C11	0.4309 (3)	0.2477 (2)	0.3398 (2)	0.0823 (7)
C12	0.4619 (2)	0.2084 (2)	0.4302 (2)	0.0744 (6)
C13	0.4502 (3)	0.2483 (2)	0.5626 (2)	0.0810 (7)
C14	0.0881 (2)	0.25864 (15)	0.5201 (2)	0.0717 (6)
C15	−0.0429 (3)	0.3047 (2)	0.4712 (2)	0.1093 (9)
C16	0.4012 (2)	0.3267 (2)	0.6089 (2)	0.0787 (6)
C17	0.3660 (3)	0.4026 (2)	0.5664 (2)	0.0851 (7)
C18	0.3191 (3)	0.4710 (2)	0.6125 (3)	0.1016 (8)
C19	0.3048 (3)	0.4666 (3)	0.7033 (3)	0.1107 (10)
C20	0.3393 (3)	0.3934 (3)	0.7464 (2)	0.1087 (10)
C21	0.3864 (3)	0.3250 (2)	0.6996 (2)	0.0951 (8)

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

F1—C17	1.334 (3)	C5—C6	1.534 (4)
F2—C18	1.349 (3)	C6—C7	1.504 (3)
F3—C19	1.331 (4)	C7—C8	1.518 (3)
F4—C20	1.337 (3)	C8—C9	1.518 (4)
F5—C21	1.345 (3)	C9—C10	1.523 (3)
O1—C13	1.431 (3)	C10—C11	1.533 (3)
O1—C12	1.466 (3)	C11—C12	1.492 (3)
O2—C14	1.356 (2)	C13—C16	1.501 (3)
O2—C1	1.437 (2)	C14—C15	1.492 (3)
O3—C14	1.188 (3)	C16—C21	1.370 (3)
C1—C2	1.518 (3)	C16—C17	1.384 (3)
C1—C12	1.538 (3)	C17—C18	1.363 (4)
C1—C13	1.550 (3)	C18—C19	1.372 (4)
C2—C3	1.509 (3)	C19—C20	1.350 (5)
C3—C4	1.519 (3)	C20—C21	1.369 (4)
C4—C5	1.513 (4)		
C13—O1—C12	92.1 (2)	C16—C13—C1	121.9 (2)
C14—O2—C1	118.8 (2)	O3—C14—O2	123.9 (2)
O2—C1—C2	112.2 (2)	O3—C14—C15	126.3 (2)
O2—C1—C12	108.4 (2)	O2—C14—C15	109.8 (2)
C2—C1—C12	116.2 (2)	C21—C16—C17	115.9 (3)
O2—C1—C13	114.4 (2)	C21—C16—C13	119.3 (3)
C2—C1—C13	117.8 (2)	C17—C16—C13	124.7 (2)
C12—C1—C13	84.9 (2)	F1—C17—C18	117.7 (3)
C3—C2—C1	112.7 (2)	F1—C17—C16	120.6 (2)
C2—C3—C4	115.8 (2)	C18—C17—C16	121.6 (3)
C5—C4—C3	114.8 (2)	F2—C18—C17	118.9 (3)
C4—C5—C6	113.5 (2)	F2—C18—C19	120.5 (3)
C7—C6—C5	113.6 (2)	C17—C18—C19	120.7 (3)
C6—C7—C8	115.7 (2)	F3—C19—C20	121.7 (4)
C9—C8—C7	114.8 (2)	F3—C19—C18	119.5 (4)
C8—C9—C10	115.1 (2)	C20—C19—C18	118.8 (3)
C9—C10—C11	114.6 (2)	F4—C20—C19	119.3 (4)
C12—C11—C10	115.7 (2)	F4—C20—C21	120.6 (4)
O1—C12—C11	112.6 (2)	C19—C20—C21	120.1 (3)
O1—C12—C1	90.7 (2)	F5—C21—C20	117.6 (3)
C11—C12—C1	123.1 (2)	F5—C21—C16	119.5 (3)
O1—C13—C16	114.0 (2)	C20—C21—C16	122.8 (3)
O1—C13—C1	91.6 (2)		

Data collection and cell refinement; CAD-4-VAX diffractometer software (Enraf–Nonius, 1988). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(pyridiniopropionate) Hydrogen Bromide

XIAO-MING CHEN† AND THOMAS C. W. MAK*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong

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Abstract

A novel anhydrous 2:1 acid adduct of a betaine derivative, pyridiniopropionate (ppbet), has been prepared, $C_{16}H_{19}N_2O_4^+.Br^-$ (I). X-ray crystallography revealed that the carboxylate groups of a pair of ppbet molecules are bridged by a proton in an unusual non-coplanar configuration to form a U-shaped dimeric cation $[(\mathrm{ppbet})_2\mathrm{H}]^+$, featuring a very strong hydrogen bond of length 2.450 (6) Å.

