Table 3. *Pertinent observed distances* (Å), *angles* (°) *and chemical shifts* (*p.p.m.*) *in the two diastereoisomers* (1) *and* (2) *with e.s.d.'s in parentheses*

	O3—C6″	O3—C7″*b*	O3—C—C1″—C6″	δC6″	δC7″*b*	δH(C7″*b*)
(1)	3.178 (4)	3.125 (3)	74.5 (3)	30.471	15.763	0.53
(2)	2.96 (1)	3.37 (1)	39 (1)	30.137	16.091	0.81

explain some typical differences in chemical shifts in the observed ^{1}H and ^{13}C NMR spectra by comparing the intramolecular distances of the stereoisomers as found in the crystallographic study. Pertinent observed geometry and chemical shifts are given in Table 3. The C7″*b*—O3 and C6″—O3 interactions are the only conformational differences in the two stereoisomers which may conceivably influence the chemical shifts δC6″, δC7″*b* and δH(C7″*b*). In (1), the carbonyl O atom of the camphanic ester moiety points in the direction of C7″*b*, whereas in (2) it is oriented more towards C6″, as can be seen from Fig. 3.

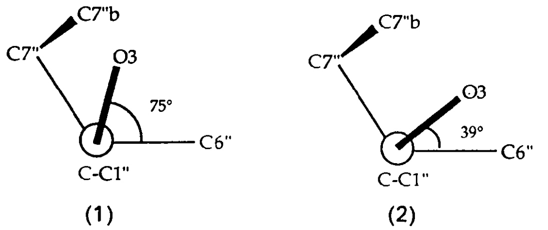

Fig. 3. Newman projection along the C—C1″ bond. Only the relevant atoms are shown.

A carbonyl group affects the chemical shifts of neighbouring nuclei (Williams & Fleming, 1987). We observe a correlation between the chemical shift values of a given nucleus and the distance from the nucleus to the carbonyl O atom. The structure with a C or an H atom closer to the carbonyl O atom gives a chemical shift at higher field. In (1), both H(C7″*b*) and C7″*b* are shifted to higher field, whereas in (2) C6″ is shifted upfield. Thus, it seems likely that the conformations of the two esters observed in the solid state are preserved in solution. The different intramolecular interactions also result in another difference in the ^{1}H spectra. The C5″ and C6″ methylene protons in (1) show a characteristic *ABCD* pattern, whereas in (2) the *ABCD* coupling system is influenced by the carbonyl group, resulting in a complicated coupling system. The trend is that this new coupling system is found at higher field. The reason for the different twisting of the camphanic esters around the C—C1″ bond is as yet unknown, but the crystallographic study corroborates the conclusions drawn from the NMR studies.

Thus, the X-ray crystallographic study verifies the configurations of the two camphanic esters. NMR studies support the results found in the crystallographic study. In spite of considerable differences in physical properties, such as solubility and melting point, relatively small differences in interatomic distances are observed.

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Structure of 4-Iodo-*trans*-cinnamic Acid and a Study of Carboxyl Group Disorder

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Abstract. (*E*)-3-(4-Iodophenyl)propenoic acid, $C_9H_7IO_2$, $M_r = 274.05$, monoclinic, $P2_1/n$, $a = 4.118\ (2)$, $b = 6.274\ (4)$, $c = 34.672\ (2)$ Å, $\beta = 90.32°$, $V = 895.7\ (9)$ Å^3, $Z = 4$, $D_x = 2.03$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 34.90$ cm^{-1}, $F(000) = 520$, $T = 153$ K, $R = 0.037$, $wR = 0.043$ for 1098

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reflections. The crystal structure is characterized by O—H···O, C—H···O and I···I interactions and resembles the packing of 4-iodobenzoic acid and 4-chlorocinnamic acid. The Cambridge Structural Database has been used to study the disorder of the carboxyl group in 47 benzoic acids and 25 cinnamic acids.

