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

O(3)—C(3)	1.234 (6)	C(9)—C(11)	1.541 (6)
O(17)—C(22)	1.355 (7)	C(9)—C(10)	1.545 (6)
O(17)—C(17)	1.458 (5)	C(11)—C(12)	1.540 (6)
C(1)—C(10)	1.519 (8)	C(12)—C(13)	1.526 (7)
C(1)—C(2)	1.524 (7)	C(13)—C(14)	1.530 (6)
C(2)—C(3)	1.482 (7)	C(13)—C(18)	1.536 (6)
C(3)—C(4)	1.450 (8)	C(13)—C(17)	1.561 (6)
C(4)—C(5)	1.348 (7)	C(14)—C(15)	1.515 (8)
C(5)—C(6)	1.493 (8)	C(15)—C(16)	1.567 (7)
C(5)—C(10)	1.513 (6)	C(16)—C(17)	1.549 (7)
C(6)—C(7)	1.528 (7)	C(17)—C(20)	1.457 (8)
C(7)—C(8)	1.532 (6)	C(20)—C(21)	1.176 (7)
C(8)—C(14)	1.526 (6)	O(22)—C(22)	1.202 (7)
C(8)—C(9)	1.550 (7)	C(22)—C(23)	1.503 (8)
C(22)—O(17)—C(17)	119.4 (4)	C(13)—C(12)—C(11)	110.6 (4)
C(10)—C(1)—C(2)	112.1 (5)	C(12)—C(13)—C(14)	109.5 (4)
C(3)—C(2)—C(1)	111.7 (5)	C(12)—C(13)—C(18)	110.7 (4)
O(3)—C(3)—C(4)	120.4 (6)	C(14)—C(13)—C(18)	112.7 (4)
O(3)—C(3)—C(2)	121.2 (6)	C(12)—C(13)—C(17)	115.8 (4)
C(4)—C(3)—C(2)	118.3 (5)	C(14)—C(13)—C(17)	99.8 (3)
C(5)—C(4)—C(3)	122.0 (5)	C(18)—C(13)—C(17)	107.9 (4)
C(4)—C(5)—C(6)	120.1 (5)	C(15)—C(14)—C(8)	119.4 (4)
C(4)—C(5)—C(10)	122.1 (5)	C(15)—C(14)—C(13)	104.8 (4)
C(6)—C(5)—C(10)	117.6 (4)	C(8)—C(14)—C(13)	112.4 (3)
C(5)—C(6)—C(7)	113.6 (4)	C(14)—C(15)—C(16)	104.4 (4)
C(6)—C(7)—C(8)	111.2 (4)	C(17)—C(16)—C(15)	105.6 (4)
C(14)—C(8)—C(7)	111.8 (4)	C(20)—C(17)—O(17)	108.7 (4)
C(14)—C(8)—C(9)	109.5 (4)	C(20)—C(17)—C(16)	111.5 (4)
C(7)—C(8)—C(9)	109.0 (4)	O(17)—C(17)—C(16)	113.4 (4)
C(11)—C(9)—C(10)	111.4 (4)	C(20)—C(17)—C(13)	112.4 (4)
C(11)—C(9)—C(8)	112.4 (4)	O(17)—C(17)—C(13)	107.1 (3)
C(10)—C(9)—C(8)	111.5 (4)	C(16)—C(17)—C(13)	103.6 (4)
C(5)—C(10)—C(1)	111.7 (4)	C(21)—C(20)—C(17)	179.4 (5)
C(5)—C(10)—C(9)	111.6 (4)	O(22)—C(22)—O(17)	123.2 (5)
C(1)—C(10)—C(9)	111.9 (4)	O(22)—C(22)—C(23)	127.6 (6)
C(12)—C(11)—C(9)	112.5 (4)	O(17)—C(22)—C(23)	109.2 (6)
C(13)—C(17)—O(17)—C(22)	172.9 (5)		
C(16)—C(17)—O(17)—C(22)	59.2 (6)		
C(17)—O(17)—C(22)—O(22)	−0.6 (9)		
C(17)—O(17)—C(22)—C(23)	179.9 (5)		

Table 3. *C—H···O hydrogen-bond parameters (Å, °)*

As H-atom positions are theoretical (C—H 1.09 Å), no e.s.d.'s are given for parameters involving H atoms.

