Acta Cryst. (1984). C**40**, 1474–1475

Structure of 1,1'-Di(4-pyridyl)-2,2',6,6'-bi(4-piperidone)* Dihydrochloride Dihydrate, $C_{20}H_{22}N_4O_2^{2+}.2Cl^-.2H_2O$

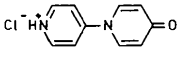
By C. J. Cheer, J. P. Cosgrove and B. M. Vittimberga

Department of Chemistry, University of Rhode Island, Kingston, RI 02881, *USA*

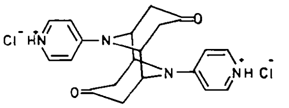
(*Received* 21 *November* 1983; *accepted* 10 *May* 1984)

Abstract. $M_r = 457{\cdot}35$, monoclinic, $P2_1/c$, $a = 10{\cdot}3282\,(19)$, $b = 12{\cdot}1735\,(19)$, $c = 8{\cdot}2311\,(13)$ Å, $\beta = 92{\cdot}456\,(14)^\circ$, $V = 1033{\cdot}9\,(3)$ Å^3, $Z = 2$, $D_m = 1{\cdot}437$, $D_x = 1{\cdot}469$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}473$ cm^{-1}, $F(000) = 480$, $T = 295\,(2)$ K, $R(R_w) = 0{\cdot}0434\,(0{\cdot}0408)$ for 1513 observed independent reflections $[I > 2{\cdot}5\sigma(I)]$. The dimer lies on a center of symmetry and contains a molecule of water hydrogen-bonded to both the carbonyl oxygen and the chloride ion. The piperidone rings have a distorted chair conformation, flattened at the carbonyl group. The pyridine rings are planar with the nitrogens of the piperidone groups out of this plane.

Introduction. As part of a study of the photoelectron-abstraction reactions of six-membered heteroaromatic nitrogen compounds with alcohols (Vittimberga & Morrocchi, 1981), we recently examined the photoreduction of *N*-(4-pyridyl)-4-pyridone hydrochloride (1). Irradiation of an aqueous 2-propanol solution of (1) results in the formation of a number of different compounds, among which was the highly crystalline dimer (2), the crystal structure of which is the subject of this communication.



(1)



(2)

Experimental. Well formed crystals deposited on addition of ethanol to aqueous solution of (2). Crystal, air-stable, approximately 0·2 × 0·2 × 0·25 mm chosen for data collection. Density by flotation in carbon tetrachloride–hexane. Lattice parameters determined by least-squares fit of positions of 12 automatically centered reflections, between 2θ 5·99 and 29·60°. Nicolet *R*3*m*/*E* auto-diffractometer; 2032 reflections collected in the range $3{\cdot}5 < 2\theta < 45^\circ$ and index range h 0–12, k 0–14, l −9–+9 by variable speed (6·00–29·30° min^{-1}) Wyckoff (ω) scans, 3 check reflections ($\bar{5}00$, $\bar{3}00$, $0\bar{1}1$) measured after each 48 reflections; data corrected for slight (0·9896–1·0029) variation in check reflections; Lp but no absorption corrections; 1513 reflections with $I > 2{\cdot}5\sigma(I)$ considered observed and used in refinement. Structure solved using the Nicolet *SHELXTL* (Nicolet XRD Corp., Fremont, CA) version of *MULTAN* (Germain, Main & Woolfson, 1971). Positional and thermal parameters for non-hydrogen atoms refined, based on F, by blocked-cascade least squares, all hydrogen-atom positions located from a difference Fourier map. Hydrogen-atom thermal parameters set at 1·2 × that of their bonded atoms, not refined. Final discrepancy indices, $R = 0{\cdot}0434$, $R_w = 0{\cdot}0408$ and $R_G = 0{\cdot}0451$ for 1513 reflections. $w = 1/\sigma^2(|F_o|) + 0{\cdot}0002(F_o)^2$, $R_w = \sum(||F_o| - |F_c||w^{1/2})/\sum(|F_o|w^{1/2})$ and $R_G = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$. $(\Delta/\sigma)_{\max} = 0{\cdot}082$: max., min. height in final difference Fourier synthesis $= 0{\cdot}31, -0{\cdot}24$ e Å^{-3}. All calculations performed using a Data General Eclipse computer with *SHELXTL* programs, which use scattering factors from *International Tables for X-ray Crystallography* (1974).†

