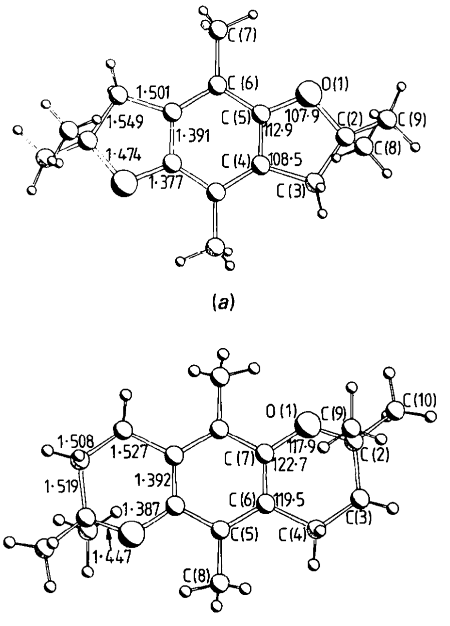

(a)

(b)

Fig. 1. (*a*) One molecule of (I) with selected bond lengths (Å, $\sigma = 0{\cdot}002$ Å) and angles (°, $\sigma = 0{\cdot}1°$). (*b*) One molecule of (II) with selected bond lengths (Å, $\sigma = 0{\cdot}004$ Å) and angles (°, $\sigma = 0{\cdot}2°$).

molecules must depend on the angle between the O p_z orbital and the normal to the benzene-ring plane, 8° in (I) and 18° in (II) (e.s.d.'s 0·1 and 0·3°); these angles are equivalent to the torsion angles C(4)—C(5)—O(1)—C(2) and C(6)—C(7)—O(1)—C(2) (0° would allow maximum overlap). It is entirely consistent, then, that (I) should form a radical more readily than (II).

ESR spectroscopy (Smith *et al.*, 1984) allows the cation radicals to be compared; the benzylic proton hyperfine coupling constants give average values of 0·618 and 0·136 mT for the radicals (I*R*) and (II*R*) respectively. These values show that much more spin density is present in the heterocyclic ring of the difuran cation radical (I*R*) due to the tendency towards maximum overlap. It has been shown (MacLean *et al.*, 1985) that for some heterocyclic cations most bond lengths and angles are not greatly affected by the addition of a delocalized electron to give the (neutral) radical. ESR data for the cation radical (II*R*) yielded separate values for the axial and equatorial proton coupling constants of 0·237 and 0·035 mT, respectively, and from these the angle between the axial C—H bond, C(3)—H(31), and the normal to the benzene-ring plane is calculated to be 6° (Morton, 1964). The crystallographic results give an angle of 25 (3)° for the parent compound (II), showing that there *is* a significant change in conformation on addition of a delocalized electron.

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References

Burton, G. W., Le Page, Y., Gabe, E. J. & Ingold, K. U. (1980). *J. Am. Chem. Soc.* **102**, 7791–7792.
Frampton, V. L., Skinner, W. A., Cambour, P. & Bailey, P. S. (1960). *J. Am. Chem. Soc.* **82**, 4632–4634.
Gould, R. O. (1984). Personal communication.
MacLean, G. K., Passmore, J., Sudheedra Rao, M. N., Schriver, M. J., White, P. S., Bethell, D., Pilkington, R. S. & Sutcliffe, L. H. (1985). *J. Chem. Soc. Dalton Trans.* pp. 1405–1416.
Morton, J. R. (1964). *J. Chem. Phys.* **41**, 2956–2957.
Motherwell, W. D. S. (1976). *PLUTO*. A program for plotting molecular and crytal structures. Univ. of Cambridge, England.
Sheldrick, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
Smith, I. M., Sutcliffe, L. H., Wiesner, S., Lubitz, W. & Kurreck, K. (1984). *J. Chem. Soc. Faraday Trans.* 1, **80**, 3021–3036.

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Dipyridinium Bis(hydrogen oxalate)–Oxalic Acid

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Abstract. $2C_5H_6N^+.2C_2HO_4^-.C_2H_2O_4$, $M_r = 428{\cdot}4$, monoclinic, $P2_1/n$, $a = 3{\cdot}725\,(1)$, $b = 8{\cdot}908\,(2)$, $c = 26{\cdot}842\,(4)$ Å, $\beta = 92{\cdot}94\,(2)°$, $V = 889{\cdot}5\,(6)$ Å^3, $Z = 2$, $D_x = 1{\cdot}599$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 1{\cdot}31$ cm^{-1}, $F(000) = 444$, $T = 296$ K, $R = 0{\cdot}049$ for 1179 observations (of 1838 unique data). The structure

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consists of pyridinium and hydrogen oxalate ions in general positions, and a centrosymmetric oxalic acid molecule. These three moieties are involved in hydrogen bonding in nonplanar sheets, stacked along the [10$\bar{1}$] direction. The hydrogen oxalate anion is nonplanar, exhibiting a torsion angle about its central C—C bond of 14·9 (4)°.