C—H···O	H···O	C···O	C—H···O	H···O═C
C21—H···O3^{i}	2.18	3.097 (7)	140	145
C4—H···O22^{ii}	2.49	3.578 (7)	172	161

Symmetry codes: (i) $\frac{3}{2} - x, 1 - y, z + \frac{3}{2}$; (ii) $\frac{1}{2} - x, 1 - y, z - \frac{3}{2}$.

Table 4. *Selected IR stretching frequencies (FTIR; cm^{-1})*

	In CCl_4	Crystal	$\Delta\nu$
$\nu_{\equiv C-H}$	3309.5	3238.5	−71.0
$\nu_{C═O}$ (C3═O3)^{a}	1678.4	1668.2	−10.2
$\nu_{C═O}$ (C22═O22)^{a}	1751.5	1751.1	−0.4

^{a} Assignment of the two $\nu_{C═O}$ bands is unambiguous since the ν_{CO} value for the ester C22═O22 must be at appreciably higher wavenumbers than that of the ketone C3═O3.

H atoms were treated using a riding model (*SHELXL*93; Sheldrick, 1993) with C—H = 1.09 Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1177). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Triphenylpropargylphosphonium Bromide

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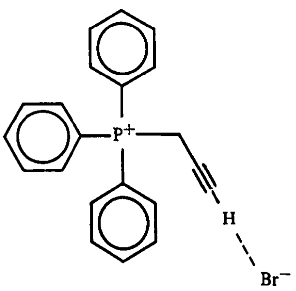
Abstract

The asymmetric crystal unit of the title compound, $C_{21}H_{18}P^{+}.Br^{-}$, contains two formula units of similar geometry. The alkynyl residues of both independent cations donate hydrogen bonds to bromide ions with

$H\cdots Br^-$ distances of 2.66 and 2.58 Å. This represents $C—H\cdots Br^-$ hydrogen bonding of considerable strength.

Comment

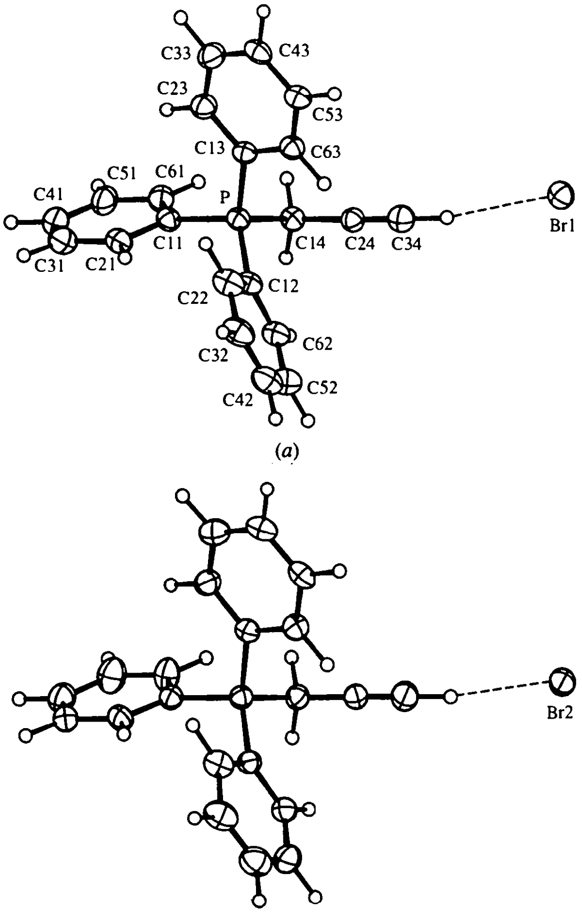
The crystal structure of the title compound, (I), was determined primarily in order to characterize the contact geometries of the organic cation with the Br^- counterion. Of particular interest is the behaviour of the alkynyl residue which is known to be one of the strongest C—H hydrogen-bond donors (Desiraju, 1991; Steiner, 1994; Lutz, van der Maas & Kanters, 1994).



