

The central carbon skeleton of (2) comprises a system of three *trans*-fused rings which all have tetrahedral atoms with the exception of C(9) and C(11). It is a new diterpene compound with an *ent*-pimarane skeleton and a *p*-bromobenzoate substituent at C(3).

The *A* ring is distorted from the ideal chair form because of the axial methyl–methyl interaction,  $C(19)\cdots C(20) = 3.302(16)$  Å. Rings *B* and *C* have a twist-boat and half-chair form, respectively. At the *A/B* and *B/C trans* junctions, torsion angles  $C(4)–C(5)–C(10)–C(1)$ ;  $C(6)–C(5)–C(10)–C(9)$  and  $C(7)–C(8)–C(9)–C(10)$ ;  $C(14)–C(8)–C(9)–C(11)$  are  $50.9(12)$ ;  $-61.8(11)^\circ$  and  $37.4(11)$ ;  $-12.2(14)^\circ$ , respectively.

In the *A* ring, the C(3) *p*-bromobenzoate group is in the equatorial position and the C(10) methyl group is axial. The carboxy group of the *p*-bromobenzoate substituent is oriented to minimize transannular repulsions between its O atoms and the C(4) methyl groups. The pertinent torsion angles are:  $C(21)–O(1)–C(3)–C(2) = -86.2(11)$ ;  $C(21)–O(1)–C(3)–C(4) = 144.7(9)$  and  $C(21)–O(1)–C(3)–H(3) = 28^\circ$ , placing the C=O group *syn* to the C(3)–H bond (Mathieson, 1965; Chothia & Pauling, 1970).

The phenyl ring shows normal geometry,  $1.378(17)$  Å and  $120.0(11)^\circ$  for the mean  $C(sp^2)–C(sp^2)$  bond distance and the mean internal angle. This mean bond distance is close to that given by Sutton (1965) [ $1.395(5)$  Å] and Brisse & Sygusch (1974) ( $1.379$  Å).

Examination of the three-dimensional packing of the molecules within the crystalline lattice (shown in Fig. 2) reveals that there are no unusually short intermolecular contacts and the molecules are packed at normal van der Waals distance.

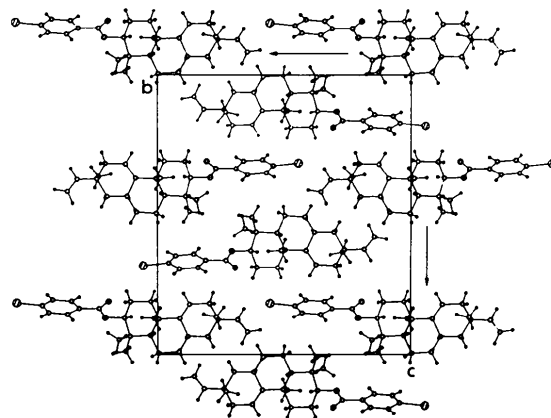


Fig. 2. The packing arrangement as viewed along *a*.

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## Structure of the 1:1 Adduct Formed by *p*-Nitrophenol with Triphenylarsine Oxide

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**Abstract.**  $C_6H_5NO_3 \cdot As(C_6H_5)_3O$ ,  $M_r = 461.35$ , monoclinic,  $P2_1/n$ ,  $a = 8.847(1)$ ,  $b = 15.879(2)$ ,  $c = 15.704(2)$  Å,  $\beta = 100.47(1)^\circ$ ,  $V = 2169.4(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.390(5)$  (floatation),  $D_x = 1.412(2)$  g cm<sup>-3</sup>,

$\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 16.86$  cm<sup>-1</sup>,  $F(000) = 944$ , room temperature. Final  $R = 0.055$  for 1337 observed reflections. The adduct is formed by hydrogen bonding between the O atoms of the arsine oxide and

*p*-nitrophenol, with an O...O distance of 2.555 (8) Å. The As atom was found to have a nearly tetrahedral coordination [mean C-As-C 108 (2)°]. As in other nitrophenols, the benzene ring is planar. The dihedral angle between the benzene and nitro-group planes is 4.8°.

**Introduction.** It was shown by Lechat (1984) that the distance  $R_{O...O}$  in adducts formed by strong or medium hydrogen bonds, and where the donor and acceptor atoms are O atoms, may be correlated with the value of the differences of  $pK_a$  of the acids and bases involved in the adducts. The relation developed is based on the analysis of eight adducts in which the hydrogen bond occurs only between the acids and the bases. This crystal-structure determination has been undertaken in order to gather structural information for an adduct involving a strong hydrogen bond.

