Table 3. *Intermolecular distances (Å) and angles (°) about the methyl groups* C(17)H$_3$ *and* C(18)H$_3$

	x	y	z				
C(18)	0·6623 (5)	−0·1119 (4)	1·2215 (1)	C(18)—O(4)	3·158 (4)	C(18)—H(181)—O(4)	121 (3)
H(181)	0·7374 (46)	−0·1874 (41)	1·2339 (13)	C(18)—H(181)	0·918 (35)	C(18)—H(182)—O(4)	92 (2)
H(182)	0·5264 (48)	−0·1213 (37)	1·2352 (12)	C(18)—H(182)	1·090 (36)	C(18)—H(183)—O(4)	83 (2)
H(183)	0·7350 (45)	−0·0145 (41)	1·2351 (12)	C(18)—H(183)	1·072 (35)		
O(4)	0·6593 (5)	−0·3370 (3)	1·3098 (1)	H(181)—O(4)	2·583 (36)		
				H(182)—O(4)	2·929 (33)		
				H(183)—O(4)	3·433 (33)		
C(17)	0·8841 (6)	0·2413 (5)	0·7174 (1)	C(17)—O(1)	3·217 (4)	C(17)—H(171)—O(1)	72 (2)
H(171)	0·7628 (57)	0·2060 (45)	0·7134 (13)	C(17)—H(171)	0·938 (41)	C(17)—H(172)—O(1)	130 (2)
H(172)	0·9174 (51)	0·3191 (43)	0·6950 (14)	C(17)—H(172)	0·971 (39)	C(17)—H(173)—O(1)	not calc.
H(173)	0·9671 (51)	0·1380 (44)	0·7131 (13)	C(17)—H(173)	1·115 (39)		
O(1)	0·8521 (4)	0·3373 (3)	0·6045 (1)	H(171)—O(1)	3·330 (38)		
				H(172)—O(1)	2·510 (39)		
				H(173)—O(1)	>3·5		

2·70 Å], but for methylene (CH$_2$) and methyl (CH$_3$) groups this was not necessary, and in the cases considered the angle C—H⋯O varied from 102 to 147° and the distance H⋯C could be larger than 2·6 Å. It was suggested that this could be due to steric hindrance from other atoms of the methylene or methyl groups.

Examination of the distances about the methyl groups (Table 3) suggests that there is a hydrogen bond C(18)—H(181)⋯O(4), and there also appears to be a weak hydrogen bond, C(17)—H(172)⋯O(1). However, the latter bond is only slightly shorter than the van der Waals distance given by Bondi (1964) (3·28 Å) and so must be very weak indeed. The first of these tends to cause the molecules to lie in puckered chains parallel to **c**.

References

Bondi, A. (1964). *J. Phys. Chem.* 68, 441–451.
Brown, C. J. & Yadav, H. R. (1984). *Acta Cryst.* C40, 564–566.
Cruickshank, D. W. J. (1956). *Acta Cryst.* 9, 747–753.
Germain, G., Main, P. & Woolfson, M. M. (1970). *Acta Cryst.* B26, 274–285.

Hirshfeld, F. L. & Rabinovich, D. (1973). *Acta Cryst.* A29, 510–513.
International Tables for X-ray Crystallography (1968). Vol. III, pp. 270–276. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
Mason, R. (1964). *Acta Cryst.* 17, 547–555.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
Nardelli, M. (1982). *PARST. A System of Computer Routines for Calculating Molecular Parameters from the Results of Crystal Structure Analysis.* Univ. of Parma, Italy.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.
Pauling, L. (1960). *The Nature of the Chemical Bond*, p. 260. Ithaca: Cornell Univ. Press.
Paulus, E. F. (1984). *Z. Kristallogr.* 167, 65–72.
Paulus, E. F., Rieper, W. & Wagner, D. (1983). *Z. Kristallogr.* 165, 137–149.
Sheldrick, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.
Sutor, D. J. (1963). *J. Chem. Soc.* pp. 1105–1110.
Whitaker, A. (1983a). *Z. Kristallogr.* 163, 19–30.
Whitaker, A. (1983b). *Z. Kristallogr.* 163, 139–149.
Whitaker, A. (1984a). *Z. Kristallogr.* 166, 177–188.
Whitaker, A. (1984b). *Z. Kristallogr.* 167, 225–233.
Whitaker, A. (1985a). *Z. Kristallogr.* 170, 213–223.
Whitaker, A. (1985b). *Z. Kristallogr.* 171, 17–22.
Whitaker, A. (1986). *Acta Cryst.* C42, 1566–1569.
Whitaker, A. & Walker, N. (1985). *Z. Kristallogr.* 171, 7–15.
Whitaker, A. & Walker, N. (1987). *Acta Cryst.* C43, 2137–2141.
Wilson, A. J. C. (1976). *Acta Cryst.* A32, 994–996.
Wilson, A. J. C. (1978). *Acta Cryst.* A34, 474–475.