(I)

The crystal structure contains two formula units per asymmetric crystal unit (Fig. 1), which are related by a pseudo centre of symmetry at x/a = 0.609 (4), y/b = 0.248 (5) and z/c = 0.614 (2). The geometry of the cations is similar but with a substantial difference in the orientation of one phenyl ring [torsion angle C14—P—C12—C22 = 155.7 (5) and 166.2 (5)° in molecules *A* and *B*, respectively]. In both cations, the alkynyl residue donates a short and almost-linear hydrogen bond to a bromide ion; the corresponding $H\cdots Br^-$ distances are 2.66 and 2.58 Å for cations *A* and *B*, respectively. In the region of alkynyl C—H stretching frequencies, the IR absorption spectrum shows a relatively broad and asymmetric band peaking at 3149.8 cm^{-1} (the asymmetry is presumably due to the composition of two individual bands from the two symmetry-independent alkynyl groups). This is one of the lowest solid-state alkynyl C—H stretching frequencies reported, indicating a considerable strength in the $C—H\cdots Br^-$ hydrogen bonds. [In a different alkynyl salt, propargylamine hydrochloride, $NH_3^+—CH_2—CC—H\cdots Cl^-$ (Steiner, 1995), the $C—H\cdots Cl^-$ interaction with $H\cdots Cl$ = 2.63 Å is associated with an alkynyl C—H stretching frequency of 3247 cm^{-1}.]

In addition to the alkynyl $C—H\cdots Br^-$ contacts, the cations are tightly coordinated with bromide ions, as shown in Fig. 2 for cation *B*. All three phenyl rings and the propargyl CH_2 group are involved in short contacts to Br^- (geometries are listed in Table 3 for $H\cdots Br^-$ distances shorter than 3.2 Å). For these contacts, one can debate whether they may be regarded as 'hydrogen



(*a*)

(*b*)

Fig. 1. Molecular structure and atom labelling in (*a*) molecule *A* and (*b*) molecule *B* of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

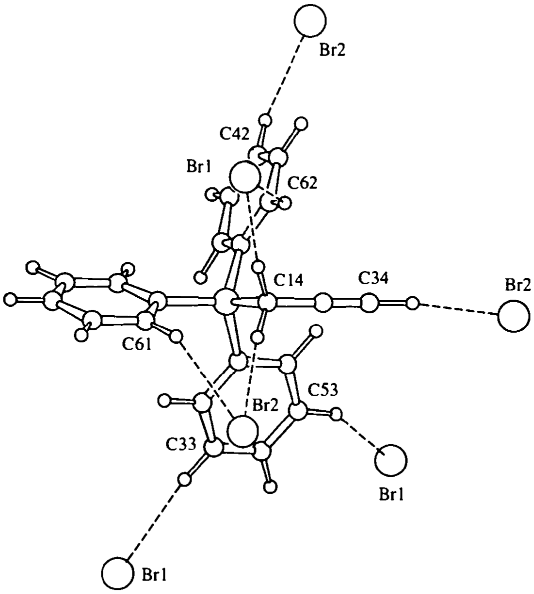


Fig. 2. Contacts to Br^- shorter than $H\cdots Br^-$ = 3.2 Å in cation *B*.

bonds' or if they are merely the result of the electrostatic attraction of Br^- by the central charge of the cation. Generally, the discussion of how $R^+C—H\cdots X^-$ contacts should be interpreted is not yet closed; only for the special case of $R^+—CC—H\cdots X^-$ interactions do the particular vibrational properties of the alkynyl C—H bond allow direct deduction of the hydrogen-bonding nature from the vibrational spectra.

Experimental

The title compound is commercially available (Lancester) and was recrystallized from MeOH.

