

# Ammonium 2,7-dimethyl-5-bora-1,4,6,9-tetroxa-spiro[4.4]nonane-3,8-dionate (ammonium borodilactate)

P. A. Angeli Mary,  
S. Dhanuskodi, S. Thamocharan  
and V. Parthasarathi\*

Department of Physics, Bharathidasan  
University, Tiruchirappalli 620 024, India

Correspondence e-mail: vpsarati@yahoo.com

## Key indicators

Single-crystal X-ray study

$T = 293$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å

$R$  factor = 0.026

$wR$  factor = 0.103

Data-to-parameter ratio = 9.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $\text{NH}_4^+\cdot\text{C}_6\text{H}_8\text{BO}_6^-$ , the trivalent boron is tetrahedrally bonded to four O atoms of the two lactate ions having a chiral carbon in each. Two of the O atoms are covalently bonded [1.4259 (13) Å] to the boron, while there is an extended B—O bonds [1.5177 (14) Å] between the boron and each of the other two O atoms. There are distortions in the tetrahedral angles around boron ranging from 104.47 (5) to 115.35 (15)°. The structure is stabilized by a network of N—H···O hydrogen bonds involving the H atoms of the ammonium cation and the O atoms of the borodilactate anion. The UV–vis transmittance window of this non-linear optical crystal is in the range 240–1250 nm.

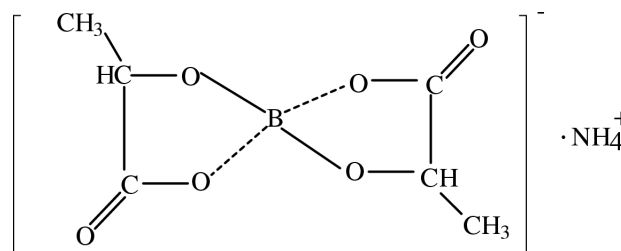
Received 29 November 2001

Accepted 5 December 2001

Online 14 December 2001

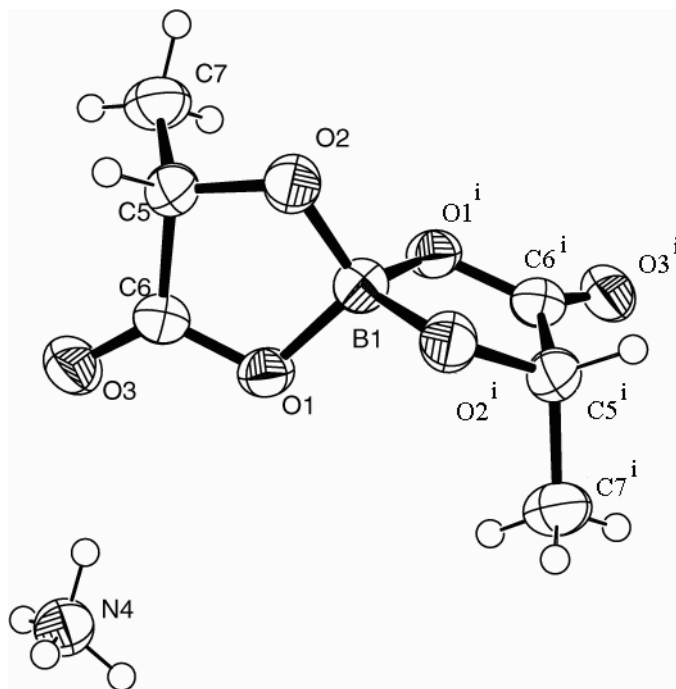
## Comment

The structure determination of the title compound, (I), was undertaken to investigate the environment around boron and the hydrogen bonds involving the ammonium cation. Non-linear optical (NLO) materials play a vital role in advancing laser technology and opto-electronic applications, such as optical computing, optical data storage and optical communication. Since it is reported that semi-organic NLO materials combine the large non-linearity of organics and favourable crystal growth properties of inorganic salts (Jiang & Fang, 1999; Jiang *et al.*, 2001), we have prepared the title compound, which crystallizes in the noncentrosymmetric space group  $C222_1$  with  $Z = 4$ .