Discussion. Atomic coordinates are listed in Table 1, bond lengths and angles in Table 2. Fig. 1 shows a perspective drawing of the structure of the dimer with the numbering scheme used. The structure is dimeric and centrosymmetric. From the list of bond lengths in Table 2, a significant shortening of the C(1)—C(2) and C(4)—C(5) bonds is evident. Since no such bond shortening in the comparable bonds is apparent in the structure of a 4-(*N*,*N*-dimethylamino)pyridinium ion solvate of a bis[μ-salicylato(2−)-*O*,*O*′,*O*″]-bis[nitrato-dioxouranate(IV)] complex (Nassimbeni, Rodgers & Haigh, 1976), its appearance here may be due to some systematic error, rather than a change in π-bond order for those bonds. The pyridinium ring is canted slightly

---

* 11,12-Di(4-pyridyl)-11,12-diazatricyclo[5.3.1.1^{2,6}]dodecane-4,9-dione.

† Lists of structure factors, anisotropic thermal parameters, hydrogen-atom coordinates and details of least-squares molecular planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39459 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/84/081474-02$01.50

Table 1. *Atom coordinates* (×10^4) *and temperature factors* (Å^2 × 10^3)

	x	y	z	U*
C(1)	584 (3)	4871 (2)	−2232 (4)	43 (1)
C(2)	1706 (3)	5274 (2)	−1542 (4)	37 (1)
C(3)	2451 (2)	4627 (2)	−435 (3)	24 (1)
C(4)	1912 (2)	3615 (2)	−12 (3)	38 (1)
C(5)	783 (3)	3269 (2)	−750 (4)	44 (1)
C(6)	4269 (2)	5988 (2)	−331 (3)	22 (1)
C(7)	4559 (2)	6701 (2)	1173 (3)	28 (1)
C(8)	5255 (2)	6101 (2)	2532 (3)	27 (1)
C(9)	4846 (2)	4941 (2)	2809 (3)	29 (1)
C(10)	4502 (2)	4301 (2)	1233 (3)	22 (1)
O(1)	6061 (2)	6559 (1)	3427 (2)	40 (1)
O(2)	8070 (2)	5852 (2)	5716 (3)	68 (1)
N(1)	142 (2)	3885 (2)	−1852 (3)	40 (1)
N(2)	3642 (2)	4963 (2)	155 (2)	22 (1)
Cl	7926 (1)	1721 (1)	651 (1)	41 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U tensor.

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

C(1)–C(2)	1·360 (4)	C(1)–N(1)	1·327 (4)
C(2)–C(3)	1·408 (3)	C(3)–C(4)	1·402 (3)
C(3)–N(2)	1·366 (3)	C(4)–C(5)	1·358 (4)
C(5)–N(1)	1·331 (4)	C(6)–C(7)	1·531 (3)
C(6)–N(2)	1·469 (3)	C(6)–C(10a)	1·539 (3)
C(7)–C(8)	1·494 (3)	C(8)–C(9)	1·494 (3)
C(8)–O(1)	1·223 (3)	C(9)–C(10)	1·542 (3)
C(10)–N(2)	1·469 (3)	C(10)–C(6a)	1·539 (3)

C(2)–C(1)–N(1)	121·6 (3)	C(1)–C(2)–C(3)	120·1 (2)
C(2)–C(3)–C(4)	116·1 (2)	C(2)–C(3)–N(2)	121·5 (2)
C(4)–C(3)–N(2)	122·4 (2)	C(3)–C(4)–C(5)	120·3 (2)
C(4)–C(5)–N(1)	121·5 (3)	C(7)–C(6)–N(2)	109·5 (2)
C(7)–C(6)–C(10a)	112·5 (2)	N(2)–C(6)–C(10a)	108·6 (2)
C(6)–C(7)–C(8)	113·6 (2)	C(7)–C(8)–C(9)	116·3 (2)
C(7)–C(8)–O(1)	121·4 (2)	C(9)–C(8)–O(1)	121·9 (2)
C(8)–C(9)–C(10)	113·9 (2)	C(9)–C(10)–N(2)	110·1 (2)
C(9)–C(10)–C(6a)	110·8 (2)	N(2)–C(10)–C(6a)	108·9 (2)
C(1)–N(1)–C(5)	120·3 (2)	C(3)–N(2)–C(6)	123·9 (2)
C(3)–N(2)–C(10)	124·2 (2)	C(6)–N(2)–C(10)	111·6 (2)

