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The Crystal and Molecular Structure of (*S*)-1′-Ethoxycarbonyloxyethyl 6β-[(Hexahydro-1*H*-azepin-1-yl)methyleneamino]penicillanate Hydrochloride (Bacmecillinam* Hydrochloride)

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(*S*)-1′-Ethoxycarbonyloxyethyl 6β-[(hexahydro-1*H*-azepin-1-yl)methyleneamino]penicillanate hydrochloride, $C_{20}H_{31}O_6N_3S.HCl$, orthorhombic, $P2_12_12_1$, $a = 22{\cdot}447\ (5)$, $b = 14{\cdot}700\ (3)$, $c = 7{\cdot}546\ (2)$ Å, $Z = 4$. The structure was solved by direct methods and refined by least-squares procedures against 2168 diffractometer-collected reflexions to a final linear R value of 0·052. The chlorine anion is hydrogen-bonded to the cation. The crystal structure seems to be further stabilized by electrostatically favourable molecular packing in addition to the van der Waals forces.

Introduction

Many semisynthetic penicillins carrying an acyl moiety on the 6-amino group have been prepared in search of penicillins with improved oral absorption, resistance to penicillinase, and increased activity towards Gram-negative bacilli. A new type of *N*-substituted 6-amino-penicillanic acid with enhanced activity against Gram-negative bacteria, the 6β-amidinopenicillanic acids, was described by Lund & Tybring (1972). One member of this series, 6β-[(hexahydro-1*H*-azepin-1-yl)methylene-amino]penicillanic acid (mecillinam), was selected for further study. It was found that the morphological response of *E. coli* bacteria to mecillinam was different from that to ampicillin and benzylpenicillin (Melchior, Blom, Tybring & Birch-Andersen, 1973) and that mecillinam did not inhibit murein transpeptidase (Park & Burman, 1973). Furthermore, it was shown by Spratt (1975) that mecillinam bound preferentially to a penicillin-binding protein, protein 2, which is involved in the maintenance of cell shape, rather than to the proteins involved in elongation or septum formation. Thus the mode of action of mecillinam appears to be different from that of penicillins.

Mecillinam itself is poorly absorbed by the oral route (Roholt, Nielsen & Kristensen, 1975), and thus esters of mecillinam have been developed which are well absorbed after oral administration and hydrolysed *in vivo* giving mecillinam. Examples of such esters are the pivaloyloxymethyl ester, pivmecillinam (Lund & Tybring, 1972; Roholt *et al.*, 1975) and the 1′-ethoxy-carbonyloxyethyl ester, bacmecillinam (Bamberg, Ekström, Forsgren, Magni, Pring & Sjöberg, 1977), the structure of which is given in Fig. 1. An X-ray structure analysis of bacmecillinam hydrochloride having the (*S*)-configuration for the ester group has now been performed in order to obtain information about the conformational features of an amidinopenicillanic acid derivative.

* Proposed international nonproprietary name.

Experimental

The crystals of the title compound were prepared in the laboratories of Astra Läkemedel AB (Ekström, Molin, Pring, Csöregh & Palm, 1977).

Preliminary X-ray investigations using oscillation, De Jong–Bouman and precession photographic techniques showed that the crystal symmetry is orthorhombic with space group $P2_12_12_1$. Powder photographs were taken by a Guinier–Hägg focusing camera using Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}54056$ Å) and potassium chloride ($a = 6{\cdot}29228$ Å) as an internal standard. The least-squares-refined unit-cell dimensions obtained from the X-ray powder pattern are: $a = 22{\cdot}447\ (5)$, $b = 14{\cdot}700\ (3)$ and $c = 7{\cdot}546\ (2)$ Å. Three-dimensional intensity data were collected with a PW 1100 single-crystal diffractometer. Graphite-monochromatized Cu $K\alpha$ radiation was used. The selected single crystal had the approximate dimensions 0·3 × 0·3 × 0·5 mm. The intensities of 2546 independent reflections with $\theta \leq 65°$ were measured. The net intensities were corrected for Lorentz–polarization, absorption ($\mu = 24{\cdot}6$ cm^{-1}) and extinction effects. In the refinement of the structure, 2168 structure factors with $F > 6\sigma(F)$, where $\sigma(F)$ is the estimated standard deviation, were used.

