$wR = 0.059$
$S = 1.955$
1358 reflections
145 parameters
H atoms riding (C—H 0.95 Å)
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{\max} = 0.003$

Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $0.18(1) \times 10^{-5}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Cl1 | 0.39882 (6) | 0.0936 (3) | 0.00000 | 0.0658 (3) |
| Cl2 | 0.44907 (7) | 0.6548 (3) | 0.24897 (8) | 0.0660 (3) |
| C1 | 0.5098 (2) | 0.008 (1) | −0.0047 (2) | 0.0448 (9) |
| C2 | 0.5405 (3) | −0.152 (1) | −0.0644 (3) | 0.056 (1) |
| C3 | 0.6307 (3) | −0.224 (1) | −0.0690 (3) | 0.061 (1) |
| C4 | 0.6847 (3) | −0.134 (1) | −0.0134 (3) | 0.058 (1) |
| C5 | 0.7328 (3) | 0.388 (1) | 0.2314 (3) | 0.065 (1) |
| C6 | 0.7020 (3) | 0.550 (1) | 0.2901 (3) | 0.073 (1) |
| C7 | 0.6134 (4) | 0.633 (1) | 0.2974 (3) | 0.067 (1) |
| C8 | 0.5590 (3) | 0.545 (1) | 0.2401 (3) | 0.053 (1) |
| C9 | 0.5320 (2) | 0.282 (1) | 0.1184 (2) | 0.0448 (9) |
| C10 | 0.7075 (2) | 0.126 (1) | 0.1091 (3) | 0.056 (1) |
| C11 | 0.5625 (2) | 0.114 (1) | 0.0564 (2) | 0.0411 (9) |
| C12 | 0.6538 (2) | 0.033 (1) | 0.0506 (2) | 0.047 (1) |
| C13 | 0.5861 (2) | 0.376 (1) | 0.1763 (2) | 0.044 (1) |
| C14 | 0.6778 (2) | 0.293 (1) | 0.1716 (3) | 0.049 (1) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cl1—C1 | 1.745 (4) | C6—C7 | 1.411 (8) |
| Cl2—C8 | 1.756 (4) | C7—C8 | 1.376 (7) |
| C1—C2 | 1.339 (6) | C8—C13 | 1.397 (6) |
| C1—C11 | 1.434 (6) | C9—C11 | 1.385 (6) |
| C2—C3 | 1.421 (7) | C9—C13 | 1.389 (6) |
| C3—C4 | 1.352 (7) | C10—C12 | 1.391 (6) |
| C4—C12 | 1.415 (6) | C10—C14 | 1.388 (7) |
| C5—C6 | 1.327 (7) | C11—C12 | 1.447 (5) |
| C5—C14 | 1.423 (7) | C13—C14 | 1.453 (5) |
| | | | |
| Cl1—C1—C2 | 118.5 (3) | C12—C10—C14 | 123.3 (4) |
| Cl1—C1—C11 | 117.5 (3) | C1—C11—C9 | 124.8 (3) |
| C2—C1—C11 | 124.0 (4) | C1—C11—C12 | 115.5 (3) |
| C1—C2—C3 | 119.2 (4) | C9—C11—C12 | 119.7 (3) |
| C2—C3—C4 | 120.4 (5) | C4—C12—C10 | 123.0 (4) |
| C3—C4—C12 | 121.6 (4) | C4—C12—C11 | 119.3 (4) |
| C6—C5—C14 | 121.4 (4) | C10—C12—C11 | 117.7 (4) |
| C5—C6—C7 | 122.2 (5) | C8—C13—C9 | 124.8 (4) |
| C6—C7—C8 | 117.4 (4) | C8—C13—C14 | 116.6 (4) |
| Cl2—C8—C7 | 117.2 (4) | C9—C13—C14 | 118.6 (4) |
| Cl2—C8—C13 | 118.8 (3) | C5—C14—C10 | 123.2 (4) |
| C7—C8—C13 | 124.1 (4) | C5—C14—C13 | 118.4 (4) |
| C11—C9—C13 | 122.3 (3) | C10—C14—C13 | 118.4 (4) |

The crystal used for analysis was mounted in a capillary to prevent sublimation. The structure with the opposite sense of the polar axis was refined under identical circumstances, however, no significant coordinate shifts or differences in agreement indices were noted. The reported configuration was arbitrarily chosen.