Introduction. The crystal structures of 4-halocinnamic and benzoic acids are related and are stabilized by halogen···halogen interactions, and strong (O—H···O) and weak (C—H···O) hydrogen bonding (Taylor & Kennard, 1982; Desiraju, 1991). The structures of 4-chlorobenzoic acid (4-CBA; Miller, Paul & Curtin, 1974), 4-chlorocinnamic acid (4-CCA; Glusker, Zacharias & Carrell, 1975), 4-bromobenzoic acid (4-BBA; Ohkura, Kashino & Haisa, 1972) and 4-iodobenzoic acid (4-IBA; Baughman & Nelson, 1984) have been reported previously. The structure of 4-bromocinnamic acid has not been reported. In this paper, we describe the crystal structure of 4-iodocinnamic acid (4-ICA). This compound was studied in order to examine more closely the I···I contacts which were anticipated. The study of this compound also provided an opportunity to update previous results regarding carboxyl group disorder (Dieterich, Paul & Curtin, 1974; Dunitz & Strickler, 1968) with the Cambridge Structural Database (CSD; Allen, Kennard & Taylor, 1983). Finally, it was sought to understand the crystal packing of the title compound, in the context of the other structures mentioned above.

Experimental. 4-ICA (m.p. 533–544 K) was prepared by refluxing 4-iodotoluene with *N*-bromosuccinimide in CCl_4 for 5 h (Hall & Turner, 1955). After cooling, the succinimide was filtered off. The solvent was evaporated to obtain 4-iodobenzyl bromide, which was refluxed with hexamethylenetetramine in 50% aqueous acetic acid for 2 h, to obtain the hexaminium salt. Hydrolysis with conc. HCl resulted in the formation of 4-iodobenzaldehyde (m.p. 350 K) from which 4-ICA was obtained by condensation with malonic acid. The white solid was recrystallized from a 1:2 acetone–ethyl acetate mixture. Intensity data were collected on an irregularly shaped block 0.4 × 0.4 × 0.3 mm on a Nicolet *R*3*m* diffractometer. Unit-cell parameters were obtained from 25 reflections in the range $5 < 2\theta < 30°$. The ω-scan method was used with a scan width of 2.6° and scan speed between 0.30 and 8.06 min^{-1}. A total of 1557 reflections (1150 unique) were collected with $4 < 2\theta < 50°$ in the range $0 \leq h \leq 5$, $0 \leq k \leq 8$, $-42 \leq l \leq 42$. Of these, 1098 unique reflections were found to be non-zero with $I \geq 3.0\sigma(I)$. Two standard reflections ($0\bar{1}4$ and $0,1,\overline{11}$) were measured every 98 reflections and showed less than 2% variation. Absorption corrections were applied based on ψ scans. The structure was solved by heavy-atom methods and refined using the *SHELXTL* (Sheldrick, 1978) package. The non-H atoms were refined anisotropically and the H atoms H(2), H(3), H(5), H(6), H(7) and H(8) were allowed to ride with the corresponding C atoms. Refinement converged at $R = 0.037$, $wR = 0.043$, $S = 1.708$, $(\Delta/\sigma)_{\max} = 0.035$. The maximum and minimum peaks in the final difference Fourier map were 0.99 and -1.12 e Å^{-3}, respectively (near the I atom). The scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Atomic positions and equivalent isotropic temperature factors are listed in Table 1.* The bond lengths and angles are given in Table 2. Fig. 1 is an *ORTEP* (Johnson, 1976) diagram of the molecule of 4-ICA showing the atomic numbering scheme. The angle between the mean plane of the phenyl ring and the best plane of the atoms C(1), C(7), C(8), C(9), O(1) and O(2) is 13.82 (1)°. The corresponding angles in 4-CCA, 4-CBA, 4-BBA and 4-IBA are 14.1, 1.9, 5.7 and 3.0°, respectively. The alkene–carbonyl conformation in 4-ICA is *anti* (C═C—C═O torsion angle ≃ 180°) which is unusual since the *syn* conformation (C═C—C═O torsion angle ≃ 0°) is more common for *trans*-cinnamic acids (Leiserowitz, 1976). Molecules of 4-ICA crystallize as centrosymmetric hydrogen-bonded dimers with an O···O distance of 2.592 (2) Å. Fig. 2 shows that these dimers are themselves linked by C—H···O hydrogen bonds [C2—H2···O1 3.46 (1) Å, 117.9 (8)°; C3—H3···O1 3.47 (1) Å, 119.3 (7)°; C2—H2···O2 3.63 (1) Å, 150.0 (8)°; C8—H8···O2 3.50 (1) Å, 156.1 (9)°] to form ribbons which extend along [$\bar{1}$10] and [110]. Though the H-atom positions are calculated, the C···O distances are reasonable and it may be inferred that these C—H···O bonds are of moderate strength (Desiraju, 1991). Successive ribbons are therefore inclined and related by glide-plane operations (or alternatively a screw-axis operation since the ribbon contains molecules related by a centre of symmetry). These ribbons are connected by I···I contacts of 4.132 (3) Å; the geometry of these contacts is shown in Fig. 3. It may be noted that halogen···halogen interactions C—*X*···*X*—C (*X* = Cl, Br, I) are characterized by the two C—*X*···*X* angles, θ_1 and θ_2 (Sakurai, Sundaralingam & Jeffrey, 1963; Ramasubbu, Parthasarathy & Murray-Rust, 1986; Desiraju & Parthasarathy, 1989). In the so-called Type I contacts, $\theta_1 = \theta_2$, this

