

Funding for this work was provided by the Natural Sciences and Engineering Research Council of Canada and the Fonds FCAR (Ministère de l'Éducation du Québec).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1426). Services for accessing these data are described at the back of the journal.

## References

- Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1973). *NRC Crystallographic Computer Programs for the IBM/360*. Accession Nos. 133–147. *J. Appl. Cryst.* **6**, 309–346.
- Cambridge Structural Database (1998). Version V5.15. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
- Connac, F., Habbadi, N., Lucchese, Y., Dartiguenave, M., Lamandé, L., Sanchez, M., Simard, M. & Beauchamp, A. L. (1997). *Inorg. Chim. Acta*, **256**, 107–114.
- Connac, F., Lucchese, Y., Dartiguenave, M., Coulais, Y. & Beauchamp, A. L. (1998). *J. Inorg. Chem. Acta*. Submitted.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Habbadi, N., Connac, F., Dartiguenave, M., Beauchamp, A. L. & Souiri, A. (1999). In preparation.
- Habbadi, N., Dartiguenave, M., Lamandé, L., Sanchez, M., Simard, M., Beauchamp, A. L. & Souiri, A. (1998). *New J. Chem.* pp. 983–987.
- Hogerheide, M. P., Ringelberg, S. N., Janssen, M. D., Boersma, J., Spek, A. L. & van Koten, G. (1996). *Inorg. Chem.* **35**, 1195–1200.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1996). *SHELXL96. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

*Acta Cryst.* (1999). **C55**, 683–685

## *tert*-Butylammonium hydrogen phenyl phosphate

SANTIAGO REINOSO, PABLO VITORIA, MARIA UGALDE, JUAN M. GUTIÉRREZ-ZORRILLA,\* ANTONIO LUQUE AND PASCUAL ROMÁN

*Departamento de Química Inorgánica, Facultad de Ciencias, Universidad del País Vasco, Apartado 644, E-48080 Bilbao, Spain. E-mail: qipguloj@lg.ehu.es*

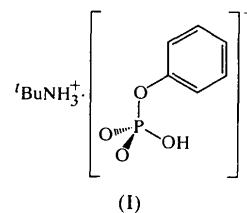
(Received 23 October 1998; accepted 7 December 1998)

## Abstract

The title compound,  $(\text{Me}_3\text{C})\text{NH}_3^+\cdot\text{PhOPO}_3\text{H}^-$ , contains hydrogen phenyl phosphate anions connected by electrostatic interactions and hydrogen bonds to *tert*-butylammonium cations, forming a two-dimensional network.

## Comment

There are three structurally characterized phenyl phosphate salts with inorganic cations (Svetich & Caughlan, 1963; Caughlan & ul Haque, 1967; Glowiak & Wnek, 1985) and only one with an organic cation (Kneeland *et al.*, 1993). Three examples of hydrogen phenyl phosphate salts have been structurally characterized (Kennard *et al.*, 1967; Glowiak & Szemik, 1986; Kral *et al.*, 1996). The present study of the title compound, (I), was undertaken in order to obtain a deeper insight into the effect of the cation on the crystal packing, the strength of the intermolecular contacts and the chemical properties of organoammonium phenyl phosphates.



The asymmetric unit of the title compound (Fig. 1) contains one  $\text{C}_6\text{H}_5\text{PO}_4^-$  anion and one  $\text{C}_4\text{H}_{12}\text{N}^+$  cation. The hydrogen phenyl phosphate anions form dimeric units through the strong  $\text{O1}—\text{H1}\cdots\text{O3}$  hydrogen bond [2.5912(16) Å]. The interaction between these dimers takes place through three hydrogen bonds involving the  $\text{NH}_3^+$  group of the *tert*-butylammonium cations. This hydrogen-bond network generates a two-dimensional structure (Fig. 2), with the layers parallel to the  $(10\bar{1})$  plane and each layer containing a hydrophilic central zone formed by the terminal O atoms and the  $\text{NH}_3^+$  group. The aromatic rings and methyl groups emerge above and below this central zone to form the corresponding hydrophobic zone with the adjacent layers (Fig. 3).