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD-4 Operations Manual*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: direct methods (*MULTAN*80; Main *et al.*, 1980). Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN CIF IN*.

The purchase of the diffractometer was made possible by a National Science Foundation chemical instrumentation grant, which we gratefully acknowledge. We thank the ACS Petroleum Research Fund for partial support of this work.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, together with a unit-cell stereopacking diagram, have been deposited with the IUCr (Reference: FG1096). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# *n*-Butyl(carboxymethyl)dimethylammonium Bromide and (Carboxymethyl)ethyldimethylammonium Bromide

RAINER RUDERT,[a] BURKHARD SCHULZ,[a] GÜNTER RECK,[a] DIETER VOLLHARDT[b] AND JÖRG KRIWANEK[b]

[a]*Bundesanstalt für Materialforschung und -prüfung, Rudower Chaussee 5, 12489 Berlin, Germany, and* [b]*Institut für Kolloid- und Grenzflächenforschung, Rudower Chaussee 5, 12489 Berlin, Germany*

(*Received 23 January 1995; accepted 21 August 1995*)

## Abstract

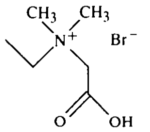
The title compounds, $C_6H_{14}NO_2^+.Br^-$ and $C_8H_{18}NO_2^+.Br^-$, each crystallize forming three-dimensional networks of $Br^-\cdots N^+$ contacts and $Br^-\cdots H—O$ hydro-

gen bonds. *n*-Butyl(carboxymethyl)dimethylammonium bromide has two molecules in the asymmetric unit. The orientation of the alkyl chain relative to the polar part of the molecule is different in the two compounds.

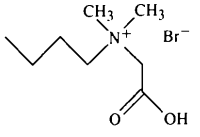
## Comment

In a systematic study, analogies between the crystal structures and properties of monomolecular layers of homologous *N*-*n*-alkylcarboxybetaines at the water surface have been investigated. It is of interest, therefore, whether structure analogies between the three-dimensional crystals and the two-dimensional monolayers resulting from comparable lateral intermolecular interactions in the layer planes can be found. The homologous *N*-*n*-alkyl-*N*,*N*-dimethylammonioacetic acid hydrobromides of general formula $RN^+(CH_3)_2CH_2COOH.Br^-$ are suitable candidates for a systematic investigation of the effect of alkyl chain length on the molecular packing within the crystal. It is well known that the surface activity of amphiphiles decreases with decreasing chain length. Amphiphiles containing only short alkyl chains are no longer surface active and no self-assembly can be observed. It is the objective of this work to obtain information on the special structural features of *N*-*n*-alkylcarboxybetaines with short alkyl chains.

This is the third publication in a series of crystal structures of *N*-*n*-alkylcarboxybetaines. In the preceding publications of this series, the structures of the *n*-octyl and *n*-undecyl analogs of the title compounds were presented (Rudert, Schulz, Reck, Vollhardt & Kriwanek, 1995*a*,*b*). In the following discussion, the two title compounds will be referred to as ethyl betaine, (I), and butyl betaine, (II).