Comment

As zwitterions with terminal quaternary ammonium and carboxylate groups, betaine and its derivatives are good proton acceptors, and very strong hydrogen bonds are found in crystalline acid adducts such as $[(\mathrm{bet})_2\mathrm{H}]\mathrm{Cl.H_2O}$ (bet = $Me_3N^+CH_2CO_2^-$) (Chen & Mak, 1990*a*) and $[(\mathrm{pybet})_2\mathrm{H}]\mathrm{Cl.H_2O}$ (pybet = $C_5H_5N^+CH_2CO_2^-$) (Chen & Mak, 1990*b*). In the strongly hydrogen-bonded dimeric cations of these two betaine–acid adducts, the pair of carboxylate groups are centrosymmetrically related with an O···O distance of *ca* 2.45 Å. It is found that the carboxylate group of betaines is significantly affected by

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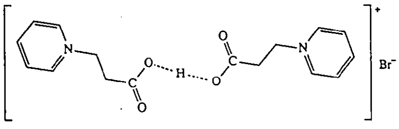
† On leave from the Department of Chemistry, Zhongshan University, Guangzhou 510275, People's Republic of China.

the positively charged N atom and such an effect can be reduced by the introduction of an additional methylene group as a spacer (Chen & Mak, 1991). In this paper, we report the preparation and structure of an acid adduct of a higher analogue of betaine, pyridiniopropionate ($C_5H_5N^+CH_2CH_2CO_2^-$, ppbet), namely bis(pyridiniopropionate) hydrogen bromide, (I), which turns out to be the first anhydrous example in its class.



(I)

As illustrated in Fig. 1, a pair of ppbet molecules are bridged by a proton to form a U-shaped dimeric cationic system, resulting in a short hydrogen bond between two carboxylate O atoms [O···O = 2.450 (6) Å], which qualifies it as a 'very strong' hydrogen bond (Emsley, 1980). The O···O distance is compatible with those found in analogous hydrogen-bonded dimeric betaine derivatives: $[(\text{pybet})_2\text{H}]\text{Cl.H}_2\text{O}$ [2.436 (6) Å] (Chen & Mak, 1990*a*) and $[(\text{bet})_2\text{H}]\text{Cl.H}_2\text{O}$ [2.454 (3) Å] (Chen & Mak, 1990*b*). The geometric similarity between the two carboxylate groups suggests that the $[(\text{ppbet})_2\text{H}]^+$ cation is more similar to Type *A* than Type *B* acid salts (Speakman, 1972). It is interesting that the two carboxy fragments participating in the hydrogen bonding are significantly non-coplanar, the dihedral angle between the O(11)—C(11)—O(12) and O(21)—C(21)—O(22) carboxylate moieties being 36°. Thus, the conformation of the hydrogen bond in the ppbet dimeric cation is different from the coplanar configuration found in the other two betaine dimeric cations as well as in a variety of common carboxylic acid salts (Emsley, 1980; Speakman, 1972).

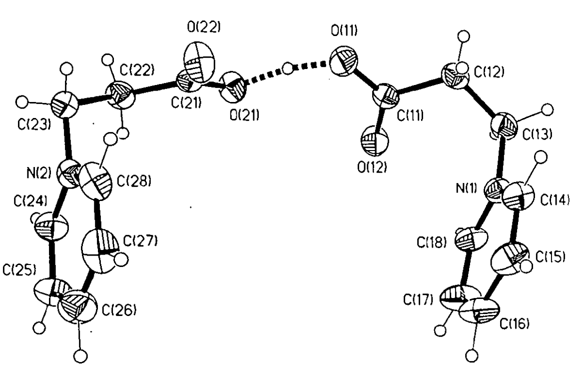


Fig. 1. Displacement ellipsoid plot (50% probability) of the hydrogen-bonded pyridiniopropionate dimeric cation, $[(\text{ppbet})_2\text{H}]^+$, with the atom-numbering scheme.

