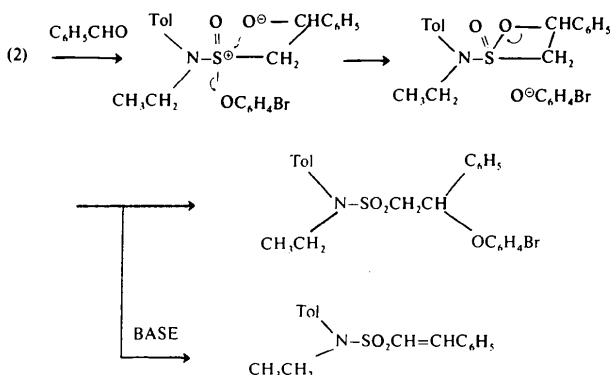


The O(2)–S–O(3) bond angle is 119.4 (3)° in agreement with that in related compounds (Kálmán, 1967; Kálmán *et al.*, 1971; Cameron *et al.*, 1973, 1974).

The molecular packing is shown in Fig. 2. The molecule is a racemate and two enantiomers are related by a center of symmetry. The shortest intermolecular contact of 3.29 Å is seen between C(2) and C(3). The molecules are held together by van der Waals forces in the crystal.

Compound (4) is identified as the title compound. Thus the reaction mechanism can be deduced as follows.



References

- ASHIDA, T. (1981). *HBLSVI. The Universal Crystallographic Computing System - Nagoya*, pp. 65–70.
- BULLOUGH, R. K. & WHEATLEY, P. J. (1957). *Acta Cryst.* **10**, 233–237.
- CAMERON, A. F., HAIR, N. J. & MORRIS, D. G. (1973). *J. Chem. Soc. Perkin Trans. 2*, pp. 1951–1954.
- CAMERON, A. F., HAIR, N. J. & MORRIS, D. G. (1974). *Acta Cryst.* **B30**, 221–225.
- CHALKLEY, G. R., SNODIN, D. J., STEVENS, G. & WHITING, M. C. (1970). *J. Chem. Soc. C*, pp. 682–686.
- CHALKLEY, G. R., SNODIN, D. J., STEVENS, G. & WHITING, M. C. (1978). *J. Chem. Soc. Perkin Trans. 1*, pp. 1580–1587.
- COREY, E. J. & CHAYKOVSKY, M. J. (1965). *J. Am. Chem. Soc.* **87**, 1353–1364.
- International Tables for X-ray Crystallography* (1962). Vol. III, 2nd ed. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
- JORDAN, T., SMITH, H. W., LOHR, L. L. JR & LIPSCOMB, W. N. (1963). *J. Am. Chem. Soc.* **85**, 846–851.
- KÁLMÁN, A. (1967). *Acta Cryst.* **22**, 501–507.
- KÁLMÁN, A., DUFFIN, B. & KUCSMAN, A. (1971). *Acta Cryst.* **B27**, 586–594.
- OKUMA, K., TANAKA, Y. & OHTA, H. (1981). *J. Am. Chem. Soc.* **103**, 5976–5977.
- TRUTER, M. R. (1962). *J. Chem. Soc.* pp. 3393–3399.
- WHEATLEY, P. J. (1954). *Acta Cryst.* **7**, 68–72.

Acta Cryst. (1985). **C41**, 463–465

Structure of 2-[5'-Aminocyclohexanespiro-4'-(4'*H*-imidazol)-2'-yl]-1-methylpyridinium Iodide, C₁₄H₁₉N₄⁺.I⁻

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Abstract. $M_r = 370.235$, tetragonal, $I4_1/a$, $a = 31.475$ (6), $c = 6.446$ (1) Å, $V = 6385.64$ (5) Å³, $Z = 16$, $D_x = 1.5404$ (3) g cm⁻³, $F(000) = 2944$, $\text{Mo K}\alpha$, $\mu = 19.765$ cm⁻¹, $\lambda = 0.7107$ Å, room temperature, $R = 0.024$ for 1643 unique observed reflections. The reaction of 5'-amino-2'-(2-pyridyl)cyclohexanespiro-4'-4'*H*-imidazole with methyl iodide takes place at the pyridine N atom giving the pyridinium salt. The pyridine ring is planar, the five-membered ring is near planar and the cyclohexane ring adopts a slightly flattened chair conformation. The molecules are held together by van der Waals contacts and N–H...N hydrogen bonds.

Introduction. The reaction of 5'-amino-2'-(2-pyridyl)-cyclohexanespiro-4'-4'*H*-imidazole, previously studied by X-ray diffraction (Avendaño, Ramos, Bellanato, Smith-Verdier, Florencio & García-Blanco, 1984), with methyl iodide in acetonitrile (Avendaño & Ramos, 1984) afforded crystals of the title compound. Among all possible alkylated products on any of the four N atoms which are present, this study shows that the reaction takes place at the pyridine N atom giving the pyridinium salt.