Table 3. *Ring-puckering and asymmetry parameters for* N(2), C(6), C(7), C(8), C(9), C(10)

q_2 = 0·1665 (22) Å
q_3 = 0·4935 (19) Å
φ_2 = 6·62 (72)°
Q_T = 0·5209 (19) Å
θ_2 = 18·65 (25)°

$\Delta C_s\lvert$N(2)$\rvert$	0·0137 (14)	$\Delta C_s\lvert$N(2)–C(10)$\rvert$	0·2899 (12)
$\Delta C_2\lvert$N(2)$\rvert$	0·2295 (9)	$\Delta C_2\lvert$N(2)–C(10)$\rvert$	0·0580 (11)
$\Delta C_s\lvert$C(6)$\rvert$	0·0955 (15)	$\Delta C_s\lvert$C(6)–N(2)$\rvert$	0·2921 (11)
$\Delta C_2\lvert$C(6)$\rvert$	0·2241 (10)	$\Delta C_2\lvert$C(6)–N(2)$\rvert$	0·0386 (12)
$\Delta C_s\lvert$C(7)$\rvert$	0·1092 (13)	$\Delta C_s\lvert$C(7)–C(6)$\rvert$	0·2784 (11)
$\Delta C_2\lvert$C(7)$\rvert$	0·2221 (9)	$\Delta C_2\lvert$C(7)–C(6)$\rvert$	0·0965 (12)

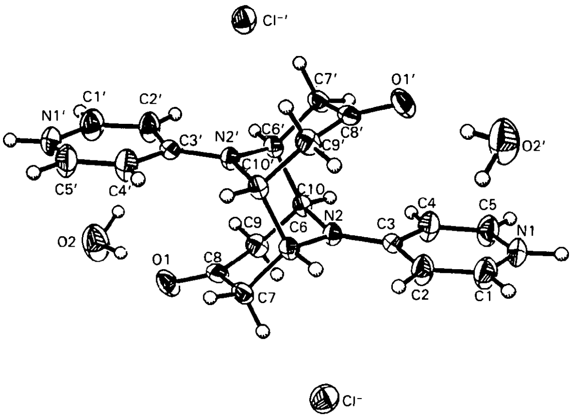


Fig. 1. Perspective drawing with 50% probability thermal ellipsoids showing the numbering of atoms. (Hydrogen atoms are shown with arbitrary radii of 0·15 Å.)

at its connection to N(2), the N(2) atom displaced 0·143 (2) Å from the mean plane of the pyridinium ring. It is also twisted slightly with respect to N(2); the angle of the mean plane of the pyridinium ring to the plane defined by C(3), C(6) and C(10) is 6·57 (8)°. The N(2) atom itself deviates from planarity; it lies −0·039 (2) Å outside the plane of C(3), C(6) and C(10).

From ring-puckering and asymmetry-parameter calculations (Nardelli, 1983) shown in Table 3, it may be seen that the piperidone ring exists in a distorted chair conformation, significantly flattened $|\theta_2 = 18{\cdot}65\ (25)^{\circ}|$ at the carbonyl apex. The water of crystallization is hydrogen-bonded to the ketone oxygen [O(1)···H(102) distance 1·928 (35) Å] and to the chloride ion [Cl$^-$···H(202) distance 2·076 (39) Å], while the chloride ion is in turn associated with the proton attached to the pyridinium nitrogen atom [Cl$^-$···H(N1) distance 2·182 (33) Å].

We are grateful to Professor M. Nardelli (Parma) for ring-puckering and asymmetry-parameter calculations.

References

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.
Nassimbeni, L. R., Rodgers, A. L. & Haigh, J. M. (1976). *Inorg. Chim. Acta*, **20**, 149–153.
Vittimberga, B. M. & Morrocchi, S. (1981). *J. Org. Chem.* **46**, 34–38.