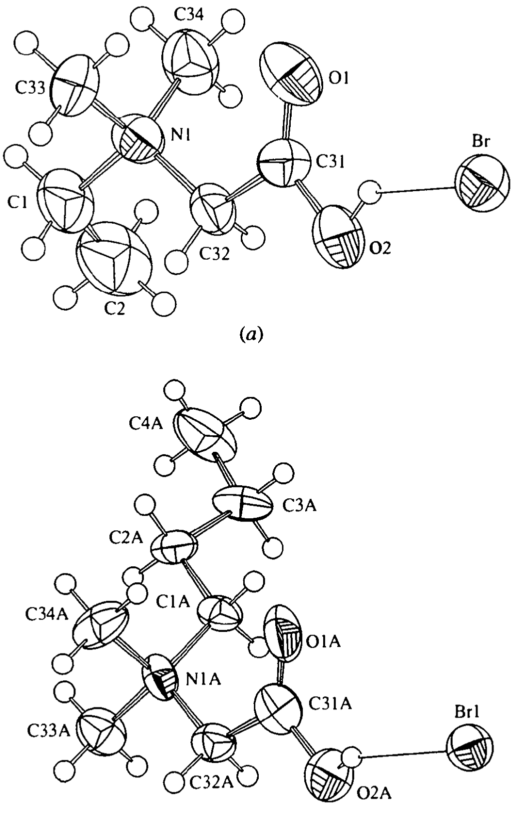
(I)



(II)

Ethyl betaine has one molecule in the asymmetric unit, whereas the asymmetric unit of butyl betaine contains two independent molecules, *A* and *B*, with slightly different conformations, and two independent Br$^-$ anions. The orientation of the alkyl chain relative to the polar part of the molecule, and therefore the torsion angles C31—C32—N1—C2 and C32—N1—C1—C2, are different in the two compounds (Tables 2 and 4; Fig. 1).

Atoms O1, O2, C31 and C32 are coplanar in all molecules, the maximum deviation from the least-squares planes being less than 0.01 Å. The distance of the N atom from this plane is 0.13 (2) Å in ethyl betaine, and 0.26 (3) and −0.08 (5) Å in molecules *A* and *B*, respectively, of butyl betaine. Consequently, the distance between the partially negative O1 atom and the N1 atom is rather short, being 2.895 (8) Å in ethyl betaine, and 2.96 (1) and 2.95 (1) Å in butyl betaine. So far, this type of conformation has been found in all other alkyl betaine compounds.



(*a*)

(*b*)

Fig. 1. *PLATON* (Spek, 1990) drawings of (*a*) ethyl betaine and (*b*) molecule *A* of butyl betaine. The ellipsoids enclose 50% probability and hydrogen bonds are symbolized by thin lines.

The Br$^-\cdots$N$^+$ contacts and Br$^-\cdots$H—O hydrogen bridges build up a three-dimensional network. Because four C atoms are tetrahedrally bonded to the N atom, there are four potential coordination sites above the centers of the tetrahedral faces. The crystal structure of tetramethylammonium bromide (Cheban, Dvorkin, Rotaru & Malinovskii, 1987; Evans & Hughes, 1990) may serve as a model for this type of Br$^-\cdots$N$^+$ interaction. One of these sites is occupied by the O1 atom of the same molecule, while the other three sites are occupied by Br$^-$ anions. One exception is molecule *B* of butyl betaine, which is fourfold coordinated by Br$^-$ anions, the fourth Br$^-$ being at a distance of 4.025 (7) Å from atom O1*B*.

Each Br$^-$ anion is coordinated by three or four N atoms, the distances being 4.161 (7), 4.285 (7) and 4.310 (7) Å for ethyl betaine, 4.294 (8), 4.311 (7), 4.655 (7) and 4.805 (7) Å for Br1 of butyl betaine, and

4.225 (7), 4.242 (7) and 4.697 (7) Å for Br2 of butyl betaine. The Br···O distances of the hydrogen bonds are 3.102 (6) Å for ethyl betaine, and 3.075 (7) and 3.122 (7) Å for butyl betaine. Similar contacts exist in longer chain betaine compounds (*e.g.* octyl betaine and undecyl betaine; Rudert *et al.*, 1995*a*,*b*), as well as in betaine hydrobromide itself (Clastre, 1964). In contrast to the longer chain betaines, the title compounds do not form layers.