It is notable that the geometry of the carboxylate group in the ppbet dimeric cation is slightly different to the geometries of those in the analogous bet and pybet species. The O—C—O bond angle [average 125.2 (5)°] in the ppbet dimeric cation is smaller than those in the bet [126.5 (2)°] and pybet [127.3 (3)°] cations, concomitant with a markedly larger C—C—O(H) bond angle [average 114.2 (4)°, *versus* 110.8 (3) and 110.0 (3)° in the bet and pybet dimeric cations, respectively]. This can be attributed to the fact that with the addition of one more methylene unit between the carboxylate group and the positively charged N atom, the inductive effect is reduced. This observation is in accord with the trend established for a number of metal complexes of betaines (Chen & Mak, 1993).

Experimental

Solid 3-bromopropionic acid (6.2 g) was dissolved in pyridine (40 ml) and the mixture was stirred at room temperature overnight. After removal of excess pyridine under reduced pressure at 333 K, a yellowish powder was obtained which was dissolved in a minimum amount of hot pyridine (338 K). Upon slow cooling of the resulting solution, a crop of very hygroscopic crystals (8.6 g, yield 90%) was deposited.

Crystal data

$C_{16}H_{19}N_2O_4^+.Br^-$
$M_r = 383.2$
Monoclinic
$C2/c$
$a = 32.108$ (6) Å
$b = 9.244$ (2) Å
$c = 12.043$ (3) Å
$\beta = 103.63$ (2)°
$V = 3474$ (1) Å^3
$Z = 8$
$D_x = 1.465$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.5$–14°
$\mu = 2.36$ mm^{-1}
$T = 295$ K
Prismatic
0.50 × 0.42 × 0.40 mm
Colorless

Data collection

Nicolet *R*3*m*/*V* diffractometer
ω–2θ scans
Absorption correction: empirical (ψ scan)
$T_{\min} = 0.538$, $T_{\max} = 0.874$
4143 measured reflections
3953 independent reflections
2316 observed reflections [$F_o \geq 6.0\sigma(F_o)$]

$R_{\text{int}} = 0.022$
$\theta_{\max} = 27.5°$
$h = -41 \rightarrow 40$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 15$
2 standard reflections monitored every 125 reflections intensity variation: ±2.0%

Refinement

Refinement on *F*
$R = 0.061$
$wR = 0.076$
$S = 1.35$
2316 reflections
209 parameters

$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -0.72$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: $\chi = 0.00004$

H-atom parameters not refined
$w = 1/(\sigma^2|F_o| + 0.002|F_o|^2)$
$(\Delta/\sigma)_{\max} = 0.008$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	$U_{\rm eq}$
Br(1)	0.56560 (2)	0.32825 (6)	1.04460 (5)	0.0544 (2)
O(12)	0.3795 (1)	0.1116 (4)	0.7692 (4)	0.058 (2)
O(11)	0.3529 (1)	0.3259 (4)	0.7087 (4)	0.058 (1)
C(11)	0.3834 (2)	0.2407 (5)	0.7512 (4)	0.042 (2)
C(12)	0.4273 (2)	0.3118 (5)	0.7801 (5)	0.046 (2)
C(13)	0.4621 (2)	0.2206 (6)	0.8562 (4)	0.048 (2)
N(1)	0.4527 (1)	0.1947 (4)	0.9697 (4)	0.042 (1)
C(14)	0.4557 (2)	0.3040 (5)	1.0434 (5)	0.051 (2)
C(15)	0.4454 (2)	0.2832 (7)	1.1471 (5)	0.062 (2)
C(16)	0.4317 (2)	0.1477 (7)	1.1717 (5)	0.067 (3)
C(17)	0.4290 (2)	0.0384 (7)	1.0953 (5)	0.072 (3)
C(18)	0.4405 (2)	0.0607 (6)	0.9940 (5)	0.054 (2)
O(21)	0.2814 (1)	0.2180 (4)	0.6513 (3)	0.054 (1)
O(22)	0.2574 (1)	0.4203 (4)	0.7114 (4)	0.067 (2)
C(21)	0.2518 (2)	0.3002 (5)	0.6700 (4)	0.041 (2)
C(22)	0.2069 (2)	0.2363 (6)	0.6324 (5)	0.050 (2)
C(23)	0.1732 (2)	0.3149 (6)	0.6808 (5)	0.051 (2)
N(2)	0.1776 (1)	0.2818 (4)	0.8029 (4)	0.042 (1)
C(24)	0.1640 (2)	0.1536 (5)	0.8303 (5)	0.054 (2)
C(25)	0.1663 (2)	0.1194 (7)	0.9425 (6)	0.067 (3)
C(26)	0.1835 (2)	0.2154 (8)	1.0259 (6)	0.072 (3)
C(27)	0.1982 (2)	0.3469 (8)	0.9970 (6)	0.071 (3)
C(28)	0.1947 (2)	0.3795 (6)	0.8835 (5)	0.058 (2)