Experimental. Crystal 0.10 × 0.20 × 0.25 mm. D_m not determined. Unit-cell parameters determined by least-

squares fit of angular settings for 25 high-angle reflections. Enraf-Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences consistent with space group $I4_1/a$. $\omega-2\theta$ scanning mode. $2 \leq \theta \leq 30^\circ$. No absorption correction. 2 reference reflections monitored every 100 reflections showed no significant variation. 4632 independent reflections, 1643 observed with $I \geq 2\sigma(I)$. $R_{\text{int}} = 0.013$. Scattering factors from *International Tables for X-ray Crystallography* (1974). Structure solved by Patterson and Fourier techniques and refined by full-matrix least-

squares method. Anisotropic thermal parameters for non-H atoms, H (from ΔF synthesis) isotropic. $\sum w(\Delta F)^2$ minimized. Empirical weighting scheme giving no trends. $(\Delta/\sigma)_{\text{mean}} = 0.02$. Final $R = 0.024$, $R_w = 0.040$. Final difference Fourier synthesis showed no significant electron density. Calculation performed with the *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and programs *PARST* (Nardelli, 1982) and *PESOS* (Martinez-Ripoll & Cano, 1975) on a Digital-11/750 VAX computer.

Table 1. Atomic positional parameters and U_{eq} values ($\text{\AA}^2 \times 10^4$)

$$U_{\text{eq}} = \frac{1}{2} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos(a_i a_j)$$

	x	y	z	U_{eq}
I	0.34501 (1)	0.10939 (1)	0.72521 (6)	574
C(1)	0.3425 (2)	0.2398 (2)	0.0745 (8)	352
N(2)	0.3378 (1)	0.2770 (1)	0.2076 (7)	387
C(3)	0.3015 (2)	0.2923 (2)	0.1584 (8)	355
N(4)	0.2785 (1)	0.2726 (1)	-0.0017 (7)	437
C(5)	0.3024 (2)	0.2396 (2)	-0.0477 (8)	419
C(6)	0.3511 (2)	0.2007 (2)	0.2156 (9)	502
C(7)	0.3924 (2)	0.2031 (2)	0.3270 (9)	523
C(8)	0.4293 (2)	0.2085 (2)	0.1798 (11)	659
C(9)	0.4232 (2)	0.2480 (2)	0.0544 (9)	550
C(10)	0.3823 (2)	0.2476 (2)	-0.0652 (10)	538
N(11)	0.2973 (1)	0.3469 (1)	0.4358 (6)	383
C(12)	0.2827 (2)	0.3305 (2)	0.2528 (8)	407
C(13)	0.2500 (2)	0.3522 (2)	0.1532 (9)	444
C(14)	0.2339 (2)	0.3889 (2)	0.2346 (12)	732
C(15)	0.2489 (2)	0.4044 (2)	0.4161 (10)	563
C(16)	0.2810 (2)	0.3822 (2)	0.5151 (9)	508
N(17)	0.2931 (2)	0.2114 (2)	-0.1911 (10)	662
C(18)	0.3317 (3)	0.3263 (2)	0.5582 (10)	752

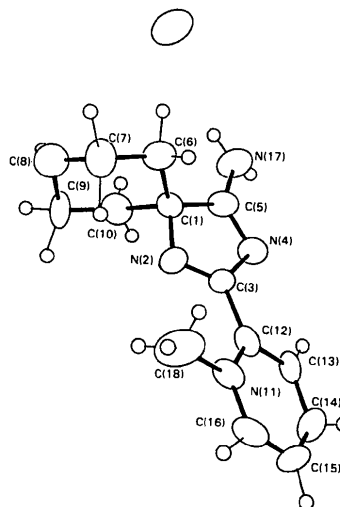


Fig. 1. A view of the molecule showing the atom numbering.

Table 2. Bond distances (\AA), bond angles ($^\circ$) and torsion angles ($^\circ$)