**Experimental.** Pale-yellow crystals of the title compound, m.p. 380–381 K, were prepared by slowly evaporating an equimolar solution of *p*-nitrophenol and triphenylarsine oxide in benzene. Technique as well as reagents were provided by Professor Tomita (Tomita, 1972). Crystal of dimensions 0.3 × 0.1 × 0.3 mm used for data collection on a Nonius CAD-4 diffractometer. Cell parameters refined from setting angles of 25 reflections in  $\theta$  range 9.0–18.5°. Three-dimensional intensity data collected using graphite-monochromated Mo  $K\alpha$  radiation.  $\omega$ - $2\theta$  scanning mode with varying interval used up to  $2\theta = 100^\circ$ . Reflections collected in range 0–9 for  $h$ , 0–17 for  $k$  and –17–17 for  $l$ . 3713 recorded independent reflections, only 1337 considered above background [ $I > 3\sigma(I)$ , where  $\sigma(I)$  based on counting statistics]. Two standard reflections measured every 1800 s and presented a maximum 7% variation throughout experiment. Data reduced to structure factors with absorption correction (numerical absorption correction based on crystal shape), max. and min. transmission factors 0.8289 and 0.6564 respectively. Structure solved by direct methods (SHELX76; Sheldrick, 1976). All non-H atoms appeared clearly in  $E$  map based on set of phases giving highest combined figure of merit. H atoms placed at their calculated positions, hydroxyl H atoms located by Fourier difference synthesis and its coordinates fixed.

Refinement carried out by full-matrix least-squares calculations with anisotropic thermal parameters for non-H atoms and isotropic thermal parameters for H atoms. Function minimized  $\sum w_i(k|F_o| - |F_c|)^2$  with  $w_i^{-1} = \sigma(F)^2 + 0.001F^2$  for observed and  $w_i = 0$  for unobserved reflections. Atomic scattering factors were those of Cromer & Waber (1974). H-atom coordinates recalculated after each refinement cycle. Refinement carried out until max. least-squares shift/e.s.d. < 1. Final  $R$  and  $wR$ , omitting unobserved reflections, 0.055 and 0.065 respectively. Reflection 040, affected by

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors (Hamilton, 1959), with e.s.d.'s in parentheses for the *p*-nitrophenol-triphenylarsine oxide adduct

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}(\text{Å}^2)$
As	777 (1)	4302 (1)	3128 (1)	3.63 (4)
O(1)	1359 (8)	3916 (4)	2254 (4)	4.6 (3)
O(2)	-73 (9)	3992 (5)	10689 (4)	5.8 (3)
O(3)	5369 (9)	4042 (6)	8677 (6)	8.3 (5)
O(4)	3569 (9)	3544 (9)	7696 (7)	8.4 (4)
N	4021 (18)	3812 (9)	8422 (9)	7.8 (6)
C(1)	1909 (8)	3788 (9)	4161 (7)	3.8 (4)
C(2)	2778 (9)	4288 (8)	4789 (7)	4.8 (4)
C(3)	3571 (19)	3886 (8)	5532 (8)	6.0 (6)
C(4)	3471 (18)	3045 (11)	5638 (9)	6.7 (6)
C(5)	2577 (16)	2551 (9)	5012 (9)	6.2 (6)
C(6)	1764 (7)	2931 (9)	4271 (7)	4.7 (5)
C(7)	1146 (9)	5484 (7)	3216 (6)	3.5 (4)
C(8)	2315 (12)	5808 (9)	2840 (6)	4.4 (4)
C(9)	2653 (16)	6661 (9)	2921 (8)	5.0 (5)
C(10)	1820 (18)	7186 (8)	3368 (8)	5.6 (5)
C(11)	650 (19)	6843 (8)	3737 (7)	5.7 (6)
C(12)	302 (8)	6014 (8)	3655 (7)	4.8 (5)
C(13)	-1359 (9)	4074 (6)	3107 (7)	3.6 (4)
C(14)	-1906 (8)	3844 (8)	3846 (7)	4.9 (5)
C(15)	-3438 (16)	3679 (9)	3821 (11)	7.6 (7)
C(16)	-4414 (18)	3769 (9)	3045 (13)	8.1 (7)
C(17)	-3909 (16)	3970 (12)	2287 (8)	8.7 (8)
C(18)	-2381 (17)	4138 (8)	2335 (8)	6.4 (6)
C(19)	947 (19)	3979 (7)	10152 (7)	4.8 (5)
C(20)	425 (19)	3735 (8)	9278 (7)	6.2 (5)
C(21)	1409 (18)	3689 (8)	8723 (7)	6.2 (5)
C(22)	2921 (17)	3863 (7)	9003 (7)	4.7 (5)
C(23)	3477 (9)	4126 (7)	9851 (8)	5.7 (5)
C(24)	2498 (8)	4172 (7)	10422 (6)	4.7 (4)