Structure determination and refinement

Preliminary structure factor phases were derived by direct methods. 220 E values ($|E| > 1{\cdot}60$) and the

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *for the non-hydrogen atoms, with estimated standard deviations in parentheses*

	x	*y*	*z*
Cl	9449 (1)	7320 (2)	4017 (2)
N(1)	8125 (2)	7907 (3)	10297 (6)
C(2)	7984 (3)	7611 (4)	12096 (7)
C(3)	7838 (3)	6573 (4)	11999 (9)
S(4)	8351 (1)	6174 (1)	10224 (3)
C(5)	8205 (3)	7188 (5)	8970 (8)
C(6)	8744 (3)	7745 (5)	8231 (8)
C(7)	8647 (3)	8356 (4)	9875 (8)
C(8)	8911 (2)	8956 (3)	10585 (6)
C(9)	7196 (4)	6399 (7)	11425 (12)
C(10)	7988 (4)	6081 (6)	13703 (11)
C(11)	7473 (3)	8156 (4)	12879 (8)
O(12)	7121 (2)	8605 (4)	12081 (6)
O(13)	7495 (2)	8092 (3)	14655 (5)
N(14)	9324 (2)	7336 (4)	8028 (6)
C(15)	9669 (3)	7122 (4)	9376 (7)
N(16)	10195 (2)	6765 (4)	9226 (6)
C(17)	10465 (4)	6540 (7)	7520 (10)
C(18)	10320 (6)	5651 (8)	6868 (13)
C(19)	10308 (8)	4876 (9)	8175 (18)
C(20)	10666 (7)	4881 (7)	9807 (19)
C(21)	10527 (5)	5548 (8)	11239 (12)
C(22)	10537 (4)	6529 (6)	10813 (10)
C(23)	7031 (3)	8531 (5)	15661 (9)
C(24)	7271 (4)	9343 (6)	16621 (13)
O(25)	6840 (2)	7888 (3)	16925 (6)
C(26)	6466 (3)	7245 (5)	16321 (9)
O(27)	6284 (2)	7175 (4)	14853 (7)
O(28)	6319 (2)	6728 (4)	17687 (7)
C(29)	5857 (4)	6047 (6)	17364 (15)
C(30)	5673 (6)	5722 (8)	19139 (18)

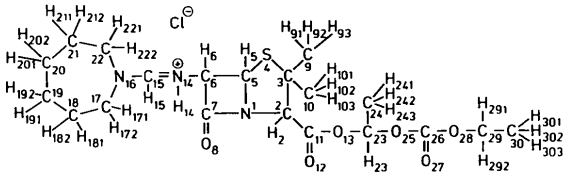

Fig. 1. Schematic drawing of the protonated bacmecillinam with atoms numbered for reference in the text.

1500 best triple relations among them were used to generate four trial phase sets by the program system *MULTAN* (Main, Woolfson & Germain, 1971). In the *E* map, computed from the phase set with the best figure of merit, 20 peaks could be recognized as a fragment of the molecule. A subsequent difference Fourier synthesis and full-matrix least-squares refinement revealed the remaining 10 non-hydrogen positions and 17 H positions. The coordinates of the remaining 14 H atoms were calculated geometrically. At this stage the real and imaginary components of the anomalous-dispersion correction for the Cl and S atoms were included in the structure factor calculations. In the last refinement of the structural model the unweighted

Table 2. *Fractional atomic coordinates* ($\times 10^3$) *for the hydrogen atoms, with estimated standard deviations in parentheses*