4,4'-Bipyridinium(2+) Dinitrate

By Timothy J. R. Weakley

Chemistry Department, Dundee University, Dundee DD1 4HN, Scotland

Abstract. C$_{10}$H$_{10}$N$_4$O$_6$, $M_r = 282·2$, monoclinic, $C2/c$, $a = 16·08$ (3), $b = 3·785$ (6), $c = 18·85$ (3) Å, $\beta = 98·16$ (2)°, $U = 1135·6$ Å^3, $Z = 4$, $D_x = 1·65$, $D_m = 1·64$ (1) Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1·5418$ Å, $\mu = 0·76$ mm^{-1}, $F(000) = 584$, $T = 291$ (1) K, $R = 0·048$ for 610 unique reflections. The planar centrosymmetric

$(4,4'\text{-bipyH}_2)^{2+}$ cations form stacks parallel to **b**. There are $N-H\cdots O$ hydrogen bonds $[N\cdots O\ 2\cdot770\ (5)\ \text{Å}]$.

Table 1. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic temperature factors* $(\text{Å}^2 \times 10^3)$

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
N(1)	3617 (2)	1635 (10)	3445 (2)	31 (1)
C(1)	4338 (3)	−3 (12)	3400 (2)	33 (1)
C(2)	4894 (2)	−693 (11)	4003 (2)	27 (1)
C(3)	4701 (2)	337 (10)	4668 (2)	21 (1)
C(4)	3936 (2)	2005 (11)	4691 (2)	27 (1)
C(5)	3404 (2)	2637 (11)	4070 (2)	31 (1)
N(2)	3426 (2)	3288 (9)	1668 (2)	28 (1)
O(1)	2905 (2)	1884 (9)	2019 (1)	37 (1)
O(2)	4075 (2)	4627 (9)	1989 (1)	45 (1)
O(3)	3286 (2)	3259 (9)	1006 (1)	45 (1)
H(N1)	3257 (29)	2120 (124)	3049 (25)	46 (12)
H(C1)	4476 (24)	−704 (114)	2959 (22)	33 (10)
H(C2)	5395 (23)	−1947 (103)	3942 (18)	23 (9)
H(C4)	3748 (23)	2540 (112)	5121 (21)	32 (10)
H(C5)	2915 (27)	3614 (116)	4057 (21)	36 (11)

Table 2. *Bond lengths* (Å) *and interbond angles* (°)

N(1)–C(1)	1·328 (5)	N(2)–O(2)	1·238 (4)
N(1)–C(5)	1·328 (5)	N(2)–O(3)	1·235 (4)
C(1)–C(2)	1·367 (5)	N(1)–H(N1)	0·90 (5)
C(2)–C(3)	1·389 (5)	C(1)–H(C1)	0·93 (4)
C(3)–C(3^i)	1·488 (6)	C(2)–H(C2)	0·96 (4)
C(3)–C(4)	1·389 (5)	C(4)–H(C4)	0·93 (4)
C(4)–C(5)	1·369 (5)	C(5)--H(C5)	0·87 (5)
N(2)–O(1)	1·257 (4)		

C(1)–N(1)–C(5)	121·8 (3)	N(1)–C(5)–C(4)	120·0 (4)
N(1)–C(1)–C(2)	120·7 (4)	O(1)–N(2)–O(2)	119·7 (3)
C(1)–C(2)–C(3)	119·5 (4)	O(1)–N(2)–O(3)	119·2 (3)
C(2)–C(3)–C(4)	117·9 (3)	O(2)–N(2)–O(3)	121·2 (3)
C(3)–C(4)–C(5)	120·1 (3)		

Hydrogen bond

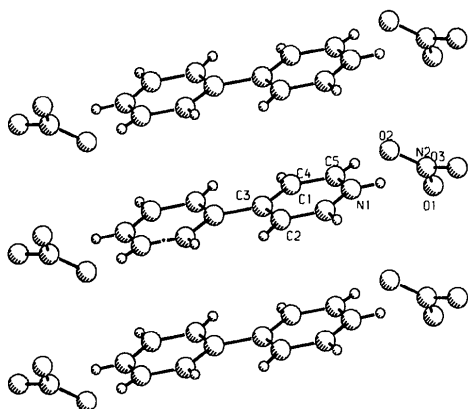|			
N(1)···O(1)	2·770 (10)	H(N1)···O(1)	1·95 (5)
		N(1)–H(N1)···O(1)	152 (4)

Symmetry code: (i) $1-x, -y, 1-z$.