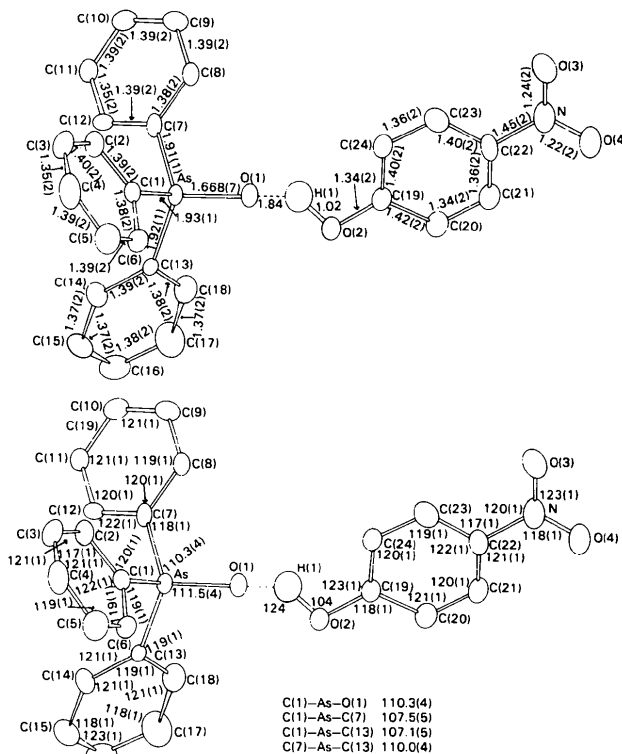


Fig. 1. Representation of the hydrogen-bonding scheme in the adduct giving bond lengths (Å) (top), angles (°) (bottom) and atomic numbering.

non-systematic error, omitted in last cycle. Difference Fourier calculations after last refinement cycle revealed max. positive and negative electron density  $0.449$  and  $-0.527 \text{ e } \text{\AA}^{-3}$  respectively.

The final atomic parameters for the non-H atoms are given in Table 1.\*

**Discussion.** The *p*-nitrophenol binds to triphenylarsine oxide through hydrogen bonding between O(1) and O(2) atoms, as was predicted.

The hydrogen bond is asymmetric and may be classified as strong (Novak, 1974). The value of the O(1)⋯H(1)–O(2) angle is  $124^\circ$  and of the O(1)⋯O(2) distance  $2.555(8) \text{ \AA}$ . This latter value agrees satisfactorily with the value [ $2.60(1) \text{ \AA}$ ] proposed by Lechat (1984).

Fig. 1 shows the bond lengths and angles in the *p*-nitrophenol–triphenylarsine oxide adduct, with the atomic numbering.

The relevant distances and angles in the *p*-nitrophenol molecule are: C–N  $1.45(2)$ , C–O  $1.34(2)$  and N–O  $1.22(2) \text{ \AA}$  (mean); O–N–O  $123(1)$ , O–N–C  $118(1)$  (mean) and O–C–C  $121(1)^\circ$  (mean). As in other nitrophenols, the benzene ring is planar, the largest distance to it being observed for the O(4) atom ( $0.11 \text{ \AA}$ ). The dihedral angle between the benzene and nitro-group planes is  $4.8^\circ$ .

The As atom in the triphenylarsine oxide molecule was found to have a nearly tetrahedral coordination [C–As–C  $108(2)^\circ$  (mean)]. The values of the As–C

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, bond lengths, angles, and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42718 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

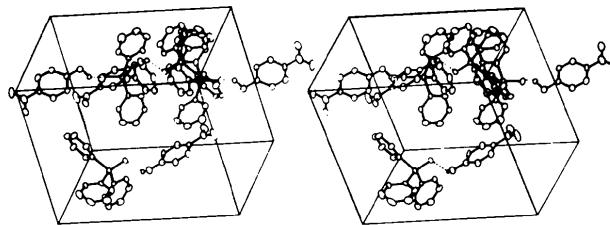


Fig. 2. Stereoview of the molecular packing diagram for the adduct formed by *p*-nitrophenol with triphenylarsine oxide.

and As=O distances are  $1.92(1)$  (mean) and  $1.668(7) \text{ \AA}$  respectively.

Crystal packing as well as hydrogen bonds are shown in Fig. 2.

All calculations, unless otherwise mentioned in the text, were performed in the Instituto de Física e Química de São Carlos, USP, on the PDP11/45 and VAX 760 computers using *SDP* crystallography programs (Frenz, 1978). This work has received the support of Universidade Federal de Goiás, CAPES, CNPq, FINEP and FAPESP which is hereby gratefully acknowledged.

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## Structure of Anticancer Antibiotic L-Alanosine

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**Abstract.**  $\text{C}_3\text{H}_7\text{N}_3\text{O}_4$ ,  $M_r = 149.11$ , orthorhombic,  $P2_12_12_1$ ,  $a = 9.107(4)$ ,  $b = 9.600(4)$ ,  $c = 6.383(8) \text{ \AA}$ ,  $V = 558.1 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.774 \text{ g cm}^{-3}$ ,  $\text{Mo } K\alpha$ ,  $\lambda = 0.71069 \text{ \AA}$ ,  $\mu = 1.73 \text{ cm}^{-1}$ ,  $F(000) = 312$ ,  $T = 138 \text{ K}$ ,  $R = 0.032$  for 603 observed data and  $0.041$  for all 685

reflections. The compound crystallizes as a zwitterion like many other  $\alpha$ -amino acids. In the crystalline state, L-alanosine is a tautomer of the published structure so that the terminal position in the chain of the molecule is occupied by the *N*-nitroso group. Conformationally,