	x	*y*	*z*
H(2)	837 (4)	759 (5)	1282 (11)
H(5)	791 (4)	699 (6)	822 (11)
H(6)	868 (4)	803 (6)	693 (11)
H(91)	693 (4)	673 (5)	1233 (11)
H(92)	711 (4)	657 (6)	1056 (12)
H(93)	712 (4)	571 (6)	1123 (11)
H(101)	839 (4)	624 (6)	1404 (11)
H(102)	767 (4)	630 (6)	1463 (11)
H(103)	790 (4)	547 (6)	1352 (11)
H(14)	945 (4)	718 (6)	718 (13)
H(15)	951 (4)	728 (6)	1036 (12)
H(171)	1043 (4)	703 (6)	664 (11)
H(172)	1092 (4)	638 (6)	768 (11)
H(181)	983 (4)	571 (5)	592 (12)
H(182)	1061 (4)	545 (6)	611 (12)
H(191)	996 (4)	485 (6)	887 (12)
H(192)	1033 (4)	438 (6)	764 (13)
H(201)	1072 (4)	437 (6)	1060 (12)
H(202)	1109 (4)	514 (6)	927 (12)
H(211)	1009 (4)	538 (6)	1149 (11)
H(212)	1073 (4)	537 (6)	1234 (13)
H(221)	1038 (4)	682 (6)	1169 (12)
H(222)	1095 (4)	671 (5)	1055 (11)
H(23)	668 (4)	869 (5)	1497 (11)
H(241)	697 (4)	973 (6)	1726 (11)
H(242)	748 (4)	972 (6)	1593 (11)
H(243)	758 (4)	916 (6)	1753 (12)
H(291)	546 (4)	637 (6)	1679 (11)
H(292)	601 (4)	566 (6)	1677 (11)
H(301)	539 (4)	525 (6)	1886 (11)
H(302)	596 (4)	538 (6)	1987 (12)
H(303)	556 (4)	624 (6)	1981 (12)

reliability index *R* reduced to 0·052 for the 2168 reflexions. The non-hydrogen atoms were allowed to vibrate anisotropically while the H atoms were given the fixed isotropic temperature factor of 5·0 Å^2, obtained from a Wilson plot. The atomic scattering factors and the real and imaginary dispersion corrections for the Cl and S atoms were those given by *International Tables for X-ray Crystallography* (1974). The fractional atomic coordinates are listed in Tables 1 and 2.* The atomic labels used are shown in Fig. 1.

Discussion

The molecular conformation of protonated (*S*)-1′-ethoxycarbonyloxyethyl 6*β*-[(hexahydro-1*H*-azepin-1-yl)methyleneamino]penicillanate, bacmecillinam, is displayed in Fig. 2. The intramolecular bond distances and angles within the cation are listed in Tables 3 and 4.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32849 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

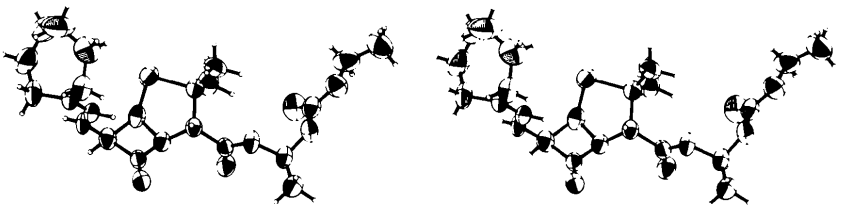

Fig. 2. Stereoscopic view of the protonated bacmecillinam. The non-hydrogen atoms are represented by their thermal ellipsoids, while the H atoms are drawn with constant radii.

The geometry of the bicyclic penicillanate moiety found in the present study is compared with that in (*S*)-1′-ethoxycarbonyloxyethyl 6β-phenylacetamidopenicillanate (Csöregh & Palm, 1977) and in the corresponding *p*-bromophenylacetamido derivative (Csöregh & Palm, 1976). However, this latter compound yields less accurate bond distances and angles owing to the presence of the Br atom.

Table 3. *Intramolecular bond distances* (Å) *between the non-hydrogen atoms of protonated bacmecillinam*

The estimated standard deviations are given in parentheses.