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55874 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: GR1002]

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}
I	0.1280 (1)	0.0429 (1)	0.2139 (1)	32 (1)
C(1)	−0.378 (2)	0.516 (1)	0.1188 (2)	31 (3)
C(2)	−0.281 (2)	0.307 (1)	0.1079 (2)	34 (3)
C(3)	−0.127 (2)	0.177 (1)	0.1343 (2)	35 (3)
C(4)	−0.079 (2)	0.250 (1)	0.1724 (2)	32 (3)
C(5)	−0.180 (2)	0.451 (1)	0.1837 (2)	32 (2)
C(6)	−0.331 (2)	0.581 (1)	0.1562 (2)	33 (3)
C(7)	−0.543 (2)	0.661 (1)	0.0920 (2)	33 (3)
C(8)	−0.610 (2)	0.632 (2)	0.0542 (2)	41 (3)
C(9)	−0.773 (2)	0.793 (2)	0.0306 (2)	40 (3)
O(1)	−0.861 (2)	0.968 (1)	0.0474 (2)	48 (2)
O(2)	−0.828 (2)	0.760 (1)	−0.0048 (2)	56 (3)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

I—C(4)	2.115 (8)	C(1)—C(2)	1.42 (1)
C(1)—C(6)	1.37 (1)	C(1)—C(7)	1.47 (1)
C(2)—C(3)	1.38 (1)	C(3)—C(4)	1.41 (1)
C(4)—C(5)	1.38 (1)	C(5)—C(6)	1.40 (1)
C(7)—C(8)	1.35 (1)	C(8)—C(9)	1.46 (1)
C(9)—O(1)	1.30 (1)	C(9)—O(2)	1.26 (1)

C(2)—C(1)—C(6)	119.3 (7)	C(2)—C(1)—C(7)	122.2 (7)
C(6)—C(1)—C(7)	118.5 (7)	C(1)—C(2)—C(3)	119.9 (7)
C(2)—C(3)—C(4)	119.3 (7)	I—C(4)—C(3)	119.4 (3)
I—C(4)—C(5)	119.2 (5)	C(3)—C(4)—C(5)	121.3 (7)
C(4)—C(5)—C(6)	118.3 (7)	C(1)—C(6)—C(5)	121.9 (8)
C(1)—C(7)—C(8)	128.5 (8)	C(7)—C(8)—C(9)	122.5 (8)
C(8)—C(9)—O(1)	117.7 (7)	C(8)—C(9)—O(2)	120.5 (8)
O(1)—C(9)—O(2)	121.8 (8)		

angle is close to 180° owing to crystal packing and other reasons.