Crystal data

$C_{21}H_{18}P^+.Br^-$
$M_r = 381.23$
Orthorhombic
$Pca2_1$
$a = 14.868$ (5) Å
$b = 11.953$ (2) Å
$c = 20.403$ (6) Å
$V = 3626.0$ (17) Å^3
$Z = 8$
$D_x = 1.397$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54176$ Å
Cell parameters from 25 reflections
$\theta = 10.3–31.0°$
$\mu = 3.879$ mm^{-1}
$T = 293$ (2) K
Rod
0.55 × 0.10 × 0.07 mm
Pale yellow

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: semi-empirical (ψ-scan; North, Phillips & Matthews, 1968)
$T_{min} = 0.82$, $T_{max} = 0.99$
2991 measured reflections
2763 independent reflections

2361 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0206$
$\theta_{max} = 59.65°$
$h = 0 \rightarrow 16$
$k = -13 \rightarrow 1$
$l = -22 \rightarrow 0$
3 standard reflections
frequency: 30 min
intensity decay: 10.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0295$
$wR(F^2) = 0.0827$
$S = 1.045$
2751 reflections
451 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 1.2098P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.001$

$\Delta\rho_{max} = 0.199$ e Å^{-3}
$\Delta\rho_{min} = -0.261$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = 0.06 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	*y*	*z*	U_{eq}
Br1	0.77297 (4)	0.40831 (5)	1.20321 (3)	0.0602 (2)
P*A*	0.38639 (10)	0.55814 (11)	0.99380 (7)	0.0412 (4)
C11*A*	0.2865 (4)	0.6335 (5)	0.9742 (3)	0.0458 (15)
C21*A*	0.2547 (5)	0.6305 (5)	0.9092 (3)	0.056 (2)
C31*A*	0.1761 (5)	0.6859 (6)	0.8936 (4)	0.070 (2)
C41*A*	0.1313 (5)	0.7469 (6)	0.9404 (4)	0.074 (2)
C51*A*	0.1625 (4)	0.7522 (6)	1.0047 (4)	0.068 (2)
C61*A*	0.2404 (4)	0.6933 (5)	1.0216 (4)	0.059 (2)
C12*A*	0.4668 (4)	0.5660 (5)	0.9287 (3)	0.0486 (15)
C22*A*	0.4623 (5)	0.4900 (5)	0.8769 (3)	0.067 (2)
C32*A*	0.5263 (6)	0.4944 (7)	0.8274 (4)	0.073 (2)
C42*A*	0.5927 (5)	0.5724 (7)	0.8294 (4)	0.076 (2)
C52*A*	0.5954 (5)	0.6496 (6)	0.8798 (4)	0.075 (2)
C62*A*	0.5323 (5)	0.6480 (5)	0.9289 (3)	0.059 (2)
C13*A*	0.3590 (4)	0.4138 (4)	1.0077 (3)	0.0428 (14)
C23*A*	0.2701 (4)	0.3806 (5)	1.0147 (4)	0.057 (2)
C33*A*	0.2521 (5)	0.2681 (5)	1.0280 (5)	0.065 (2)
C43*A*	0.3214 (5)	0.1916 (5)	1.0324 (3)	0.055 (2)
C53*A*	0.4091 (4)	0.2254 (5)	1.0250 (3)	0.0517 (14)
C63*A*	0.4287 (4)	0.3354 (4)	1.0133 (3)	0.049 (2)
C14*A*	0.4333 (4)	0.6197 (4)	1.0660 (3)	0.0442 (14)
C24*A*	0.5181 (4)	0.5667 (5)	1.0863 (3)	0.047 (2)
C34*A*	0.5844 (5)	0.5238 (6)	1.1053 (4)	0.063 (2)
Br2	0.49401 (4)	1.08460 (5)	0.52664 (3)	0.0593 (2)
P*B*	0.10650 (10)	0.94658 (12)	0.73460 (8)	0.0420 (4)
C11*B*	0.0072 (4)	0.8664 (5)	0.7553 (3)	0.0447 (14)
C21*B*	−0.0273 (4)	0.8708 (6)	0.8183 (3)	0.054 (2)
C31*B*	−0.1027 (4)	0.8098 (6)	0.8344 (4)	0.059 (2)
C41*B*	−0.1436 (5)	0.7459 (6)	0.7870 (4)	0.068 (2)
C51*B*	−0.1116 (5)	0.7426 (7)	0.7238 (4)	0.082 (2)
C61*B*	−0.0353 (5)	0.8041 (6)	0.7076 (4)	0.070 (2)
C12*B*	0.1850 (4)	0.9481 (5)	0.8006 (3)	0.0463 (14)
C22*B*	0.1669 (5)	1.0149 (6)	0.8547 (3)	0.065 (2)
C32*B*	0.2238 (6)	1.0125 (7)	0.9090 (4)	0.082 (3)
C42*B*	0.2993 (6)	0.9502 (7)	0.9069 (4)	0.081 (3)
C52*B*	0.3190 (5)	0.8852 (6)	0.8523 (4)	0.075 (2)
C62*B*	0.2617 (4)	0.8821 (5)	0.7982 (3)	0.056 (2)
C13*B*	0.0761 (4)	1.0878 (5)	0.7166 (3)	0.0458 (15)
C23*B*	−0.0131 (4)	1.1207 (6)	0.7089 (4)	0.058 (2)
C33*B*	−0.0326 (6)	1.2305 (6)	0.6949 (5)	0.071 (2)
C43*B*	0.0355 (5)	1.3074 (5)	0.6862 (3)	0.063 (2)
C53*B*	0.1236 (5)	1.2753 (5)	0.6919 (3)	0.056 (2)
C63*B*	0.1464 (4)	1.1651 (5)	0.7077 (3)	0.053 (2)
C14*B*	0.1566 (4)	0.8820 (5)	0.6630 (3)	0.0472 (15)
C24*B*	0.2362 (5)	0.9356 (5)	0.6399 (3)	0.050 (2)
C34*B*	0.3030 (5)	0.9781 (6)	0.6194 (4)	0.066 (2)