N(1)–C(2)	1·460 (7)	N(14)–C(15)	1·317 (7)
N(1)–C(5)	1·467 (8)	C(15)–N(16)	1·297 (8)
N(1)–C(7)	1·382 (7)	N(16)–C(17)	1·461 (9)
C(2)–C(3)	1·562 (8)	N(16)–C(22)	1·464 (9)
C(2)–C(11)	1·519 (8)	C(17)–C(18)	1·434 (15)
C(3)–S(4)	1·861 (6)	C(18)–C(19)	1·507 (17)
C(3)–C(9)	1·526 (11)	C(19)–C(20)	1·471 (21)
C(3)–C(10)	1·513 (10)	C(20)–C(21)	1·492 (16)
S(4)–C(5)	1·796 (7)	C(21)–C(22)	1·478 (14)
C(5)–C(6)	1·564 (9)	C(23)–C(24)	1·497 (11)
C(6)–C(7)	1·547 (8)	C(23)–O(25)	1·410 (8)
C(6)–N(14)	1·442 (8)	O(25)–C(26)	1·344 (8)
C(7)–O(8)	1·190 (7)	C(26)–O(27)	1·185 (8)
C(11)–O(12)	1·193 (7)	C(26)–O(28)	1·322 (8)
C(11)–O(13)	1·344 (7)	O(28)–C(29)	1·462 (10)
O(13)–C(23)	1·441 (8)	C(29)–C(30)	1·481 (17)

The β-lactam ring has a similar geometry in these structures. The lactam N(1) is 0·42 Å out of the plane defined by its three substituents, C(2), C(5) and C(7). The sum of the bond angles around N(1) is 334·0°.

The thiazolidine ring can adopt two different conformations in penicillins (Cooper, De Marco, Cheng & Jones, 1969; Sweet, 1972); one of them is seen in the arylacetamido derivatives mentioned above, while the five-membered ring in protonated bacmecillinam adopts the other. In this case the S atom departs 0·862 Å from the plane defined by the other four atoms in the ring (*cf.* Table 5). The C–S–C angle is 90·3 (2)°, and the carboxylate C(11) lies in an equatorial position. The angle between the best planes of the thiazolidine ring and the β-lactam group is 43°. The bond lengths in the penicillanate moiety of the bacmecillinam molecule agree well with those found in the phenylacetamido derivative with one exception: the S(4)–C(5) distance is 1·796 (7) Å in protonated bacmecillinam and 1·825 (4) Å in the phenylacetamido derivative. The bond angles in the β-lactams of these two structures are also in good agreement, but not those in the five-membered rings. These differences certainly depend on different conformations of the thiazolidine rings in these structures. In the crystal structure of ampicillin trihydrate (James, Hall & Hodgkin, 1968) the five-membered ring shows the same conformation as in the present molecule, and the bond

Table 4. *Intramolecular bond angles* (°) *involving the non-hydrogen atoms of protonated bacmecillinam*

The estimated standard deviations are given in parentheses.

C(2)–N(1)–C(5)	116·5 (4)	C(5)–C(6)–C(7)	84·8 (4)	N(16)–C(17)–C(18)	114·5 (7)
C(2)–N(1)–C(7)	122·7 (4)	C(5)–C(6)–N(14)	121·2 (5)	C(17)–C(18)–C(19)	117·9 (9)
C(5)–N(1)–C(7)	94·8 (4)	C(7)–C(6)–N(14)	117·0 (5)	C(18)–C(19)–C(20)	122·3 (11)
N(1)–C(2)–C(3)	107·0 (4)	N(1)–C(7)–C(6)	91·5 (4)	C(19)–C(20)–C(21)	119·7 (11)
N(1)–C(2)–C(11)	111·6 (4)	N(1)–C(7)–O(8)	132·3 (5)	C(20)–C(21)–C(22)	118·7 (8)
C(3)–C(2)–C(11)	112·0 (5)	C(6)–C(7)–O(8)	136·2 (6)	N(16)–C(22)–C(21)	113·6 (7)
C(2)–C(3)–S(4)	102·2 (4)	C(2)–C(11)–O(12)	126·6 (5)	O(13)–C(23)–C(24)	110·6 (5)
C(2)–C(3)–C(9)	112·0 (5)	C(2)–C(11)–O(13)	108·8 (5)	O(13)–C(23)–O(25)	106·0 (5)
C(2)–C(3)–C(10)	112·4 (5)	O(12)–C(11)–O(13)	124·5 (5)	C(24)–C(23)–O(25)	108·5 (5)
S(4)–C(3)–C(9)	109·1 (5)	C(11)–O(13)–C(23)	117·8 (4)	C(23)–O(25)–C(26)	115·6 (5)
S(4)–C(3)–C(10)	108·9 (4)	C(6)–N(14)–C(15)	123·3 (4)	O(25)–C(26)–O(27)	126·4 (6)
C(9)–C(3)–C(10)	111·8 (6)	N(14)–C(15)–N(16)	124·4 (5)	O(25)–C(26)–O(28)	107·2 (5)
C(3)–S(4)–C(5)	90·3 (2)	C(15)–N(16)–C(17)	123·1 (5)	O(27)–C(26)–O(28)	126·3 (6)
N(1)–C(5)–S(4)	105·1 (3)	C(15)–N(16)–C(22)	120·1 (5)	C(26)–O(28)–C(29)	116·1 (6)
N(1)–C(5)–C(6)	87·8 (4)	C(17)–N(16)–C(22)	116·7 (5)	O(28)–C(29)–C(30)	105·5 (8)
S(4)–C(5)–C(6)	118·8 (4)				