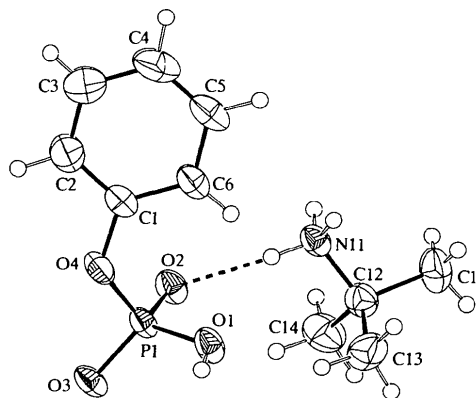


Fig. 1. View of *tert*-butylammonium hydrogen phenyl phosphate, showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as spheres of an arbitrary radius. The dashed line indicates a hydrogen bond.

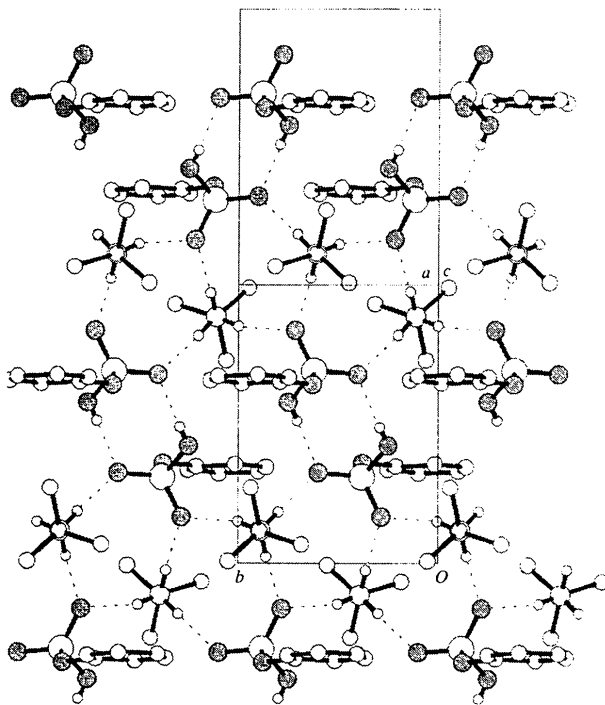
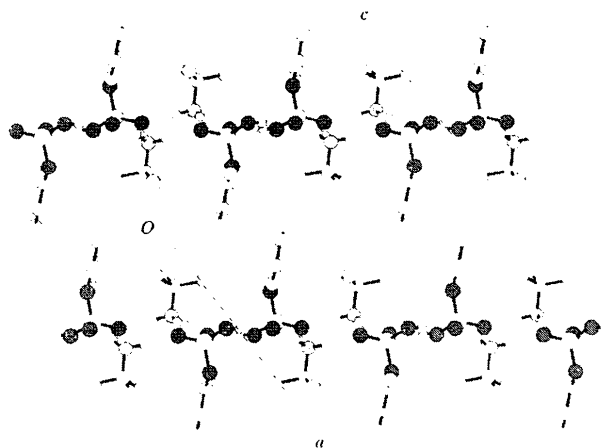
Fig. 2. View of the hydrogen-bond network in the  $(10\bar{1})$  plane.

Fig. 3. View of the hydrophobic and hydrophilic zones in the crystal structure. H atoms bonded to carbon have been omitted for clarity.

## Experimental

*tert*-Butylammonium *cyclo*-tetrametavanadate (0.88 g) and sodium phenyl phosphate (1.33 g) were dissolved in water (30 ml). The resulting yellow solution was refluxed at 373 K for 3 h, and was then filtered and kept at room temperature. Colourless crystals were obtained after several days.