(I)

The asymmetric unit of (I) contains ammonium borodilactate. The other halves are generated by twofold symmetry, with B1 and N4 lying on twofold axes. Atom B1 forms two covalent bonds [1.4259 (13) Å each] with O2 and O2<sup>i</sup> and an extended B—O bonds [1.5177 (14) Å] to each of O1 and O1<sup>i</sup> [symmetry code: (i)  $-x, y, 1/2-z$ ]. The bond angles around boron, O1—B1—O2 [104.47 (5)°], O1—B1—O1<sup>i</sup> [105.69 (13)°], O1—B1—O2<sup>i</sup> [113.33 (6)°] and O2—B1—O2<sup>i</sup> [115.35 (15)°] indicate a distorted tetrahedral environment. Similar bond lengths and deviations from the tetrahedral



**Figure 1**

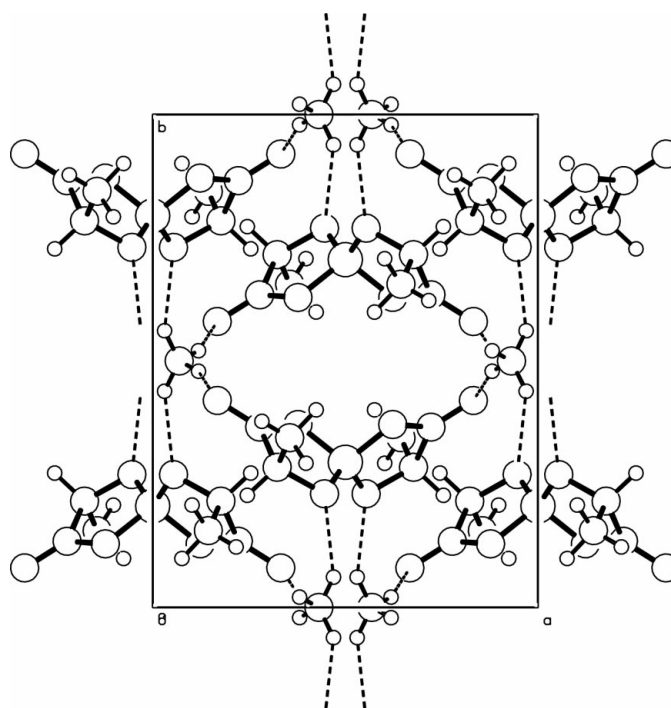
The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. [Symmetry code: (i)  $-x, y, 1/2-z$ .]

values of bond angles around boron have been reported in the literature (Stibrany & Brant, 2001; Hill *et al.*, 1997). The dihedral angle between the planes of the two lactate moieties of the borodilactate anion is  $88.3 (10)^\circ$ .

The structure is stabilized by a network of  $N-H \cdots O$  hydrogen bonds involving the H atoms of the ammonium cation and two of the O atoms (O2 and O3) of the lactate moiety (Table 2). Because of the space group symmetry, all the four H atoms of the ammonium ion are involved in hydrogen bonding with O3 and symmetry-related  $O2(-x+1/2, -y+1/2, z-1/2)$ ,  $O2(-x+1/2, y-1/2, -z+1/2)$  and  $O3(x, -y, -z)$ .

## Experimental

The title compound was prepared by mixing 3.93 g (0.025 mol) of ammonium carbonate, 3.09 g (0.05 mol) of boric acid and 9.08 g (0.1 mol) of lactic acid. The components were thoroughly dissolved in 100 ml of distilled water and the mixture was evaporated to dryness by heating at 323 K for 8 h. The yield was around 50%. Single crystals were obtained by slow evaporation of a saturated aqueous solution at 293 K. Good quality single crystals of size  $8 \times 6 \times 3$  mm were obtained over a period of two months. The melting point was measured as 489–492 K. The molecular mass was obtained as 205 amu using a Finnigan Mat-8230 GC mass spectrometer. The UV–vis spectrum of the crystal, recorded using a Varian Cary 5E UV–vis–NIR spectrophotometer, shows a transmittance window in the range 240–1250 nm. The extended UV transparency down to 240 nm makes this crystal preferred for opto-electronic applications.