lengths and angles found there agree within a few standard deviations with the values reported here for protonated bacmecillinam.

Atoms N(14), C(15), N(16), belonging to the amidino group, and their nearest neighbours, C(17), C(22) and C(6), are coplanar within 0·03 Å and the angle between the best planes through these atoms and the β-lactam ring is nearly 66° (*cf.* Table 5). The two C–N bonds in the amidino group are 1·317 (7) and 1·297 (8) Å respectively. Both are intermediate between a double and a single bond with some predominance of double-bond character. Thus the planar arrangement of the atoms is stabilized by resonance energy gained through π–π overlap.

In the hexamethyleneimine ring the two N–C bond lengths have the mean value of 1·462 Å in accordance with the average value of 1·462 Å for such bonds found in different organometallic hexamethylenedithiocarbamate and dialkyldithiocarbamate structures (Agre & Shugam, 1972, and references therein). The angles at the C atoms within the heterocyclic seven-membered ring range between 113 and 122° with a mean value of 118 (3)°; the angle at the N atom is 117°. These are all normal values for N–hexamethylene rings (Agre & Shugam, 1972). However, the mean value of 1·48 (3) Å for C–C bonds in the hexamethyleneimine ring is shorter than the normal $C(sp^3)$–$C(sp^3)$ distance of 1·537 (5) Å (Sutton, 1965). This difference is probably not statistically significant and within the margin of experimental error, especially as regards the high thermal-vibration amplitudes for the C(17)–C(22) ring atoms.

The carboxylate group and the (*S*)-1′-ethoxycarbonyloxyethyl ester chain have the same geometry as in the arylacetamido derivatives previously studied by us (Csöregh & Palm, 1976, 1977). The bond distances and angles are in good agreement with one exception: the carbonate carbonyl C–O distance is 1·185 (8) Å in bacmecillinam hydrochloride and 1·169 (6) Å in the phenylacetamido derivative. This lengthening probably reflects the involvement of the carbonyl O(27) in short intermolecular interactions in the bacmecillinam hydrochloride crystal since in the crystal of the benzylpenicillin ester the same O atom takes no part in shorter (<3·6 Å) intermolecular interactions.

At the end of the ester chain, C(29) and C(30) have large thermal vibrations (*cf.* Table 1) and therefore the difference between the observed C–C distance of 1·48 (2) Å and the commonly accepted value of 1·537 (5) Å (Sutton, 1965) cannot be considered as significant.

The mean value of 0·97 Å for the C–H bond lengths is compatible with X-ray-determined C–H distances (Stewart, Davidson & Simpson, 1965).

Stereoscopic views of the crystal structure are shown in Fig. 3. The short contact distance (3·040 Å) between N(14) and the chlorine ion (*cf.* Table 6) presumably indicates hydrogen bonding from the cation to the anion. The (N)H···Cl distance is 2·40 (10) Å, and the N–H···Cl angle is 147 (9)°.

All distances less than 3·6 Å between the cations are listed in Table 7. The shortest intermolecular distance of 3·19 Å between the methylene C(17) belonging to the hexamethyleneimine ring and the keto O(27) belonging to the carbonate ester group is notably

Table 5. *Equations of the least-squares (LS) planes, and deviations of the atoms from the planes* (Å)

The planes are expressed as $Ax + By + Cz = D$, where x, y and z are in Å relative to the axes a, b, and c. The atoms indicated with asterisks were omitted from the calculations of the least-squares planes. A negative sign means that the atom lies between the plane and the origin.