### Crystal data

$C_4H_{12}N^+ \cdot C_6H_6PO_4^-$   
 $M_r = 247.23$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069 \text{ \AA}$

### Monoclinic

$P2_1/n$

$a = 13.271(2) \text{ \AA}$

$b = 6.674(2) \text{ \AA}$

$c = 14.790(1) \text{ \AA}$

$\beta = 97.505(10)^\circ$

$V = 1298.7(4) \text{ \AA}^3$

$Z = 4$

$D_x = 1.265 \text{ Mg m}^{-3}$

$D_m$  not measured

### Data collection

Enraf–Nonius CAD-4  
 diffractometer

$\omega/2\theta$  scans

Absorption correction: none

4392 measured reflections

4093 independent reflections

2795 reflections with

$I > 3\sigma(I)$

### Refinement

Refinement on  $F$

$R = 0.037$

$wR = 0.043$

$wR(F^2) = 0.053$

$S = 3.11$

2795 reflections

217 parameters

All H-atom parameters

refined

### Cell parameters from 25

reflections

$\theta = 7.37\text{--}12.28^\circ$

$\mu = 0.21 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Prismatic

$0.78 \times 0.40 \times 0.30 \text{ mm}$

Colourless

$R_{\text{int}} = 0.009$

$\theta_{\text{max}} = 30^\circ$

$h = 0 \rightarrow 18$

$k = 0 \rightarrow 9$

$l = -20 \rightarrow 20$

3 standard reflections

frequency: 60 min

intensity decay: <2%

$w = k[(a + bF_o)^2][c$   
 $+ d(\sin\theta)/\lambda]$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 0.54 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.07 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for*  
*Crystallography* (Vol. C)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

P1—O1	1.5599 (11)	P1—O4	1.6120 (12)
P1—O2	1.4923 (11)	O4—C1	1.3819 (16)
P1—O3	1.4985 (10)		
O1—P1—O4	105.88 (6)	O3—P1—O4	103.00 (5)
O2—P1—O3	117.91 (6)	P1—O4—C1	125.37 (8)
O2—P1—O4	109.98 (6)		

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
O1—H1 $\cdots$ O3 $^i$	0.78 (3)	1.81 (3)	2.5912 (16)	178 (3)
N11—H111 $\cdots$ O2 $^{ii}$	0.91 (2)	1.95 (2)	2.8453 (17)	171 (2)
N11—H112 $\cdots$ O3 $^i$	0.92 (2)	1.91 (2)	2.8287 (17)	171 (2)
N11—H113 $\cdots$ O2 $^{iii}$	0.90 (2)	1.91 (2)	2.8101 (16)	179 (2)

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

The weighting scheme is taken from *PESOS* (Martinez-Ripoll & Cano, 1975). The C—H bond range is 0.91 (4)–1.04 (3)  $\text{\AA}$ .

Data collection: *CAD-4 Software* (de Boer & Duisenberg, 1984; Enraf–Nonius, 1989). Cell refinement: local programs. Data reduction: *XRAY76* (Stewart *et al.*, 1976). Program(s) used to solve structure: *DIRDIF92* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *XRAY76*. Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

This work was supported by Gobierno Vasco (grant PI-96/69). PV acknowledges financial support from MEC (grant AP95 30650377).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1010). Services for accessing these data are described at the back of the journal.

## References

- Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Grande, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF92 Program System*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* **A40**, C-410.
- Caughlan, C. N. & ul Haque, M. (1967). *Inorg. Chem.* **6**, 1998–2002.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Glowiak, T. & Szemik, A. W. (1986). *J. Crystallogr. Spectrosc. Res.* **16**, 79–89.
- Glowiak, T. & Wnek, I. (1985). *Acta Cryst.* **C41**, 324–327.
- Kennard, O., Watson, D. G., Fawcett, J. K., Kerr, K. A. & Coppola, O. C. (1967). *Am. Crystallogr. Assoc. Summer Meet. Abstr.* p. 28.
- Kneeland, D. M., Ariga, K., Lynch, V. M., Huang, C.-Y. & Anslyn, E. V. (1993). *J. Am. Chem. Soc.* **115**, 10042–10055.
- Kral, V., Furuta, H., Schreder, K., Lynch, V. & Sessler, J. L. (1996). *J. Am. Chem. Soc.* **118**, 1595–1607.
- Martinez-Ripoll, M. & Cano, F. H. (1975). *PESOS*. Instituto Rocasolano, CSIC, Madrid, Spain.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). *The XRAY76 System*. Technical Report TR-446. Computer Science Center, University of Maryland, College Park, Maryland, USA.
- Vetich, G. W. & Caughlan, C. N. (1963). *Acta Cryst.* **16**, A-73.