Introduction. The crystal-structure determination of the 1:1 adduct between pyridine and oxalic acid surprisingly showed that two pyridinium cations exist with one oxalic acid molecule and one oxalate anion in this species rather than with two hydrogen oxalates (Newkome, Theriot & Fronczek, 1985). In a study on the effect of solvent in the preparation of the 1:1 adduct, the title compound was crystallized from MeOH/$CHCl_3$, and the structure determination was undertaken to compare the hydrogen bonding in the two species.

Experimental. To 1·0 g (8·0 mmol) of oxalic acid dihydrate in 10% MeOH/$CHCl_3$ (40 ml) was added 0·63 g (8·0 mmol) of pyridine in $CHCl_3$ (10 ml). Slow evaporation yielded colorless prisms. Crystal size 0·10 × 0·26 × 0·56 mm, sealed in capillary. Space group from systematic absences $h0l$ with $h+l$ odd, $0k0$ with k odd; cell dimensions from setting angles of 25 reflections having $15 > \theta > 13°$. Data collection on Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, ω–2θ scans designed for $I \simeq 50\sigma(I)$, max. scan time 120 s, scan rates varied 0·39–4·0° min^{-1}. Reflections having $2 < 2\theta < 53°$, $0 \leq h \leq 4$, $0 \leq k \leq 11$, $-34 \leq l \leq 34$ measured, corrected for background, Lorentz, polarization effects. No absorption correction. Redundant $0kl$ and $0k\bar{l}$ averaged, $R_{\rm int} = 0·025$. Standard reflections 200, 020, 0,0,10, ±2·3% maximum random variation. Structure solved by direct methods, *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares based on F, using 1179 data with $I > \sigma(I)$, weights $w = \sigma^{-2}(F_o)$, with Enraf–Nonius *SDP* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974). Non-H atoms anisotropic; H atoms located by ΔF, refined isotropically. Secondary-extinction coefficient 9·6 (10) × 10^{-7}. Final $R = 0·049$ (0·12 for all data), $wR = 0·041$, $S = 1·744$ for 169 variables. Max. shift 0·09σ in final cycle, largest residual density 0·20, min. −0·24 e Å^{-3}. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.*

Table 1. *Coordinates and equivalent isotropic thermal parameters*

$$B_{\rm eq} = \tfrac{4}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac\beta_{13}\cos\beta).$$

	x	y	z	$B_{\rm eq}$ or B(Å^2)
O(1)	0·6150 (5)	0·1392 (2)	0·19055 (5)	3·44 (4)
O(2)	0·4370 (5)	−0·0654 (2)	0·14809 (5)	3·65 (4)
O(3)	0·9168 (5)	−0·0454 (2)	0·26168 (6)	4·04 (4)
O(4)	0·6078 (5)	−0·2350 (4)	0·22792 (6)	3·91 (4)
O(5)	0·3096 (6)	−0·1576 (2)	0·02607 (6)	4·96 (5)
O(6)	0·5419 (5)	0·0463 (2)	0·06306 (6)	3·73 (4)
N	−0·1833 (5)	0·5875 (2)	0·85141 (7)	3·44 (5)
C(1)	−0·0671 (7)	0·6754 (3)	0·88878 (10)	3·44 (6)
C(2)	0·1011 (7)	0·6140 (3)	0·93006 (9)	3·64 (6)
C(3)	0·1476 (7)	0·4606 (3)	0·93219 (9)	3·51 (6)
C(4)	0·0254 (7)	0·3728 (3)	0·89271 (10)	3·59 (6)
C(5)	−0·1420 (7)	0·4393 (3)	0·85271 (9)	3·59 (6)
C(6)	0·5752 (7)	0·0008 (3)	0·18514 (8)	2·59 (5)
C(7)	0·7161 (6)	−0·0965 (2)	0·22911 (8)	2·47 (5)
C(8)	0·4519 (7)	−0·0371 (3)	0·02460 (8)	2·82 (5)
H(40)	0·718 (8)	−0·295 (3)	0·2604 (10)	8·2 (8)
H(60)	0·505 (7)	−0·008 (3)	0·0962 (9)	6·4 (7)
H(1N)	−0·311 (9)	0·627 (3)	0·8205 (11)	9·5 (9)
H(1)	−0·093 (7)	0·782 (3)	0·8829 (9)	6·4 (7)
H(2)	0·172 (6)	0·679 (3)	0·9559 (9)	5·3 (7)
H(3)	0·273 (7)	0·412 (3)	0·9594 (9)	5·6 (7)
H(4)	0·059 (7)	0·269 (3)	0·8924 (9)	5·7 (7)
H(5)	−0·232 (6)	0·387 (2)	0·8228 (8)	4·2 (6)