(1) Thiazolidine ring: LS plane through N(1), C(2), C(3) and C(5)

A = 0·954	N(1)	−0·058	C(7)*	0·872
B = −0·163	C(2)	0·054	O(8)*	1·429
C = 0·252	C(3)	−0·029	C(9)*	−1·471
D = 17·522	S(4)*	0·827	C(10)*	0·734
	C(5)	0·033	C(11)*	−1·022
	C(6)*	0·913		

The r.m.s. deviation from the plane of the atoms without asterisks is 0·045 Å.

(2) β-Lactam: LS plane through N(1), C(6), C(7) and O(8)

A = 0·509	N(1)	0·003	O(8)	0·005
B = −0·659	C(5)*	0·236	N(14)*	0·977
C = 0·554	C(6)	0·003		
D = 5·925	C(7)	−0·012		

The r.m.s. deviation from the plane of the atoms without asterisks is 0·007 Å.

(3) LS plane through C(6), N(14), C(15), N(16), C(17) and C(22)

A = 0·413	C(6)	−0·001	C(17)	−0·004
B = 0·910	N(14)	−0·006	C(22)	−0·010
C = −0·023	C(15)	0·004	H(14)*	−0·083
D = 18·332	N(16)	0·017	H(15)*	0·050

The r.m.s. deviation from the plane of the atoms without asterisks is 0·009 Å.

(4) LS plane through the seven-membered ring

A = 0·98	N(16)	−0·39	C(20)	0·29
B = 0·10	C(17)	0·37	C(21)	−0·09
C = −0·16	C(18)	−0·004	C(22)	0·13
D = 22·78	C(19)	−0·31		

The r.m.s. deviation of the atoms from the plane is 0·27 Å.

Angles between the planes (with estimated standard deviations in parentheses)

Planes		Planes	
1–2	43 (2)°	2–3	66 (1)°
1–3	76 (2)	2–4	70 (7)
1–4	28 (7)	3–4	60 (7)

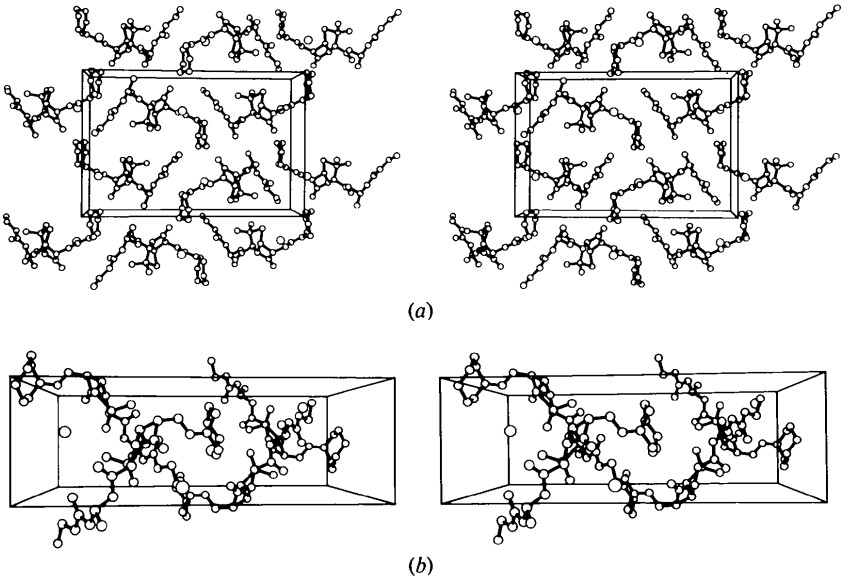

Fig. 3. Stereoscopic packing diagrams of the crystal structure viewed (*a*) along **c** and (*b*) along **b**.

Table 6. *Distances less than* 3·7 Å *between the chlorine anion and various non-hydrogen atoms of the cation*

The estimated standard deviations are in parentheses.