In the Type II contacts, $\theta_1 \simeq 90°$ and $\theta_2 = 180°$. Fig. 3 shows that the C—I···I—C geometry in the title compound, 4-ICA, is of Type II with $\theta_1 =$ 92.4 (8)° and $\theta_2 =$ 166.9 (8)°. Interestingly, a nearly identical C—I···I—C geometry is found in 4-IBA [I···I 4.055 (2) Å; $\theta_1 =$ 96.4 (3), $\theta_2 =$ 165.9 (3)°]. The C—Cl···Cl—C geometries in both 4-CCA and 4-CBA, on the other hand, are very similar and are of Type I [4-CCA: Cl···Cl 3.59 (3) Å, $\theta_1 = \theta_2 =$ 167.2 (2)°; 4-CBA: Cl···Cl 3.441 (3) Å, $\theta_1 = \theta_2 =$ 167.0 (2)°]. Furthermore, the C—Br···Br—C geometry in 4-BBA is of Type II [Br···Br 3.91 (3) Å, $\theta_1 =$ 163.7 (6), $\theta_2 =$ 92.6 (5)°]. In general, Type II is more common than Type I but the extent to which it is preferred depends on the particular halogen atom. The data of Ramasubbu, Parthasarathy & Murray-Rust (1986) show that Type II outnumbers Type I by a factor of 2:1 for Cl···Cl, 3:1 for Br···Br and 7:1 for I···I. Perhaps Type II is favoured because I is more polarizable. A case in point is the I···I contact of 3.985 Å in 3-iodobenzoic acid, a compound whose crystal packing (Patil, Curtin & Paul, 1984) shows many features in common with that of the title compound.

Concerning the I···I distance, it has been observed (Nyburg & Faerman, 1985) that there is a marked dependence of this distance on the C—X···X angle, θ; in other words, the van der Waals radius of I is not isotropic. The minimum I···I contact distance is *ca* 3.52 Å for $\theta = 90°$, but almost 4.26 Å for $\theta = 180°$

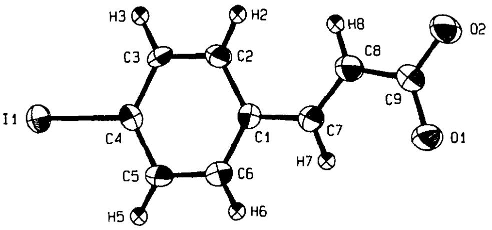

Fig. 1. *ORTEP* drawing of 4-iodocinnamic acid (4-ICA) showing the atom-labelling scheme.

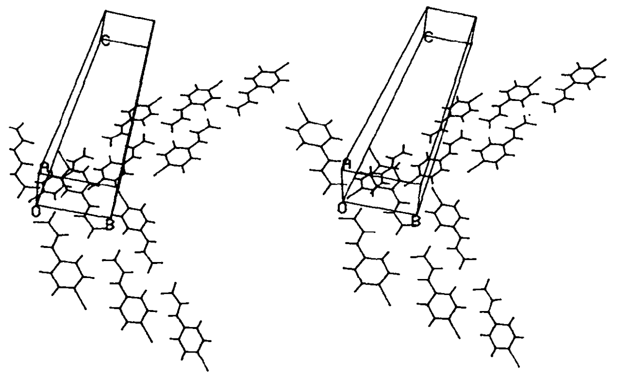

Fig. 2. Stereodrawing of the crystal structure of 4-iodocinnamic acid showing the alternating ribbon structure. The ribbons are linked by I···I contacts.

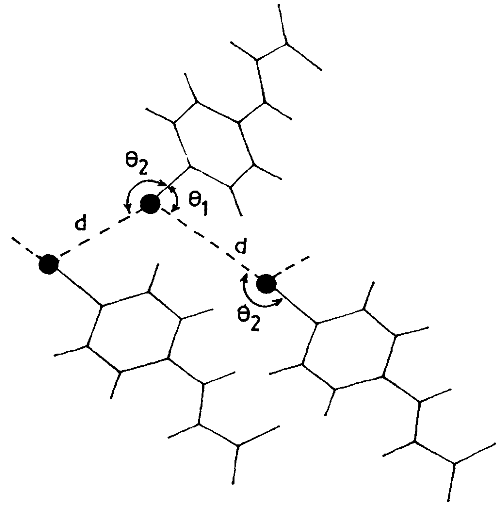

Fig. 3. View of the I···I contacts in crystalline 4-iodocinnamic acid. The I atoms are indicated. The distance d (4.132 Å) and angles θ_1 (92.4°) and θ_2 (166.9°) are marked.