Fig. 1. Cation and anion stacks extending in the direction of **b**.

Introduction. The structures of several series of adducts of 4,4'-bipyridine (4,4'-bipy), H_2O and lanthanide nitrates have been determined (Bukowska-Strzyzewska & Tosik, 1978; Al-Rasoul & Weakley, 1982; Weakley, 1982, 1984). The title compound was obtained by accident during an attempt to prepare an adduct containing $Lu(NO_3)_3$. Its structure was determined because no structures of salts of the doubly-protonated cation $(4,4'\text{-bipyH}_2)^{2+}$ are known, with the exception of $(4,4'\text{-bipyH}_2)$ (Cu_2Cl_6) (Bukowska-Stryzewska & Tosik, 1979), from a low-resolution analysis $(R = 0\cdot15)$, and two forms of $(4,4'\text{-bipyH}_2)_2(Sb_2Cl_{10})$ (Lipka, 1980, 1983).

Experimental. Colourless prisms elongated on **b** from EtOH vapour diffusion into aqueous solution. Density by flotation in $CHBr_3$/EtOH. Data recorded photographically from two fragments of dimensions ca $0\cdot2 \times 0\cdot3 \times 0\cdot2$ mm for r.l. layers $h0-3l$ and $hk0-6$; equi-inclination Weissenberg films scanned by use of a microdensitometer (SERC service, Daresbury Laboratory); few reflexions beyond $\theta = 40°$ are above background; $R_{int} = 0\cdot040$ for 610 unique data. Structure solved and refined (on F) by use of *SHELX*76 (Sheldrick, 1976), with scattering factors from *International Tables for X-ray Crystallography* (1974). For direct-methods calculations ca 850 'unobserveds' were added to the data set with $|F|$ set at $0\cdot2|F_o|_{min}$. The ten non-hydrogen atoms were located in an E map in $C2/c$; a second E map calculated on the assumption of space group Cc confirmed the centre of symmetry. Five unique H atoms subsequently located in a difference map and refined. Full-matrix least squares, minimizing $\sum w(|F_o| - |F_c|)^2$, convergence at $R = 0\cdot048$, $wR = 0\cdot054$, anisotropic thermal parameters for C, N and O, 111 parameters, unit weights, $(\Delta/\sigma)_{max}$ $0\cdot033$, final difference map flat within limits $+0\cdot21$, $-0\cdot25$ e Å^{-3}; attempts to refine g in weighting scheme $w = k[1 + gF^2]^{-1}$ resulted in oscillating R with several large Δ/σ in all cycles. Final positional parameters are given in Table 1, and bond lengths and interbond angles in Table 2.*

Discussion. The $(4,4'\text{-bipyH}_2)^{2+}$ cations lie on crystal inversion centres and form stacks parallel to **b** (Fig. 1). The anions, which lack imposed symmetry, form intervening stacks. The mean planes of the cations are separated by $3\cdot35$ (1) Å and the normals to the planes are inclined at $27\cdot7$ (1)° to the stack axis; the corresponding values for the anions are $3\cdot32$ (1) Å, $27\cdot8°$. The C_5N rings are planar [max. deviation C(3),

0·006 (4) Å] but the two ring mean planes of each cation are separated by 0·030 Å. The bond lengths and angles in the cation agree well with the values for (4,4'-bipyH$_2$)$_2$(Sb$_2$Cl$_{10}$) (Lipka, 1980) and for the protonated ring in (4,4'-bipyH)[Ce(4,4'-bipy)-(NO$_3$)$_4$(H$_2$O)$_2$] (Bukowska-Strzyzewska & Tosik, 1978), in particular as regards the increase in the ring angle at N compared with that in unprotonated 4,4'-bipy. The dihedral angle of zero between the C$_5$N ring planes contrasts with the angles of 3·1° in (4,4'-bipyH$_2$)$_2$(Sb$_2$Cl$_{10}$) and ca 22° in the unstable form of the latter compound (Lipka, 1983). The dihedral angles for the neutral and monoprotonated molecules in (4,4'-bipyH)$_2$[μ-(4,4'-bipy)Nd$_2$(NO$_3$)$_8$(H$_2$O)$_2$].2(4,4'-bipy) and [Ho(NO$_3$)$_3$(H$_2$O)$_3$].2(4,4'-bipy) range from zero to 36° (Weakley, 1984) and the dication can clearly adapt in the same way to the local requirements of crystal packing because of negligible resistance to