		Unit-cell translation along axes			
A	*B*	*a*	*b*	*c*	Distances (Å)
Cl···N(14)		0	0	0	3·040 (5)
Cl···C(15)		0	0	−1	3·549 (6)
Cl···C(6)		0	0	0	3·606 (7)
Cl···C(2)		0	0	−1	3·619 (7)
Cl···C(22)		0	0	−1	3·628 (9)
Cl···C(17)		0	0	0	3·675 (9)

shorter than the sum of the van der Waals radii of a methyl group and an O atom (3·40 Å, Pauling, 1960). Sutor (1963) asserts that this type of short CH···O intermolecular contact can be regarded as a weak hydrogen bond, especially when the C atom in the short contact is directly attached to a more electronegative atom or group and thus could be activated, which is the case in the present structure. On the other hand, the (C)H···O distance of 2·51 (9) Å observed here is by no means abnormally short and the C—H···O angle of 125 (7)° differs from 180° by an amount which appreciably exceeds those associated with hydrogen bonds (Calabrese, McPhail & Sim, 1970; Green, 1974). Sim (1967) suggests that short C—H···O contacts may represent situations in which two atoms have been forced closer together than the ideal distance for free atoms in order that the molecules may achieve more favourable packing elsewhere.

Table 7. *Intermolecular distances less than* 3·6 Å *between the non-hydrogen atoms of the cation*

The estimated standard deviations are in parentheses.

Atom *B* is generated from the coordinates of Table 1 using the unit-cell translation shown together with the following symmetry operations.

Superscript	Atom at
None	x,y,z
(i)	$\frac{1}{2}-x,-y,\frac{1}{2}+z$
(ii)	$\frac{1}{2}+x,\frac{1}{2}-y,-z$
(iii)	$-x,\frac{1}{2}+y,\frac{1}{2}-z$

		Unit-cell translation along axes			
A	*B*	*a*	*b*	*c*	Distances (Å)
C(17)	O(27^{ii})	0	1	2	3·187 (10)
C(22)	O(28^{ii})	0	1	3	3·306 (10)
O(12)	C(24^{i})	1	2	−1	3·329 (11)
C(10)	O(28)	0	0	−1	3·474 (10)
C(22)	O(25^{ii})	0	1	3	3·493 (10)
C(22)	C(26^{ii})	0	1	3	3·503 (11)
O(8)	C(18^{iii})	2	0	1	3·552 (13)
O(8)	C(21^{iii})	2	0	2	3·579 (11)
C(5)	O(25)	0	0	−1	3·582 (8)
O(8)	C(19^{iii})	2	0	1	3·599 (15)

For crystal structures this represents configurations of lowest energy for all intermolecular interactions. Table 7 shows that all intermolecular contact distances less than 3·6 Å occur in this crystal structure between negatively charged O atoms on the one hand and various C atoms on the other, most of which probably have small positive atomic charges. Thus the crystal

structure seems to be stabilized by electrostatically favourable molecular packing in addition to the conventional van der Waals forces.

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The Crystal and Molecular Structure of 2,4-Hexadiynylene Bis(*p*-chlorobenzenesulfonate)

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2,4-Hexadiynylene bis(*p*-chlorobenzenesulfonate) crystallizes in the triclinic space group $P\bar{1}$ with one molecule in a unit cell of dimensions $a = 8{\cdot}941$ (1), $b = 11{\cdot}170$ (1), $c = 5{\cdot}030$ (2) Å, $\alpha = 100{\cdot}81$ (1), $\beta = 91{\cdot}19$ (3), and $\gamma = 94{\cdot}19$ (1)°. The structure was solved by direct methods and refined by full-matrix least squares to a final R for 1723 observed reflections of 0·045. The centrosymmetric molecules pack in columns along the c axis. The details of the packing, dominated by non-bonded Cl–Cl and Cl–C(phenyl) interactions, clearly explain why the molecule does not undergo solid-state polymerization upon thermal or X-ray irradiation.

Introduction

Considerable effort has been expended during the past decade on the solid-state polymerization of organic molecules. The mechanism for such polymerization by one class of compounds, the diacetylenes, was first proposed by Wegner (1969) and later elaborated upon by Baughman (1974). Since the reactivity of the