**Figure 2**

The molecular packing viewed down the *c* axis.

## Crystal data

$C_6H_{12}BNO_6$   
 $M_r = 204.98$   
 Orthorhombic,  $C222_1$   
 $a = 9.3254 (11) \text{ \AA}$   
 $b = 11.9482 (15) \text{ \AA}$   
 $c = 8.5578 (9) \text{ \AA}$   
 $V = 953.53 (19) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.428 \text{ Mg m}^{-3}$   
 $D_m = 1.41 \text{ Mg m}^{-3}$

$D_m$  measured by flotation method  
 Cu  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 20\text{--}30^\circ$   
 $\mu = 1.09 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Prismatic, white  
 $0.15 \times 0.12 \times 0.09 \text{ mm}$

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.854, T_{\max} = 0.909$   
 988 measured reflections  
 871 independent reflections  
 870 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$   
 $\theta_{\text{max}} = 69.7^\circ$   
 $h = -8 \rightarrow 11$   
 $k = -8 \rightarrow 14$   
 $l = 0 \rightarrow 10$   
 2 standard reflections  
 frequency: 120 min  
 intensity decay: negligible

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.026$   
 $wR(F^2) = 0.103$   
 $S = 1.05$   
 871 reflections  
 90 parameters  
 All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.12 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.027 (3)  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.06 (19)

**Table 1**  
Selected geometric parameters (Å, °).

O1—B1	1.5177 (14)	O2—B1	1.4259 (13)
O2—B1—O2 <sup>i</sup>	115.35 (15)	O2—B1—O1	104.47 (5)
O2—B1—O1 <sup>i</sup>	113.33 (6)	O1 <sup>i</sup> —B1—O1	105.69 (13)

Symmetry code: (i)  $-x, y, \frac{1}{2} - z$ .

**Table 2**  
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N4—H41...O3	0.87 (2)	2.124 (19)	2.9600 (12)	160 (2)
N4—H42...O2 <sup>i</sup>	0.89 (3)	2.14 (3)	2.9494 (10)	150 (4)

Symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$ .

All H atoms were located from a difference map and were included in the structure-factor calculations with  $U_{\text{iso}}(\text{H})$  equal to 1.1  $U_{\text{eq}}$  of their respective carrier atom and their coordinates were refined. There are two chiral C atoms [C5 and C5<sup>i</sup>; symmetry code: (i)  $-x, y, 1/2 - z$ ] in the lactate moieties. The number of Friedel pairs measured was 117. The absolute configuration of the lactate anion could not be established unambiguously in the present study, because the structure contains only light atoms. However, the reported coordinates correspond to an *S* configuration.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997);

program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL97*, *PARST* (Nardelli, 1983) and *PLATON* (Spek, 2001).

The authors sincerely thank Professors R. Jeyaraman and K. Panchanatheswaran, Department of Chemistry, Bharathidasan University, Tiruchirappalli, for fruitful discussion and also Professor V. Balasubramanian, M.G.V.'s Pharmacy College, Nashik, for his kind help in the synthesis of the title compound. One of the authors (PAM) is grateful to the University Grants Commission, New Delhi, for the award of a Teacher Fellowship during the IX plan period.

## References

- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Hill, G. S., Manojlovic Muir, L., Muir, K. W. & Puddephatt, R. J. (1997). *Organometallics*, **16**, 525–530.
- Jiang, M. H. & Fang, Q. (1999). *Adv. Mater.* **11**, 1147–1151.
- Jiang, X. N., Xu, D., Yuan, D., Lu, M., Guo, G. H., Wang, X. & Fang, Q. (2001). *J. Cryst. Growth*, **222**, 755–759.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2001). *PLATON*. Utrecht University, The Netherlands.
- Stibrany, R. T. & Brant, P. (2001). *Acta Cryst.* **C57**, 644–645.
- Zsolnai, L. (1997). *ZORTEP*. University of Heidelberg, Germany.