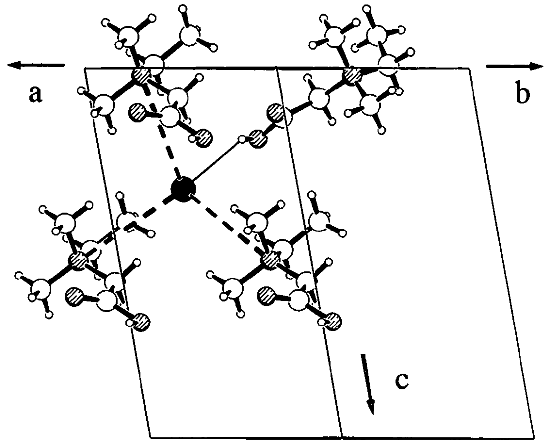


Fig. 2. *SCHAKAL*92 (Keller, 1992) drawing of the Br coordination in ethyl betaine, viewed in the [110] direction. The filled circle is Br and the shaded circles are N and O. The hydrogen bond is symbolized by a thin line and the Br···N contacts by dotted lines.

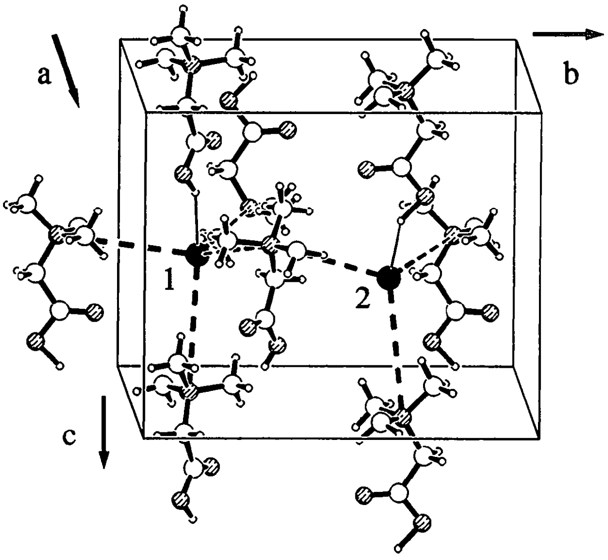


Fig. 3. *SCHAKAL*92 drawings of the Br coordinations in butyl betaine (symbols as in Fig. 2). For clarity, the last three C atoms of the butyl chains are not shown.

## Experimental

Both title compounds were synthesized according to a detailed description given for the preparation of *N*-*n*-alkyl-*N*,*N*-dimethylammonioacetic acid bromides (Wüstneck, Kriwanek, Herbst, Wasow & Haage, 1992). A mixture of equimolar quantities of *N*,*N*-dimethylglycine butyl ester and ethyl or butyl bromide were refluxed for 7 h in dry methanol. The product was hydrolyzed by addition of methanolic KOH and refluxing for 1 h. Afterwards, aqueous hydrobromic acid (48%) was added until the solution became acidic. Finally, surplus inorganic salt was removed and *N*-ethyl- or *N*-*n*-butyl-*N*,*N*-dimethylammonioacetic acid bromide crystallized on cooling. The product was filtered off, dried over $P_2O_5$ under vacuum and recrystallized repeatedly from dry acetone containing small amounts of methanol.