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

P*A*—C11*A*	1.783 (6)	P*B*—C12*B*	1.783 (6)
P*A*—C14*A*	1.789 (5)	P*B*—C13*B*	1.786 (6)
P*A*—C12*A*	1.791 (6)	P*B*—C11*B*	1.811 (6)
P*A*—C13*A*	1.795 (5)	P*B*—C14*B*	1.812 (6)
C14*A*—C24*A*	1.470 (9)	C14*B*—C24*B*	1.426 (9)
C24*A*—C34*A*	1.177 (9)	C24*B*—C34*B*	1.192 (9)
C11*A*—P*A*—C14*A*	107.6 (3)	C12*B*—P*B*—C13*B*	108.2 (3)
C11*A*—P*A*—C12*A*	111.3 (3)	C12*B*—P*B*—C11*B*	111.3 (3)
C14*A*—P*A*—C12*A*	109.2 (3)	C13*B*—P*B*—C11*B*	110.0 (3)
C11*A*—P*A*—C13*A*	109.4 (3)	C12*B*—P*B*—C14*B*	110.1 (3)
C14*A*—P*A*—C13*A*	110.7 (3)	C13*B*—P*B*—C14*B*	109.9 (3)
C12*A*—P*A*—C13*A*	108.6 (3)	C11*B*—P*B*—C14*B*	107.3 (3)
C24*A*—C14*A*—P*A*	112.8 (4)	C24*B*—C14*B*—P*B*	114.6 (4)
C34*A*—C24*A*—C14*A*	177.0 (7)	C34*B*—C24*B*—C14*B*	178.3 (7)

C14*A*—P*A*—C11*A*—C21*A*	157.4 (5)
C14*A*—P*A*—C12*A*—C22*A*	155.7 (5)
C14*A*—P*A*—C13*A*—C23*A*	106.2 (6)
C11*A*—P*A*—C14*A*—C24*A*	−178.3 (4)
C14*B*—P*B*—C11*B*—C21*B*	158.2 (5)
C14*B*—P*B*—C12*B*—C22*B*	166.2 (5)
C14*B*—P*B*—C13*B*—C23*B*	107.6 (6)
C11*B*—P*B*—C14*B*—C24*B*	179.8 (5)

Table 3. *Parameters of the C—H···Br contacts (Å, °)*

As H-atom positions are theoretical (refined using a riding model), no e.s.d.'s are given for parameters involving H atoms.

