	3.14	132	3.842 (3)
C134—H134···C31*g*	3.27	136	4.005 (3)
C213—H213···C11*g*	3.24	132	3.935 (3)
C223—H223···C13*g*	3.22	126	3.860 (3)
C224—H224···C11*g*^{iii}	2.75	148	3.591 (3)
C225—H225···C21*g*^{iv}	2.60	159	3.506 (3)
C234—H234···C33*g*	3.29	125	3.902 (3)
C314—H314···C41*g*^{v}	3.10	120	3.668 (3)
C335—H335···C41*g*^{vi}	3.38	147	4.210 (3)
C413—H413···C43*g*^{v}	3.07	143	3.867 (3)
C424—H424···C32*g*^{vi}	3.03	111	3.490 (3)

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

Data were collected during 66 h of X-ray exposure time. Reflections were measured with scan angle $\Delta\omega$ = (0.56 + 0.35 tanθ)°; horizontal and vertical apertures were (3.00 + 1.50 tanθ)° and 4.00 mm, respectively. The unit-cell parameters were checked for the presence of higher lattice symmetry (Spek, 1988). H atoms were included in the refinement at calculated positions and thereafter allowed to ride on their parent C atoms with U_{iso}(H) = 1.2U_{eq}(C). The reported R value is calculated for the reflections with $I > 2\sigma(I)$, wR is calculated for all observed reflections [$I > -3\sigma(I)$]. The somewhat high value of $\Delta\rho_{max}$ (0.83 e Å^{-3}) and its position close to P3 may be associated with this atom's lone pair of electrons but have no further chemical significance.

Data collection: locally modified *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1997). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1260). Services for accessing these data are described at the back of the journal.

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Quininium Hydrogen (*S*,*S*)-Tartrate Hemihydrate, a Salt with a Unique Conformation of the Hydrogen Tartrate Ion

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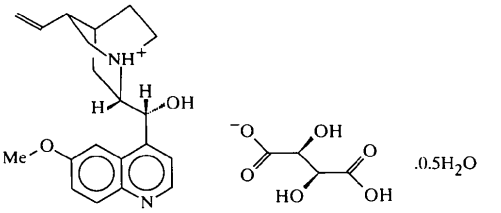
Abstract

Two independent ion pairs [(6-methoxy-4-quinolyl)(5-vinyl-1-azoniabicyclo[2.2.2]octan-2-yl)methanol hydrogen 2,3-dihydroxybutanedioate] and a water molecule are found in the asymmetric unit of $2C_{20}H_{25}N_2O_2^+.2C_4H_5O_6^-.H_2O$. The two cations are virtually identical, but the two anions have markedly different stereochemistries. One of these anions adopts a unique conformation not observed previously for hydrogen tartrate ions. The packing resembles the arrangement in cinchonidinium (*S*)-mandelate, with hydrogen-bonded chains of alternating cations and anions. The herringbone stacking of the quinoline ring systems of the cations resembles the pattern seen in other cinchona structures.

Comment

A traditional method used to isolate the pure enantiomers from a racemic mixture is through the formation of diastereomeric compounds. The racemate is reacted with a suitable resolving agent, *i.e.* an optically active compound with which it can form diastereomeric salts. The resulting salts may differ so much in their solubility that separation of the enantiomers can be achieved.

As part of our investigations of the factors that influence the suitability of a resolving agent, we are investigating the diastereomeric salts formed by the cinchona alkaloids and optically active tartaric acid. Both the cinchona alkaloid quinine and tartaric acid are frequently used as resolving agents for racemic acids and bases, respectively, and the salt, (I), formed by the reaction of quinine with optically pure (*S*,*S*)-tartaric acid was an obvious candidate for structure determination.



(I)

Two independent ion pairs (*A* and *D*) are found in the asymmetric unit. Like the free base, protonated quinine is a rather rigid molecule. In accordance with this, the two cations have almost identical geometry and stereochemistry (Fig. 1), and compare well with the geometry of the quininium ion in its mandelate salt (Gjerløv & Larsen, 1997*b*). The only significant variation of the stereochemistry involves the vinyl group, which is the most flexible part of the cation. In the present structure, the C24—C25—C26—C27 torsion angles are 127.5 (2) and 116.0 (2)° (for the ions labelled *A* and *D*, respectively), close to the average value found in a comparison of different compounds of cinchona alkaloids (Gjerløv & Larsen, 1997*a*). In the quininium mandelate salt, the corresponding torsion angle is 114.2 (2)° (Gjerløv & Larsen, 1997*b*).

The two anions adopt significantly different conformations in the crystal, as shown in Fig. 1. A search in the Cambridge Structural Database (Allen & Kennard, 1993) for hydrogen tartrate ions resulted in 89 salts of organic cations. In all these compounds, the hydrogen tartrate ions have an extended conformation with the backbone torsion angles (C1—C2—C3—C4) in a narrow range of ±16° around 180°. The *A* anion conforms well with this picture, with a torsion angle of 172.80 (13)°, whereas the equivalent angle in the *D* anion is −48.5 (2)°. This first example of a hydrogen tartrate ion in a quite unique conformation is likely to be an effect of the crystal packing.

Each cation has two hydrogen-bond donors (O18 and N2) and only one hydrogen-bond acceptor (O18), whereas each hydrogen tartrate ion has three potential hydrogen-bond donors and six acceptor atoms. One water molecule with two donor H atoms and one acceptor is also present in the structure. All potential