### Ethyl betaine, (I)

*Crystal data*

$C_6H_{14}NO_2^+.Br^-$
$M_r = 212.09$
Monoclinic
*Cc*
$a = 12.108\,(7)$ Å
$b = 7.277\,(3)$ Å
$c = 10.835\,(9)$ Å
$\beta = 107.58\,(5)°$
$V = 910\,(2)$ Å$^3$
$Z = 4$
$D_x = 1.55$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 11$–$17°$
$\mu = 4.423$ mm$^{-1}$
$T = 294$ K
Plate
0.45 × 0.40 × 0.03 mm
Colorless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scans (Fair, 1990)
$T_{min} = 0.5745$, $T_{max} = 0.9998$
3201 measured reflections
1741 independent reflections

1381 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.125$
$\theta_{max} = 24.97°$
$h = -14 \rightarrow 14$
$k = -8 \rightarrow 8$
$l = -12 \rightarrow 12$
2 standard reflections
frequency: 30 min
intensity decay: 1.55%

*Refinement*

Refinement on *F*
$R = 0.052$
$wR = 0.061$
$S = 1.354$
1381 reflections
92 parameters
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0016F_o^4]$
$(\Delta/\sigma)_{max} = 0.036$

$\Delta\rho_{max} = 0.95$ e Å$^{-3}$
$\Delta\rho_{min} = -0.50$ e Å$^{-3}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
Absolute configuration: determined by *R* value

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$) *for* (I)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

| | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| Br | 0.3250 | 0.2044 (1) | 0.8030 | 0.0624 (3) |
| O1 | 0.1228 (6) | 0.611 (1) | 0.6489 (5) | 0.078 (3) |
| O2 | 0.1869 (5) | 0.3905 (9) | 0.5449 (5) | 0.070 (3) |
| N1 | 0.0202 (5) | 0.7976 (9) | 0.4051 (5) | 0.052 (3) |
| C1 | −0.0130 (8) | 0.855 (2) | 0.2652 (8) | 0.091 (5) |
| C2 | −0.089 (1) | 0.745 (3) | 0.173 (1) | 0.103 (7) |
| C31 | 0.1309 (6) | 0.542 (1) | 0.5523 (6) | 0.050 (3) |
| C32 | 0.0800 (6) | 0.611 (1) | 0.4172 (6) | 0.049 (3) |
| C33 | 0.0982 (8) | 0.941 (1) | 0.4773 (8) | 0.070 (4) |
| C34 | −0.0892 (6) | 0.787 (1) | 0.4463 (8) | 0.072 (4) |

Table 2. *Selected geometric parameters (Å, °) for* (I)

| | | | |
|---|---|---|---|
| O1—C31 | 1.192 (9) | N1—C33 | 1.47 (1) |
| O2—C31 | 1.31 (1) | N1—C34 | 1.52 (1) |
| N1—C1 | 1.51 (1) | C1—C2 | 1.39 (2) |
| N1—C32 | 1.52 (1) | C31—C32 | 1.494 (9) |
| C1—N1—C32 | 108.0 (7) | N1—C1—C2 | 118 (1) |
| C1—N1—C33 | 105.8 (7) | O1—C31—O2 | 126.2 (7) |
| C1—N1—C34 | 108.5 (6) | O1—C31—C32 | 126.8 (8) |
| C32—N1—C33 | 112.1 (5) | O2—C31—C32 | 107.0 (6) |
| C32—N1—C34 | 111.3 (6) | N1—C32—C31 | 115.5 (6) |
| C33—N1—C34 | 110.9 (7) | | |
| C32—N1—C1—C2 | 61.0 (13) | O1—C31—C32—N1 | 5.3 (12) |
| C1—N1—C32—C31 | 173.4 (7) | O2—C31—C32—N1 | −174.5 (7) |

**Butyl betaine, (II)**

*Crystal data*

$C_8H_{18}NO_2^+.Br^-$
$M_r = 240.15$
Orthorhombic
$P2_12_12_1$
$a = 11.110$ (7) Å
$b = 13.428$ (5) Å
$c = 15.038$ (5) Å
$V = 2243$ (2) Å$^3$
$Z = 8$
$D_x = 1.42$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10–14°$
$\mu = 3.596$ mm$^{-1}$
$T = 294$ K
Prismatic
0.70 × 0.60 × 0.28 mm
Colorless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: refined from $\Delta F$ (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.16$, $T_{\max} = 0.37$
2244 measured reflections
2244 independent reflections