Discussion. The structure contains hydrogen oxalate ions hydrogen bonded in chains along the b axis. These chains are linked by oxalic acid molecules donating hydrogen bonds to O(2) of hydrogen oxalate ions in neighboring parallel chains. The resulting nonplanar, hydrogen-bonded sheets are stacked along the [10$\bar{1}$] direction, as illustrated in Fig. 1. Pyridinium ions are hydrogen bonded to the carbonyl O atom of each hydrogen oxalate in this array. Fig. 2 portrays the thermal ellipsoids and numbering scheme, and bond lengths and angles are given in Table 2. The oxalic acid lies on a center of symmetry and is thus planar; the C(8)—O(5) distance of 1·199 (2) Å, as in the 1:1 adduct (Newkome, Theriot & Fronczek, 1985), is short compared to other oxalic acid species [1·204 (2)–1·223 (1) Å] (Sabine, Cox & Craven, 1969; Stevens & Coppens, 1980; Currie, Speakman & Curry, 1967).

Although most hydrogen oxalates are nearly planar this one is *not*, with a relatively large O(3)—C(6)—C(7)—O(1) torsion angle of 14·9 (4)° [Tellgren & Olovsson (1971); see Haas (1964) and Pedersen (1968) for other examples]. As in this case, most hydrogen oxalate species form linear chains with hydrogen bonding occurring from —COH of one molecule to carboxylate —CO of another molecule. This hydrogen bond, O(4)—H(40)—O(1′), has O···O distance 2·623 (2), H···O distance 1·55 (3) Å, and angle 173 (2)°. The carboxylate O atom which hydrogen bonds is usually *cis* to the carbonyl and has a substantially longer bond to C than the non-hydrogen-bonded carboxylate O (Adams, 1978; Thomas, 1975; Thomas & Liminga, 1978; Thomas & Pramatus, 1975; Thomas & Renne, 1975; Vijayalakshmi & Srinivasan,

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* Lists of anisotropic thermal parameters and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43133 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1983). In this case, however, the C(6)—O(1) and C(6)—O(2) bonds are nearly identical due to the additional hydrogen bonding occurring between O(2)—H(60)—O(6′), O···O 2·538 (2), H···O 1·52 (3) Å, angle 171 (2)°.

The pyridinium moiety is planar [maximum deviation 0·004 (3) Å] and forms a hydrogen bond to the carbonyl of the hydrogen oxalate [N—O(3) 2·792 (2) Å, N—H—O 138 (2)°]. The pyridinium ion also forms a longer interaction with O(1) of the next hydrogen oxalate ion along the *b*-axis chain. This interaction has N···O(1) distance 3·098 (2), H(1N)···O(1) distance 2·38 (3) Å, and N—H···O angle 129 (2)°. This interaction is similar to that found between pyridinium and oxalate species in dipyridinium oxalate–oxalic acid (Newkome, Theriot & Fronczek, 1985) and may best be thought of as an asymmetric bifurcated hydrogen bond. Pyridinium C—N distances average 1·329 (2) Å; C—C distances range 1·350 (3)–1·378 (3) Å, both short with respect to expected aromatic bond lengths, but similar to those found in dipyridinium oxalate–oxalic acid and other pyridinium salts (Newkome, Theriot & Fronczek, 1985, and references cited therein).

Table 2. *Bond distances* (Å) *and angles* (°)

