

(2-Pyridylmethyl)ammonium pyridine-2-carboxylate: the product of oxidative degradation of bis(2-pyridylmethyl)amine

Anders Døssing,^{a*} Martin C. Skands^a and
Anders Østergaard Madsen^b

^aDepartment of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark, and ^bCentre for Crystallographic Studies, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark
Correspondence e-mail: dossing@kiku.dk

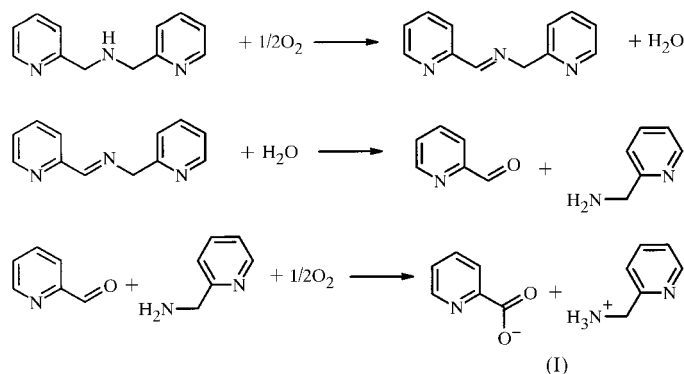
Received 5 July 2001

Accepted 19 September 2001

The title compound, $C_6H_9N_2^+ \cdot C_6H_4NO_2^-$, has been formed by oxidative degradation of neat bis(2-pyridylmethyl)amine. Hydrogen bonds link the ions into infinite chains along the *a* axis.

Comment

The amine bis(2-pyridylmethyl)amine is a versatile synthetic intermediate widely used in the preparation of polypyridyl ligands. The amine is usually distilled prior to use, and during the course of our studies in this field (Døssing *et al.*, 1996, 1997) it has puzzled us that colourless needles begin to form after a couple of months' storage of the distilled amine. In order to characterize this decomposition product, a single crystal was subjected to structure determination, which showed that the title salt, (I), consisting of a (2-pyridylmethyl)ammonium cation and a pyridine-2-carboxylate anion, had formed. A possible mechanism for the formation of (I) is shown below.



In support of this mechanism, close scrutiny of a ¹H NMR spectrum of a concentrated solution of aged bis(2-pyridylmethyl)amine in CD₃CN indeed revealed the presence of low-

intensity peaks that could originate from pyridine-2-carboxaldehyde (7.61, 7.91, 8.77 and 10.00 p.p.m. in CD₃CN). It is important to emphasize that these peaks are absent from the spectrum of freshly distilled bis(2-pyridylmethyl)amine. The presence of traces of impurities might catalyse the oxidative degradation. A similar (Fe^{III}-promoted) oxidative degradation of a polypyridyl compound has been reported by Renz *et al.* (1999).

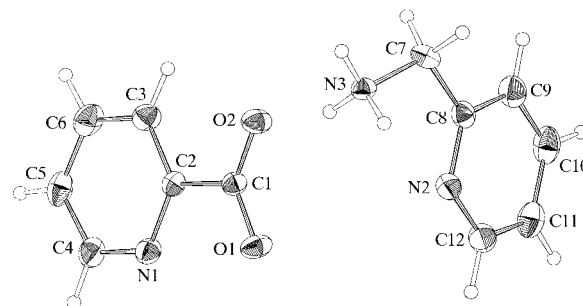


Figure 1

A view of the molecule of (I), with displacement ellipsoids drawn at the 50% probability level and H atoms shown as spheres of arbitrary radii.

The Cambridge Structural Database (Allen & Kennard, 1993) contains numerous structural reports of the pyridine-2-carboxylate anion, whereas the structure of the (2-pyridylmethyl)ammonium cation has no precedent. The bond lengths and angles in the cation and anion are normal. The pyridyl rings of the two ions are almost orthogonal [87.4 (5)°].

The structure of (I) shows four hydrogen bonds (Table 1) linking the ions into infinite chains along the *a* axis. The carboxyl O atoms and the pyridyl N atom of the anion act as hydrogen-bond acceptors, with the donor being the aliphatic N atom of the cation.

Experimental

Freshly distilled bis(2-pyridylmethyl)amine (Larsen *et al.*, 1986) was left in a closed flask for about three months, during which time colourless needles of (I) formed. The mother liquor was decanted off, and the crystals were washed with diethyl ether and dried in air.

Crystal data

$C_6H_9N_2^+ \cdot C_6H_4NO_2^-$
 $M_r = 231.25$
Monoclinic, $P2_1/c$
 $a = 6.4233$ (9) Å
 $b = 9.0728$ (18) Å
 $c = 20.265$ (3) Å
 $\beta = 95.700$ (11)°
 $V = 1175.1$ (3) Å³
 $Z = 4$

$D_x = 1.307$ Mg m⁻³
Cu $K\alpha$ radiation
Cell parameters from 20 reflections
 $\theta = 39.3$ – 43.8°
 $\mu = 0.75$ mm⁻¹
 $T = 122$ K
Needle, colourless
0.19 × 0.06 × 0.02 mm

Data collection

Enraf-Nonius CAD-4
diffractometer
 $\omega/2\theta$ scans
4776 measured reflections
2412 independent reflections
2140 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.025$

$\theta_{max} = 75^\circ$
 $h = -8 \rightarrow 8$
 $k = 0 \rightarrow 11$
 $l = 0 \rightarrow 25$
5 standard reflections
frequency: 167 min
intensity decay: 4.5%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.119$
 $S = 1.00$
 2412 reflections
 207 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.18 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 (Sheldrick, 1997)
 Extinction coefficient: 0.0120 (14)

1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

We thank Mr Flemming Hansen for help with the crystallographic experiment.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1143). Services for accessing these data are described at the back of the journal.

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N3-H1N3\cdots O1^i$	0.946 (16)	1.913 (16)	2.7672 (13)	149.0 (13)
$N3-H2N3\cdots O2$	0.933 (16)	1.885 (17)	2.7722 (13)	157.9 (14)
$N3-H3N3\cdots N1^{ii}$	0.927 (17)	2.396 (16)	3.0694 (13)	129.4 (13)
$N3-H3N3\cdots O1^{ii}$	0.927 (17)	1.956 (17)	2.8117 (12)	152.5 (14)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1+x, y, z$.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *DREADD* (Blessing, 1987); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick,

References

- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
 Blessing, R. H. (1987). *Crystallogr. Rev.* **1**, 3–58.
 Døssing, A., Hazell, A. & Toftlund, H. (1996). *Acta Chem. Scand.* **50**, 95–101.
 Døssing, A., Toftlund, H., Hazell, A., Bourassa, J. & Ford, P. C. (1997). *J. Chem. Soc. Dalton Trans.* pp. 335–339.
 Enraf-Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf-Nonius, Delft, The Netherlands.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Larsen, S., Michelsen, K. & Pedersen, E. (1986). *Acta Chem. Scand. Ser. A*, **40**, 63–76.
 Renz, M., Hemmert, C., Gornitzka, H. & Meunier, B. (1999). *New J. Chem.* **23**, 773–776.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.