2052 observed reflections $[I > \sigma(I)]$
$\theta_{\max} = 25.01°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 17$
2 standard reflections frequency: 30 min intensity decay: 1.23%

*Refinement*

Refinement on $F$
$R = 0.053$
$wR = 0.052$
$S = 2.190$
2052 reflections
224 parameters
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.045$
$\Delta\rho_{\max} = 0.53$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.23$ e Å$^{-3}$

Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: 0.89 × 10$^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å$^2$) *for* (II)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Br1 | 0.57465 (9) | 0.17574 (8) | 0.38006 (7) | 0.0509 (5) |
| Br2 | 0.40039 (9) | 0.14508 (7) | 0.90787 (7) | 0.0496 (4) |
| O1*A* | 0.2340 (7) | 0.2165 (7) | 0.3213 (5) | 0.074 (5) |
| O1*B* | 0.7443 (7) | 0.0837 (5) | 0.8710 (6) | 0.063 (4) |
| O2*A* | 0.3128 (6) | 0.1338 (6) | 0.4347 (5) | 0.062 (4) |
| O2*B* | 0.6591 (6) | 0.2323 (5) | 0.8852 (6) | 0.059 (4) |
| N1*A* | −0.0071 (6) | 0.1558 (5) | 0.3849 (5) | 0.039 (4) |
| N1*B* | 0.9833 (6) | 0.1785 (5) | 0.8663 (4) | 0.036 (3) |
| C1*A* | −0.0079 (9) | 0.0958 (7) | 0.2979 (5) | 0.037 (4) |
| C1*B* | 0.9877 (9) | 0.1193 (7) | 0.7806 (5) | 0.042 (5) |
| C2*A* | −0.1211 (9) | 0.0999 (7) | 0.2445 (5) | 0.041 (5) |
| C2*B* | 1.113 (1) | 0.0797 (8) | 0.7580 (6) | 0.050 (5) |
| C3*A* | −0.114 (1) | 0.0220 (8) | 0.1724 (6) | 0.050 (5) |
| C3*B* | 1.110 (1) | 0.0213 (8) | 0.6716 (7) | 0.060 (6) |
| C4*A* | −0.222 (1) | 0.019 (1) | 0.1145 (8) | 0.077 (8) |
| C4*B* | 1.234 (1) | −0.0053 (9) | 0.6397 (6) | 0.059 (6) |
| C31*A* | 0.2234 (9) | 0.1688 (7) | 0.3889 (7) | 0.049 (5) |
| C31*B* | 0.7517 (9) | 0.1720 (7) | 0.8749 (7) | 0.049 (5) |
| C32*A* | 0.1081 (8) | 0.1413 (7) | 0.4332 (5) | 0.041 (4) |
| C32*B* | 0.8660 (8) | 0.2340 (6) | 0.8717 (6) | 0.040 (5) |
| C33*A* | −0.1061 (9) | 0.1229 (8) | 0.4470 (6) | 0.053 (5) |
| C33*B* | 1.0792 (9) | 0.2564 (6) | 0.8685 (6) | 0.045 (5) |
| C34*A* | −0.025 (1) | 0.2663 (7) | 0.3655 (7) | 0.055 (6) |
| C34*B* | 0.999 (1) | 0.1151 (7) | 0.9478 (5) | 0.045 (5) |

Table 4. *Selected geometric parameters (Å, °) for* (II)