[the conventional or isotropic van der Waals radius for I is 1.97 Å (Bondi, 1964)]. Such observations have been variously interpreted as arising from elliptically shaped halogen atoms (Nyburg & Faerman, 1985) or from weak bonding between neighbouring halogen atoms (Desiraju & Parthasarathy, 1989). Fig. 3 shows that each I atom is linked to two screw-related neighbours by I···I contacts of 4.132 (3) Å.

Disorder of the carboxyl group has been studied previously (Dieterich, Paul & Curtin, 1974) and it has been noted that there is a correlation between $|\Delta r|$, the difference between the two C—O distances, and $|\Delta\varphi|$, the difference between the two C—C—O angles. This correlation is a geometrical one and arises from a twofold rotation about the C—C bond axis. Clearly, when $|\Delta r|$ and $|\Delta\varphi|$ are both zero the carboxyl group is completely disordered. For completely ordered structures, values of $|\Delta r|$ and $|\Delta\varphi|$ were obtained from AM1 semi-empirical calculations (Dewar, Zoebisch, Healy & Stewart, 1985). Calculations on 4-dimethylaminobenzoic acid, 4-nitrobenzoic acid and 3,5-dinitrobenzoic acid gave values of $|\Delta r| = 0.128$ Å and $|\Delta\varphi| = 13.2°$ for a fully ordered benzoic acid carboxyl group. Calculations on 3,5-dinitrocinnamic acid gave values of $|\Delta r| = 0.130$ Å and $|\Delta\varphi| = 12.0°$ for a fully ordered cinnamic acid carboxyl group. Accordingly, the carboxyl group in 4-ICA is partially disordered [C(9)—O(1) 1.30 (1) Å, C(9)—O(2) 1.26 (1) Å, $|\Delta r| = 0.04$ Å; C(8)—C(9)—O(1) 117.7 (7)°, C(8)—C(9)—O(2) 120.5 (8)°, $|\Delta\varphi| = 2.8°$]. This disorder is caused by the comparable crystal environments of the O(1) and O(2) atoms, especially with regard to C—H···O hydrogen-bond-forming ability (Leiserowitz, 1976). In comparison, 4-CCA ($|\Delta r| = 0.001$ Å, $|\Delta\varphi| = 1.8°$) and 4-CBA ($|\Delta r| = 0.02$ Å, $|\Delta\varphi| = 1.4°$) are completely disordered, while 4-BBA ($|\Delta r| = 0.08$ Å, $|\Delta\varphi| = 4.7°$) and 4-IBA ($|\Delta r| = 0.05$ Å, $|\Delta\varphi| = 4°$) are partially disordered.

We have also examined the disorder in other benzoic and cinnamic acids in the CSD. Structural data for carboxylic acid structures with $R < 0.075$ were retrieved from the 1990 version of the CSD (82129 entries). A total of 47 mono-, di- and tri-substituted benzoic acids were studied. A total of 25 mono-, di-, α- and β-substituted *cis*- and *trans*-cinnamic acids were studied. The values of $|\Delta r|$ and $|\Delta\varphi|$ were calculated. As expected, when $\Delta r > 0$, $\Delta\varphi < 0$ and *vice versa*. However, we prefer to use $|\Delta r|$ and $|\Delta\varphi|$ values here. The correlation between $|\Delta r|$ and $|\Delta\varphi|$ is shown graphically in Figs. 4 and 5 for substituted benzoic and cinnamic acids, respectively. The correlation coefficients are 0.91 for benzoic acids and 0.80 for the cinnamic acids and substantiate the earlier results of Dieterich, Paul & Curtin (1974). Fig. 4 shows that *ortho*-substituted benzoic acids are more likely to be ordered than *meta*- and *para*-substituted benzoic acids. This could be due to proximity of the *ortho*-substituent to the carboxyl group. Di- and tri-substituted benzoic acids tend towards partial or complete disorder. A number of *para*-substituted benzoic acids are completely disordered ($|\Delta r| = 0.0$ Å, $|\Delta\varphi| = 0°$). This could arise from a very non-restrictive packing mode, exemplified by compounds such as *para-n*-octyloxy- and *para-n*-decyloxybenzoic acids (Bryan, Hartley, Miller & Shen, 1980). For the cinnamic acids, *para*-substitution leads to disorder. Data for only two *ortho*-substituted acids were available, but both of them are ordered. The disorder in *para*-substituted cinnamic acids could result from a symmetrical and/or weak C—H···O bond pattern, as exhibited by