torsion about the central C—C bond. The title compound, unlike the (Sb$_2$Cl$_{10}$)$^{4-}$ and (Cu$_2$Cl$_6$)$^{2-}$ salts, contains hydrogen bonds [N(1)···O(1) 2·77 Å].

References

AL-RASOUL, K. & WEAKLEY, T. J. R. (1982). *Inorg. Chim. Acta*, **60**, 191–196.

BUKOWSKA-STRZYZEWSKA, M. & TOSIK, A. (1978). *Inorg. Chim. Acta*, **30**, 189–196.

BUKOWSKA-STRZEZEWSKA, M. & TOSIK, A. (1979). *Polish J. Chem.* **53**, 2423–2428.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 148. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

LIPKA, A. (1980). *Z. Anorg. Allg. Chem.* **469**, 229–233.

LIPKA, A. (1983). *Z. Naturforsch. Teil. B*, **38**, 1615–1621.

SHELDRICK, G. M. (1976). *SHELX76. Program for crystal structure determination*. Univ. of Cambridge, England.

WEAKLEY, T. J. R. (1982). *Inorg. Chim. Acta*, **63**, 161–168.

WEAKLEY, T. J. R. (1984). *Inorg. Chim. Acta*, **95**, 317–322.

Structures of 9,9-Dimethoxy-1-methyl-7-phenylsulfonylbicyclo[4.3.0]nonan-2-one (I) and 10,10-Dimethoxy-8-phenylsulfonylbicyclo[5.3.0]decan-2-one (II)

BY J.-P. DECLERCQ

Laboratoire de Chimie physique et de Cristallographie, Université de Louvain, Bâtiment Lavoisier, place Louis Pasteur 1, B-1348 Louvain-la-Neuve, Belgium
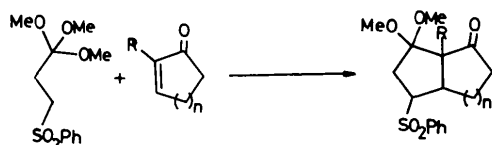
AND J. C. CARRETERO AND I. NEMERY

Laboratoire de Chimie Organique de Synthèse, Université de Louvain, Bâtiment Lavoisier, place Louis Pasteur 1, B-1348 Louvain-la-Neuve, Belgium

Abstract. (I): C$_{18}$H$_{24}$O$_5$S, M_r = 352·45, monoclinic, P2$_1$/a, a = 12·861 (2), b = 14·554 (3), c = 9·412 (1) Å, β = 97·08 (1)°, V = 1748·3 (5) Å^3, Z = 4, D_x = 1·34 g cm^{-3}, Cu Kα, λ = 1·54178 Å, μ = 18·3 cm^{-1}, $F(000)$ = 752, T = 291 K, R = 0·041 for 2801 observed reflections. (II): C$_{18}$H$_{24}$O$_5$S, M_r = 352·45, orthorhombic, P2$_1$2$_1$2$_1$, a = 12·326 (2), b = 19·182 (3), c = 7·227 (2) Å, V = 1708·7 (6) Å^3, Z = 4, D_x = 1·37 g cm^{-3}, Cu Kα, λ = 1·54178 Å, μ = 18·7 cm^{-1}, $F(000)$ = 752, T = 291 K, R = 0·045 for 1537 observed reflections. The ring fusions are *cis* and the phenylsulfonyl substituents are orientated in the *exo* position. The five-membered rings in both compounds exhibit envelope conformations, the six-membered ring in (I) has a chair conformation, and the seven-membered ring in (II) exhibits a twist-chair conformation.

Introduction. Natural and non-natural cyclopentanoids constitute an area of growing interest. In a previous communication (De Lombaert, Nemery, Roekens, Carretero, Kimmel & Ghosez, 1986) we reported a new two-step sequence that provides highly functionalized fused cyclopentanone derivatives from trimethyl 3-phenylsulfonylorthopropionate and the corresponding enone.

(I) R = Me, n = 2

(II) R = H, n = 3