| | | | |
|---|---|---|---|
| O1*A*—C31*A* | 1.21 (1) | N1*A*—C34*A* | 1.53 (1) |
| O1*B*—C31*B* | 1.19 (1) | N1*A*—C33*A* | 1.51 (1) |
| O2*A*—C31*A* | 1.30 (1) | C1*A*—C2*A* | 1.49 (1) |
| O2*B*—C31*B* | 1.32 (1) | C1*B*—C2*B* | 1.53 (1) |
| N1*B*—C1*B* | 1.52 (1) | C2*A*—C3*A* | 1.51 (1) |
| N1*B*—C32*B* | 1.50 (1) | C2*B*—C3*B* | 1.52 (1) |
| N1*B*—C33*B* | 1.49 (1) | C3*B*—C4*B* | 1.51 (2) |
| N1*B*—C34*B* | 1.50 (1) | C3*A*—C4*A* | 1.48 (2) |
| N1*A*—C1*A* | 1.54 (1) | C31*A*—C32*A* | 1.49 (1) |
| N1*A*—C32*A* | 1.48 (1) | C31*B*—C32*B* | 1.52 (1) |
| C1*B*—N1*B*—C32*B* | 109.5 (7) | N1*B*—C1*B*—C2*B* | 113.6 (8) |
| C1*B*—N1*B*—C33*B* | 111.3 (7) | C1*A*—C2*A*—C3*A* | 108.6 (8) |
| C1*B*—N1*B*—C34*B* | 113.2 (7) | C1*B*—C2*B*—C3*B* | 110.3 (8) |
| C32*B*—N1*B*—C33*B* | 105.7 (6) | C2*B*—C3*B*—C4*B* | 111.8 (9) |
| C32*B*—N1*B*—C34*B* | 109.6 (7) | C2*A*—C3*A*—C4*A* | 113.7 (9) |
| C33*B*—N1*B*—C34*B* | 107.3 (7) | O1*A*—C31*A*—O2*A* | 124.4 (9) |
| C1*A*—N1*A*—C32*A* | 110.6 (6) | O1*A*—C31*A*—C32*A* | 126.3 (9) |
| C1*A*—N1*A*—C34*A* | 110.3 (7) | O2*A*—C31*A*—C32*A* | 109.3 (8) |
| C1*A*—N1*A*—C33*A* | 111.7 (7) | O1*B*—C31*B*—O2*B* | 124.3 (9) |
| C32*A*—N1*A*—C34*A* | 109.5 (7) | O1*B*—C31*B*—C32*B* | 127.1 (9) |
| C32*A*—N1*A*—C33*A* | 106.7 (7) | O2*B*—C31*B*—C32*B* | 108.6 (7) |
| C34*A*—N1*A*—C33*A* | 107.9 (7) | N1*A*—C32*A*—C31*A* | 119.4 (7) |
| N1*A*—C1*A*—C2*A* | 116.3 (7) | N1*B*—C32*B*—C31*B* | 117.0 (7) |
| O1*A*—C31*A*—C32*A*—N1*A* | 12 (1) | | |
| O1*B*—C31*B*—C32*B*—N1*B* | −2 (1) | | |
| O2*A*—C31*A*—C32*A*—N1*A* | −168.3 (8) | | |
| O2*B*—C31*B*—C32*B*—N1*B* | 176.0 (8) | | |
| C31*A*—C32*A*—N1*A*—C1*A* | 59 (1) | | |
| C31*B*—C32*B*—N1*B*—C1*B* | 63 (1) | | |
| C32*A*—N1*A*—C1*A*—C2*A* | 177.2 (7) | | |
| C32*B*—N1*B*—C1*B*—C2*B* | 166.6 (7) | | |

For ethyl betaine, all H atoms were refined as riding, except for atom H2, which was refined independently from the position of the O2 atom. For butyl betaine, the positions of atoms H2*A* and H2*B* were found by differential Fourier synthesis. All other positions were calculated and all H atoms were refined as riding on their parent atoms.