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

O(12)—C(11)	1.225 (6)	O(11)—C(11)	1.265 (6)
C(11)—C(12)	1.522 (7)	C(12)—C(13)	1.522 (7)
C(13)—N(1)	1.488 (7)	N(1)—C(14)	1.333 (7)
N(1)—C(18)	1.350 (7)	C(14)—C(15)	1.379 (9)
C(15)—C(16)	1.383 (9)	C(16)—C(17)	1.355 (9)
C(17)—C(18)	1.371 (10)	O(21)—C(21)	1.276 (6)
O(22)—C(21)	1.213 (6)	C(21)—C(22)	1.524 (7)
C(22)—C(23)	1.529 (8)	C(23)—N(2)	1.475 (7)
N(2)—C(24)	1.331 (7)	N(2)—C(28)	1.344 (7)
C(24)—C(25)	1.372 (9)	C(25)—C(26)	1.357 (9)
C(26)—C(27)	1.378 (10)	C(27)—C(28)	1.379 (10)
O(12)—C(11)—O(11)	125.3 (5)	O(12)—C(11)—C(12)	120.4 (4)
O(11)—C(11)—C(12)	114.2 (4)	C(11)—C(12)—C(13)	114.1 (4)
C(12)—C(13)—N(1)	111.3 (5)	C(13)—N(1)—C(14)	119.4 (4)
C(13)—N(1)—C(18)	118.6 (4)	C(14)—N(1)—C(18)	122.0 (5)
N(1)—C(14)—C(15)	120.1 (5)	C(14)—C(15)—C(16)	118.5 (6)
C(15)—C(16)—C(17)	120.1 (7)	C(16)—C(17)—C(18)	120.3 (6)
N(1)—C(18)—C(17)	118.9 (5)	O(21)—C(21)—O(22)	125.0 (5)
O(21)—C(21)—C(22)	114.1 (4)	O(22)—C(21)—C(22)	120.9 (5)
C(21)—C(22)—C(23)	114.1 (4)	C(22)—C(23)—N(2)	111.8 (4)
C(23)—N(2)—C(24)	118.2 (4)	C(23)—N(2)—C(28)	120.5 (5)
C(24)—N(2)—C(28)	121.4 (5)	N(2)—C(24)—C(25)	120.4 (5)
C(24)—C(25)—C(26)	119.7 (6)	C(25)—C(26)—C(27)	119.6 (7)
C(26)—C(27)—C(28)	119.4 (6)	N(2)—C(28)—C(27)	119.5 (6)

A crystal sealed in a Lindemann glass capillary was used to collect the intensity data. An Lp correction was applied. The structure was solved by direct methods and refined anisotropically. The H atoms of ppbet were generated geometrically (C—H = 0.96 Å) and the acidic proton was located from a difference map and fixed. All H atoms were assigned isotropic displacement parameters and included in the structure-factor calculations. All computations were performed with the *SHELXTL/PC* program package (Sheldrick, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and data collection and processing parameters, and a packing diagram have been deposited with the IUCr (Reference: HL1048). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,4,6-Triphenylpyridine

J. Ondráček and J. Novotný

Department of Solid State Chemistry,
Institute of Chemical Technology, Technická 5,
166 28 Praha 6, Czech Republic

M. Petrů, P. Lhoták and J. Kuthan

Department of Organic Chemistry,
Institute of Chemical Technology, Technická 5,
166 28 Praha 6, Czech Republic

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Abstract

The crystal and molecular structures of 2,4,6-triphenylpyridine ($C_{23}H_{17}N$) obtained by X-ray analysis are compared with those obtained by quantum-chemical calculations based on the AM1 method. Both the theoretical and experimental results indicate that a disrotatory conformation is preferred. The AM1 results of the preferred conformation of a model compound (1,3,5-triphenylbenzene) are also reported.