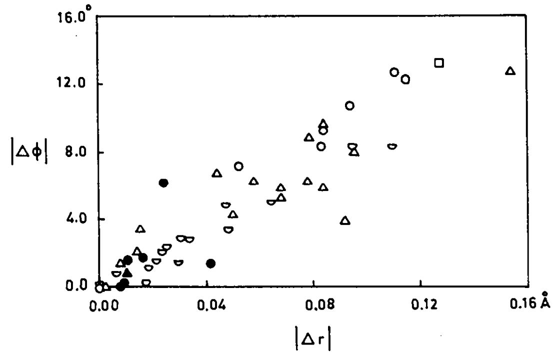

Fig. 4. Graphical representation of the correlation between $|\Delta\varphi|$ and $|\Delta r|$ for substituted benzoic acids. Circles, filled circles, half circles and triangles represent *ortho*-, *meta*-, *para*- and di- and polysubstituted acids. Unsubstituted benzoic acid is represented by a filled triangle and a square represents the ideal value for a completely ordered carboxyl group, obtained from AM1 calculations. There are one *para*- and two polysubstituted acids at the origin.

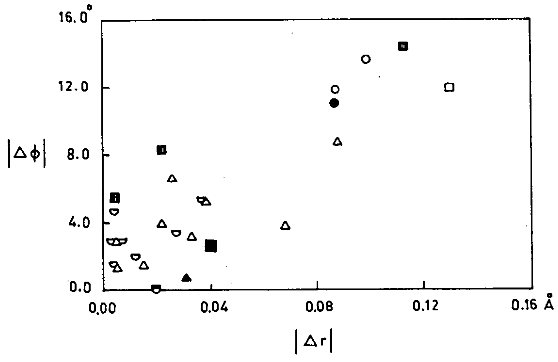

Fig. 5. Graphical representation of the correlation between $|\Delta\varphi|$ and $|\Delta r|$ for substituted cinnamic acids with the same notation as in Fig. 4 except for a filled triangle and a striped square, representing α- and β-substituted acids. A filled square represents unsubstituted *trans*-cinnamic acid. The title compound 4-ICA is included. The ideal value for a completely ordered carboxyl group, obtained as before, is represented by a square.

the title compound (Fig. 2) and which is a general packing motif.

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Structure of 1-Amino-3-(methylthio)propylphosphonic Acid

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Abstract. $C_4H_{12}NO_3PS$, $M_r = 185.18$, monoclinic, $P2_1/c$, $a = 14.508$ (8), $b = 6.095$ (4), $c = 9.532$ (5) Å, $\beta = 97.93$ (4)°, $V = 834.8$ Å^3, $Z = 4$, $D_m = 1.47$ (1), $D_x = 1.473$ (1) Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 4.8$ mm^{-1}, $F(000) = 392$, $T = 292$ K, $R = 0.052$ for 1588 observed reflexions. The molecule exists as a zwitterion with the amino group being protonated and the phosphonic acid group being ionized. The conformation of the molecule is *trans*, *gauche* and *gauche* {angles χ^1[N—C(1)—C(2)—C(3)], χ^2[C(1)—C(2)—C(3)—S] and χ^3[C(2)—C(3)—S—C(4)] are 175.7 (4), −62.5 (5) and −69.9 (5)°, respectively} and the side chain is strongly folded. There is extensive intermolecular hydrogen bonding and one of the three N—H···O hydrogen bonds is bifurcated. The crystal contains a short P—OH···O intermolecular hydrogen bond of 2.526 (3) Å.

Introduction. Aminophosphonic acids are analogues of aminocarboxylic acids, the —COOH group being replaced by a —PO_3H_2 group. These acids are of considerable interest because of their occurrence in many living organisms and their biological activity. The neutral and synthetic aminophosphonic acids and their derivatives (phosphonopeptides, phosphonolipids, phosphonoglycolipids, *etc.*) include neuroactive compounds, antibiotics and herbicides (Kafarski & Mastalerz, 1984). Their biological

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