C(1)—N(2)	1.459 (6)	C(3)—N(4)	1.405 (7)	C(7)—C(8)	1.507 (9)	N(11)—C(18)	1.489 (9)
C(1)—C(5)	1.487 (7)	C(3)—C(12)	1.472 (7)	C(8)—C(9)	1.494 (9)	C(12)—C(13)	1.391 (7)
C(1)—C(6)	1.553 (8)	N(4)—C(5)	1.313 (6)	C(9)—C(10)	1.503 (8)	C(13)—C(14)	1.366 (9)
C(1)—C(10)	1.562 (8)	C(5)—N(17)	1.315 (8)	N(11)—C(12)	1.367 (6)	C(14)—C(15)	1.353 (10)
N(2)—C(3)	1.281 (6)	C(6)—C(7)	1.489 (8)	N(11)—C(16)	1.325 (7)	C(15)—C(16)	1.384 (8)
C(6)—C(1)—C(10)	108.9 (4)	N(2)—C(3)—C(12)	124.4 (5)	C(1)—C(6)—C(7)	113.3 (5)	C(12)—N(11)—C(16)	121.3 (4)
C(5)—C(1)—C(10)	112.0 (4)	N(2)—C(3)—N(4)	118.3 (4)	C(6)—C(7)—C(8)	112.0 (5)	C(3)—C(12)—N(11)	122.0 (4)
C(5)—C(1)—C(6)	117.1 (4)	N(4)—C(3)—C(12)	117.3 (4)	C(7)—C(8)—C(9)	109.7 (5)	N(11)—C(12)—C(13)	117.5 (5)
N(2)—C(1)—C(10)	107.0 (4)	C(3)—N(4)—C(5)	102.8 (4)	C(8)—C(9)—C(10)	112.4 (5)	C(3)—C(12)—C(13)	120.5 (5)
N(2)—C(1)—C(6)	108.0 (4)	C(1)—C(5)—N(4)	111.3 (4)	C(1)—C(10)—C(9)	113.2 (5)	C(12)—C(13)—C(14)	120.8 (5)
N(2)—C(1)—C(5)	103.2 (4)	N(4)—C(5)—N(17)	124.4 (5)	C(16)—N(11)—C(18)	116.2 (5)	C(13)—C(14)—C(15)	120.5 (6)
C(1)—N(2)—C(3)	104.3 (4)	C(1)—C(5)—N(17)	124.2 (5)	C(12)—N(11)—C(18)	122.5 (4)	C(14)—C(15)—C(16)	118.2 (6)
C(6)—C(1)—C(10)—C(9)	-48.9 (6)	C(10)—C(1)—C(6)—C(7)	50.0 (6)	C(16)—N(11)—C(12)—C(13)	-0.3 (7)		
C(5)—C(1)—C(10)—C(9)	179.9 (5)	C(1)—N(2)—C(3)—N(4)	-2.5 (6)	C(18)—N(11)—C(12)—C(13)	179.1 (5)		
N(2)—C(1)—C(10)—C(9)	67.6 (6)	C(1)—N(2)—C(3)—C(12)	180.0 (5)	N(11)—C(12)—C(13)—C(14)	1.3 (8)		
C(5)—C(1)—C(6)—C(7)	178.4 (5)	N(2)—C(3)—C(12)—C(13)	161.1 (5)	C(3)—C(12)—C(13)—C(14)	-176.6 (5)		
N(2)—C(1)—C(6)—C(7)	-65.8 (6)	N(2)—C(3)—C(12)—N(11)	-16.7 (8)	C(12)—C(13)—C(14)—C(15)	-1.4 (9)		
N(2)—C(1)—C(5)—N(17)	179.2 (5)	N(2)—C(3)—N(4)—C(5)	4.1 (6)	C(13)—C(14)—C(15)—C(16)	0.3 (9)		
C(10)—C(1)—C(5)—N(4)	-112.2 (5)	C(6)—C(7)—C(8)—C(9)	58.6 (7)	C(14)—C(15)—C(16)—N(11)	0.8 (9)		
C(6)—C(1)—C(5)—N(4)	120.9 (5)	C(7)—C(8)—C(9)—C(10)	-57.7 (7)	N(4)—C(3)—C(12)—C(13)	-16.4 (7)		
N(2)—C(1)—C(5)—N(4)	2.5 (5)	C(8)—C(9)—C(10)—C(1)	54.6 (7)	N(4)—C(3)—C(12)—N(11)	165.8 (4)		
C(5)—C(1)—N(2)—C(3)	0.0 (5)	C(16)—N(11)—C(12)—C(3)	177.6 (5)	C(12)—C(3)—N(4)—C(5)	-178.2 (4)		
C(6)—C(1)—N(2)—C(3)	-124.6 (4)	C(18)—N(11)—C(12)—C(3)	-3.0 (8)	C(3)—N(4)—C(5)—C(1)	-3.7 (5)		
C(10)—C(1)—N(2)—C(3)	118.3 (5)	C(18)—N(11)—C(16)—C(15)	179.8 (6)	C(3)—N(4)—C(5)—N(17)	179.6 (6)		
C(6)—C(1)—C(5)—N(17)	-62.4 (7)	C(12)—N(11)—C(16)—C(15)	-0.8 (8)	C(1)—C(6)—C(7)—C(8)	-56.4 (7)		
C(10)—C(1)—C(5)—N(17)	64.4 (7)						

Discussion. The positional coordinates are given in Table 1.* Fig. 1 shows a projection of the molecule with the atomic numbering. Bond lengths and angles are given in Table 2.