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
C34*A*—H34*A*···Br1	2.66	3.710 (8)	161
C34*B*—H34*B*···Br2	2.58	3.643 (8)	164
C61*A*—H61*A*···Br1^i	2.95	3.929 (8)	150

C14*A*—H14*B*···Br1^{i}	2.60	3.692 (6)	178
C62*A*—H62*A*···Br2^{ii}	2.76	3.788 (7)	157
C14*A*—H14*A*···Br2^{ii}	2.71	3.782 (6)	169
C14*B*—H14C···Br1^{iii}	2.63	3.716 (6)	175
C62*B*—H62*B*···Br1^{iii}	3.13	4.009 (7)	138
C42*A*—H42*A*···Br1^{iv}	2.95	3.804 (8)	136
C33*B*—H33*B*···Br1^{v}	3.12	4.161 (8)	159
C53*B*—H53*B*···Br1^{vi}	3.16	4.089 (6)	143
C14*B*—H14D···Br2^{vii}	2.63	3.707 (6)	171
C61*B*—H61*B*···Br2^{vii}	2.99	3.948 (9)	147
C42*B*—H42*B*···Br2^{ii}	2.90	3.947 (8)	161
C53*A*—H53*A*···Br2^{viii}	3.04	3.976 (6)	144

Symmetry codes: (i) $x - \frac{1}{2}, 1 - y, z$; (ii) $1 - x, 2 - y, \frac{1}{2} + z$; (iii) $1 - x, 1 - y, z - \frac{1}{2}$; (iv) $\frac{3}{2} - x, y, z - \frac{1}{2}$; (v) $\frac{1}{2} - x, 1 + y, z - \frac{1}{2}$; (vi) $1 - x, 2 - y, z - \frac{1}{2}$; (vii) $x - \frac{1}{2}, 2 - y, z$; (viii) $1 - x, 1 - y, \frac{1}{2} + z$.

H-atom positions were refined in a riding model (*SHELXL*93; Sheldrick, 1993) with a C—H bond length of 1.09 Å.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1184). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Glycyl-L-histidinium Chloride Dihydrate: an Unusual Histidine Conformation

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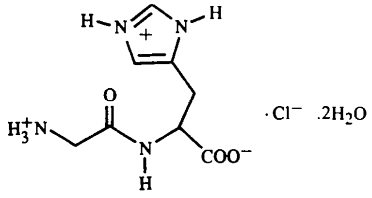
Abstract

The histidine side chain of the title compound, $C_8H_{13}N_4O_3^+.Cl^-.2H_2O$, is protonated and is incorporated in a tight N—H···*X* and C—H···*X* hydrogen-bonding pattern. The orientation of the imidazole moiety is unusual and associated with a short intramolecular C—H···O═C hydrogen bond from HisC*δ*—H to the peptide C═O. This configuration has not been observed previously with peptides.

Comment

The crystal structure of the title compound, (1), was determined primarily to study the hydrogen-bonding interactions of the histidine residue. When carrying a positive charge, the imidazole moiety of histidine is often found tightly coordinated to hydrogen-bond acceptors. Not only both N—H but also both imidazole C—H groups then donate hydrogen bonds (see Steiner, 1995, 1996).



(1)

Compound (1) was crystallized as a mono hydrochloride so the dipeptide carries positive charges at the N terminus and at the histidine side chain, and a negative charge at the C terminus (Fig. 1*a*). There are two water molecules cocrystallized for every dipeptide. This leads to a complex system of O—H···*X*, N—H···*X* and C—H···*X* hydrogen bonds (*X* = O, Cl$^-$; Table 3) that need not be discussed here in detail. The hydrogen-bonding pattern formed by the imidazole moiety of (1) is shown in Fig. 2. As in previous studies, all N—H and C—H donors are engaged in hydrogen bonding, those donated by N3—H and C8—H even being three-centered. Most remarkable is a short intramolecular C—H···O hydrogen bond from C7—H (*i.e.* HisC*δ*—H) to the peptide C═O.

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