*Acta Cryst.* (1999). **C55**, 685–687

## 7,11b-Dihydro-9,10-dimethoxy-3,11b-diphenyl[1,2,4]oxadiazolo[5,4-a]-[2,3]benzodiazepin-6(5H)-one

GIUSEPPE BRUNO,<sup>a</sup> ALBA CHIMIRRI,<sup>b</sup> ROSARIA GITTO,<sup>b</sup> FRANCESCO NICOLÒ<sup>a</sup> AND ROSARIO SCOPELLITI<sup>d</sup>

<sup>a</sup>*Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, 98166 Vill. Sant'Agata, Messina, Italy, and* <sup>b</sup>*Dipartimento Farmaco-Chimico, Università di Messina, 98168 Viale Annunziata, Messina, Italy. E-mail: giuseppe.bruno@unime.it*

(Received 28 January 1998; accepted 25 September 1998)

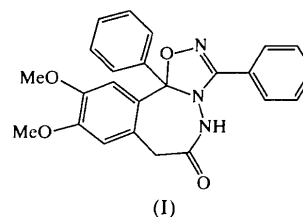
## Abstract

This paper represents one of the few structural reports on 2,3-benzodiazepines. The title compound, C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>, consists of a benzodiazepine moiety and an oxadiazole ring fused together, with the seven-membered ring in a 'boat' conformation. The molecules are linked into pairs by N—H···O hydrogen bonds. The title compound is an interesting antagonist at non-NMDA (*N*-methyl-D-aspartate) receptors.

## Comment

The unusual biological activities shown by benzodiazepine derivatives containing an additional heterocyclic ring fused to different edges of the heptatomic nucleus (Chimirri *et al.*, 1993) have stimulated the exploitation of the chemistry of this class of compounds. Previous reports claim that the biological activity of benzodiazepines can be correlated to the conformational mobility of the seven-membered ring and therefore the fusion of a heterocyclic ring can lead to an enhancement of the ring inversion barrier, thus determining a higher activity and/or specificity of action.

On this basis, in the course of our studies on structure–activity relationships of cyclofunctionalized benzodiazepines, with particular reference to their anti-convulsant effects (De Sarro *et al.*, 1992, 1993), we reported the synthesis of a series of 1,2,4-oxadiazolo-[5,4-*a*][2,3]benzodiazepine derivatives (De Sarro *et al.*, 1995), as potential antagonists at non-NMDA receptors, which constitute new interesting targets for anti-epileptic therapy (Chimirri *et al.*, 1999). In this paper, we report the results of the X-ray structure determination of 7,11b-dihydro-9,10-dimethoxy-3,11b-diphenyl[1,2,4]oxadiazolo[5,4-*a*][2,3]benzodiazepin-6(5H)-one, (I), in order to study the geometry of this new class of annelated 2,3-benzodiazepines. We then compare the structure of (I) with those of other known non-NMDA antagonists in order to clarify which structural elements are necessary for anticonvulsant activity.



(I)

There are several reports in the literature describing benzodiazepines, but only a few refer to 1,2- or 2,3-benzodiazepines (Allen & Kennard, 1993). In this paper we report the crystal structure of a 2,3-benzodiazepine which reveals that in the solid state a strong hydrogen bond occurs between molecules related by an inversion centre (see Table 2). Such interaction may be described in terms of the graph set  $R_2^2(8)$  (Bernstein *et al.*, 1995), which is typical for carboxylic acids, amides and their supramolecular association complexes (Walsh *et al.*, 1997).

The title compound consists of three fused rings: the five-membered ring has a twisted envelope conformation [ $\varphi_2 = -130.8(4)^\circ$ ] whereas the seven-membered ring shows the usual 'boat' conformation [ $\varphi_2 = 100.98(9)^\circ$ ,  $\varphi_3 = 159.6(4)^\circ$ ,  $Q = 0.9688(17) \text{ \AA}$ ,  $\theta = 78.37(10)^\circ$ ; Cremer & Pople, 1975]. The disposition of the rings is shown by the torsion angles