The molecule of the title compound contains an *N*-methylpyridinium moiety joined to a 4*H*-imidazole which has a pentamethylene group substituted at the spiranic C(1) atom.

The pyridine ring is planar (average torsion angle 0.8°) and the five-membered ring is near planar (average torsion angle 2.59°). N(2)–C(3) [1.281 (6) Å] is a localized double bond in the five-membered ring. The identity of the bond distances N(4)–C(5) [1.313 (6)] and C(5)–N(17) [1.315 (8) Å], shorter than the value usually found for a single C–N bond, reflects the conjugation of this amidine portion of the molecule (Takayanagi, Ogura, Matsuzaki, Kitajima & Nishimura, 1979).

In particular, the short C(3)–C(12) bond and the small torsion angle about this bond may be attributed to the conjugation between the imidazole and pyridinium groups. This is in good agreement with the previously studied compound 5'-amino-2'-(2-pyridyl)cyclohexanespiro-4'-4'*H*-imidazole (Avendaño, Ramos, Bellanato, Smith-Verdier, Florencio & García-Blanco, 1984).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39859 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The cyclohexane ring adopts a slightly flattened chair conformation with approximate mirror symmetry [C_s plane through C(1) and C(8), with $C_1^1 = 1.30$ (1), $C_2^{7-8} = 3.39$ (2) and $C_2^{6-7} = 8.64$ (2) (Duax & Norton, 1975)]. The deviations of C(1) and C(8) from the plane through the remaining atoms of the ring are -0.633 (5) and 0.679 (7) Å, respectively; consequently the C(6), C(1), C(10) part of the ring is a little more flattened than the opposite C(7), C(8), C(9) part.

The molecules in the crystal are held together by van der Waals contacts and are also connected by N–H...N hydrogen bonds [N(17)...N(4)($-x + \frac{1}{2}, -y + \frac{1}{2}, -z - \frac{1}{2}$) 3.043 (7), H(17)...N(4) = 2.36 (8) Å, angle N(17)–H(17)...N(4) 175.0°].

References

- AVENDAÑO, C. & RAMOS, T. (1984). Unpublished results.
 AVENDAÑO, C., RAMOS, T., BELLANATO, J., SMITH-VERDIER, P., FLORENCIO, F. & GARCÍA-BLANCO, S. (1984). *J. Mol. Struct.* In the press.
 DUAX, W. L. & NORTON, D. A. (1975). *Atlas of Steroid Structure*. New York: Plenum.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 MARTÍNEZ-RIPOLL, M. & CANO, F. H. (1975). *PESOS*. Instituto 'Rocasolano' CSIC, Madrid, Spain.
 NARDELLI, M. (1982). *PARST*. Instituto di Chimica Generale, Univ. Parma, Italy.
 STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.
 TAKAYANAGI, H., OGURA, H., MATSUZAKI, K., KITAJIMA, K. & NISHIMURA, T. (1979). *Bull. Chem. Soc. Jpn*, **52**(11), 3358–3361.

Acta Cryst. (1985). **C41**, 465–468

Structure of a 1/1 Complex of 3',5'-Di-*O*-acetyl-5-bromo-2'-deoxyuridine and 3',5'-Di-*O*-acetyl-5-iodo-2'-deoxyuridine, $C_{13}H_{15}Br_{0.5}I_{0.5}N_2O_7$

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Abstract. $M_r = 414.7$, $P2_12_12_1$, $a = 7.708$ (3), $b = 26.835$ (5), $c = 7.805$ (3) Å, $U = 1614.42$ Å³, $Z = 4$, $D_x = 1.71$ g cm⁻³, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 21.82$ cm⁻¹, $F(000) = 828$, $T = 293$ K, $R = 0.062$ for 2400 reflections (Friedel pairs not merged). The glycosidic torsion angle, χ , is -133.3 (11)°, and the sugar pucker is 2T_1 [C(1')-*exo*, C(2')-*endo*] with $P = 137.2$ (14)°. The conformation about C(4')–C(5') is *gauche-gauche* (g^+). There is one hydrogen bond,

N(3)...O(3'1) [2.914 (18) Å]. Close contacts are present between halogen and O(5'1) [average 3.21 (2) Å] and between acetyl O(5'1) and a neighbouring base ring, 2.93 (3) Å. The halogen position is occupied randomly by Br and I atoms.

Introduction. A previously determined structure in our series of substituted nucleosides, 3',5'-di-*O*-acetylthymidine (AT) (Wilson, Low, Tollin & Wilson,