For both compounds, data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD*-4 *Operations Manual*; data reduction: *MolEN PROCESS* (Fair, 1990); program(s) used to solve structures: *MULTAN*80 (direct methods; Main *et al.*, 1980); program(s) used to refine structures: *MolEN LSFM*; molecular graphics: *PLATON*92 (Spek, 1990) and *SCHAKAL*92 (Keller, 1992); software used to prepare material for publication: *MolEN CIF IN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: KA1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# 2,2′-Methylenebis(5,5-dimethyl-1,3,2-dioxaphosphorinane 2-oxide)

C. Scott Browning, Timothy E. Burrow, David H. Farrar* and Alan J. Lough

*Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1. E-mail: dfarrar@chem.utoronto.ca*

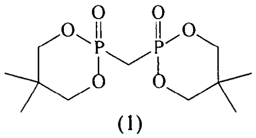
(*Received 2 October 1995; accepted 23 October 1995*)

## Abstract

The title compound, $C_{11}H_{22}O_6P_2$, contains two tetrahedral $P^V$ atoms connected by a bridging methylene group. The two P═O vectors are rotated away from each other, with an O—P···P—O torsion angle of −135.1 (1)°. Each P atom is contained in a six-membered ring with two O and three C atoms. The six-membered rings are in chair conformations, with the O atom of the P═O moiety in an equatorial position.

## Comment

Bisphosphonate compounds are under study by pharmaceutical companies because of their potential medical applications. Ethane-1-hydroxy-1,1-diphosphonic acid, $CH_3C(OH)(PO_3H_2)_2$ (EHDP), has been extensively studied (Francis & Centner, 1978) and the disodium salt of EHDP is currently used to treat osteoporosis (Berkow & Fletcher, 1992). While EHDP and many of its salts have been structurally studied, very few structures of the alkoxide derivatives of diphosphonic acid have been reported in the literature (Allen & Kennard, 1993). We are interested in the structural changes in bisphosphonate and related compounds upon complexation to transition metals. In order to gain more insight into the structures of uncoordinated bisphosphonate compounds, we undertook the crystal structure determination of the compound $CH_2[P(O)(OCH_2)_2C(CH_3)_2]_2$, (1).



(1)

The $P^V$ atoms in compound (1) have slightly distorted tetrahedral geometries. In accordance with the predictions of VSEPR (valence-shell electron-pair repulsion) theory, the six angles subtended at the P atoms involving both P═O bonds are all several degrees larger than the ideal tetrahedral value and range from 111.95 (9) to 113.97 (9)° (Bader, Gillespie & MacDougall, 1988). The remaining angles are significantly less than 109.5° and vary between 105.01 (8) and 107.18 (8)°. The two P═O bonds, P1═O1 and P2═O4, are statistically equal and average 1.461 (3) Å. These values are comparable with the distances of 1.472 (6) and 1.438 (9) Å observed in the structure of $CBr_2[P(O)(OCH_3)_2]_2$ and the distance of 1.453 (3) Å reported for $CCl_2\{P(O)[OCH(CH_3)_2]_2\}_2$ (Vepsalainen, Nupponen, Pohjala, Ahlgren & Vainiotalo, 1992). The average P═O bond length in $(RO)_3$P═O compounds is 1.449 (7) Å, while the average bond length in $R_3$P═O compounds is 1.489 (10) Å, where $R$ is a hydrocarbon group (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

The two tetrahedral P atoms are connected by a bridging methylene group (Fig. 1). The P—C11 distances are statistically equivalent and average 1.802 (5) Å. The average P—C distance in $R_3$P═O compounds is 1.801 (11) Å (Allen *et al.*, 1987). The two P tetrahedra, linked by a methylene bridge, are nearly eclipsed when viewed down the P···P vector. The torsion angle O1—P1···P2—O6 is −23.0 (1)°. The two P═O groups are rotated away from each other, with an O1—P1···P2—O4 torsion angle of −135.1 (1)°.

The P1—O2 and P1—O3 distances are indistinguishable and average 1.581 (3) Å. The P2—O5 and P2—O6 distances are statistically different (5.9$\sigma$); however, both values [1.587 (1) and 1.574 (2) Å, respectively] are comparable with the average value of 1.581 (3) Å observed for P1. Each O—P—O linkage is contained within a six-membered ring and each ring is completed by three tetrahedral C atoms. The six-membered rings