N—C(1)	1·327 (3)	N—C(1)—C(2)	119·8 (2)
N—C(5)	1·330 (3)	C(1)—C(2)—C(3)	119·0 (2)
C(1)—C(2)	1·360 (3)	C(2)—C(3)—C(4)	119·7 (2)
C(2)—C(3)	1·378 (3)	C(3)—C(4)—C(5)	119·0 (2)
C(3)—C(4)	1·375 (3)	C(4)—C(5)—N	120·3 (2)
C(4)—C(5)	1·350 (3)	C(5)—N—C(1)	122·2 (2)
C(6)—C(7)	1·535 (2)	O(3)—C(7)—O(4)	123·7 (2)
C(6)—O(1)	1·249 (2)	O(3)—C(7)—C(6)	121·2 (2)
C(6)—O(2)	1·245 (2)	O(4)—C(7)—C(6)	115·1 (2)
C(7)—O(3)	1·210 (2)	O(1)—C(6)—O(2)	127·1 (2)
C(7)—O(4)	1·298 (2)	O(1)—C(6)—C(7)	115·7 (2)
C(8)—C(8)	1·536 (4)	O(2)—C(6)—C(7)	117·2 (2)
C(8)—O(5)	1·199 (2)	O(6)—C(8)—O(5)	125·5 (2)
C(8)—O(6)	1·302 (2)	O(6)—C(8)—C(8)	112·0 (2)
N—H(1N)	1·000 (28)	O(5)—C(8)—C(8)	122·5 (2)
O(3)—H(1N)	1·970 (28)	O(3)—H(1N)—N	138 (2)
O(1)—H(40)	1·545 (26)	O(2)—H(60)—O(6)	171 (2)
O(4)—H(40)	1·083 (26)	O(1)—H(40)—O(4)	173 (2)
O(2)—H(60)	1·517 (25)		
O(6)—H(60)	1·028 (24)		
N—O(3)	2·792 (2)		
O(1)—O(4)	2·623 (2)		
O(2)—O(6)	2·538 (2)		

C—H range: 0·93(2)–0·97 (3)

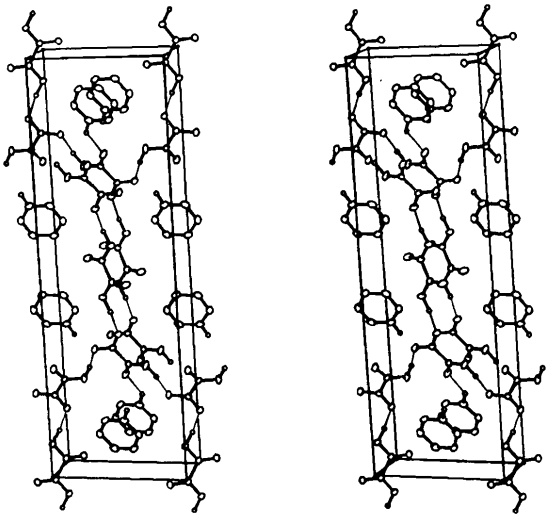

Fig. 1. Stereoscopic representation of the unit cell, illustrating hydrogen bonding. View is slightly oblique to the *a* axis, with *b* horizontal.

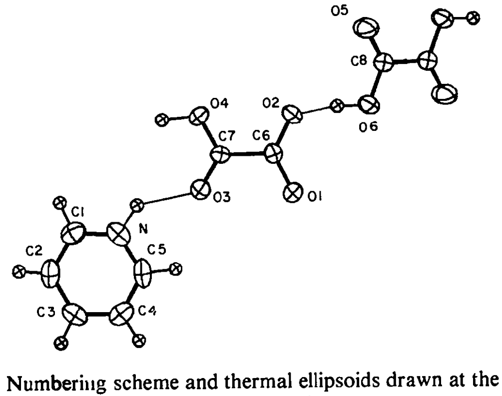

Fig. 2. Numbering scheme and thermal ellipsoids drawn at the 50% probability level.

References

ADAMS, J. M. (1978). *Acta Cryst.* B**34**, 1218–1220.

CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

CURRIE, M., SPEAKMAN, J. C. & CURRY, N. A. (1967). *J. Chem. Soc. A*, pp. 1862–1869.

FRENZ, B. & OKAYA, Y. (1980). *Enraf–Nonius Structure Determination Package*. Enraf–Nonius, Delft.

HAAS, D. J. (1964). *Acta Cryst.* **17**, 1511–1516.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

NEWKOME, G. R., THERIOT, K. J. & FRONCZEK, F. R. (1985). *Acta Cryst.* C**41**, 1642–1644.

PEDERSEN, B. F. (1968). *Acta Chem. Scand.* **22**, 2953–2964.

SABINE, T. M., COX, G. W. & CRAVEN, B. M. (1969). *Acta Cryst.* B**25**, 2437–2441.

STEVENS, E. D. & COPPENS, P. (1980). *Acta Cryst.* B**36**, 1864–1876.

TELLGREN, R. & OLOVSSON, I. (1971). *J. Chem. Phys.* **54**(1), 127–134.

THOMAS, J. O. (1975). *Acta Cryst.* B**31**, 2156–2158.

THOMAS, J. O. & LIMINGA, R. (1978). *Acta Cryst.* B**34**, 3686–3690.

THOMAS, J. O. & PRAMATUS, S. (1975). *Acta Cryst.* B**31**, 2159–2161.

THOMAS, J. O. & RENNE, N. (1975). *Acta Cryst.* B**31**, 2161–2163.

VIJAYALAKSHMI, J. & SRINIVASAN, R. (1983). *Acta Cryst.* C**39**, 908–909.