$\sigma = 0.1 - 0.2°$

Fig. 4. The ring torsional angles (°).

distances from the least-squares plane through the benzene ring of the β-carboline skeleton are given in Table 2.

The molecular structure shares features with the structure of akagerine (Dupont, Dideberg & Angenot, 1975), which also contains a tetrahydro-β-carboline ring attached to a perhydroazepino ring. Akagerine is, however, a tetracyclic molecule with —OH and —CHO groups added to the perhydroazepino ring. In akagerine the seven-membered ring is completely saturated whereas in decussine C(3)—C(14) [1·372 (4) Å] has a marked double-bond character.

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Table 2. Deviations of the heavy atoms (Å) from the least-squares plane through atoms C(8), C(9), C(10), C(11), C(12) and C(13)

N(1)	−0·054 (4)	C(13)	−0·005 (4)
C(2)	−0·043 (5)	C(14)	−0·666 (7)
C(3)	−0·230 (6)	C(15)	−1·096 (6)
N(4)	−0·073 (6)	C(16)	−1·960 (7)
C(5)	0·542 (6)	C(17)	−2·417 (8)
C(6)	−0·023 (6)	C(18)	1·699 (6)
C(7)	−0·012 (5)	C(19)	0·271 (5)
C(8)	−0·002 (4)	C(20)	−0·752 (5)
C(9)	0·006 (5)	C(21)	−1·287 (6)
C(10)	−0·003 (5)	N(22)	−2·120 (6)
C(11)	−0·004 (5)	C(23)	−0·171 (9)
C(12)	0·008 (4)		

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The Structure of 2,2'-Bipyridinium Bis(fluorosulfate)

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Abstract. $C_{10}H_{10}N_2^{2+}.2SO_3F^-$, triclinic, $P\bar{1}$, $a = 7·771$ (2), $b = 8·955$ (2), $c = 10·839$ (3) Å, $\alpha = 96·97$ (2), $\beta = 99·26$ (2), $\gamma = 107·98$ (2)°, $V = 696·21$ Å^3, $Z = 2$, D_m (flotation) $= 1·68$, $D_c = 1·70$ Mg m^{-3}. The structure was solved by direct methods and refined to a final $R(F)$ value of 6·3% for 1485 independent reflections. The molecule consists of a diprotonated bipyridinium cation involved in hydrogen bonding with surrounding fluorosulfate anions [N···O distances are 2·728 (6) and 2·764 (6) Å]. The cation exhibits a transoid configuration (distortion of 31·5° from the ideal trans configuration). Orientational disorder occurs between the F and O atoms in the fluorosulfate anions.

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Introduction. The 2,2'-bipyridine (bpy)–fluorosulfuric acid system has already been investigated by DTA, IR spectroscopy and X-ray diffraction (Belin, Pichvaï & Potier, 1980). The 1:1, 1:2 and 1:4 compounds have been characterized; the 1:1 compound is the fluorosulfate of monoprotonated 2,2'-bipyridine, while, according to spectroscopic results, the 1:2 and 1:4 compounds contain the diprotonated bipyridinium cation and the corresponding fluorosulfate (SO_3F^-) or homoconjugated $(SO_3F.HSO_3F)^-$ fluorosulfate anions.

2,2'-Bipyridine consists of two pyridine rings joined together at the 2 positions through a C—C bond and the molecule can exhibit various configurations between the *cis* and *trans* extremes. In the solid state, the molecule is in the *trans* coplanar configuration (Merritt & Schroeder, 1956); in a general way, it has been shown that monoprotonation of the base allows a nearly *cis* configuration (Dega-Szafran, 1968) owing to intramolecular hydrogen bonding; it seems that the *trans* diprotonated bipyridinium cation can be observed in 1:2 adducts with relatively strong acids (benzene- or toluenesulfonic acids) while the use of weaker acids, such as carboxylic acids, leads to the formation of the homoconjugated anions of these acids instead of the *trans* diprotonated 2,2'-bipyridinium cation.

The purpose of this work is to confirm, through an X-ray structure determination, the existence of a *trans* diprotonated cation in the compound bpy.$2HSO_3F$, as previously suspected from IR results.

The title compound was synthesized from 2,2'-bipyridine (Merck) and purified fluorosulfuric acid (Fluka); single crystals were obtained by slow cooling of a 74 mol % acid mixture. A crystal of dimensions $0.50 \times 0.16 \times 0.30$ mm was selected under a polarizing microscope and mounted in a Lindemann-glass capillary. Preliminary Weissenberg photographs showed the crystal to belong to the triclinic system. Lattice constants were determined by least-squares refinement of the angular positions of 25 reflections collected and centered on an Enraf–Nonius CAD-4 four-circle automatic diffractometer. Integrated diffraction intensities were collected at room temperature (298 K) in the range $2 < \theta < 23°$ within the four octants hkl, $h\bar{k}l$, $hk\bar{l}$, $h\bar{k}\bar{l}$ using graphite-monochromated Mo $K\alpha$ radiation; the profile analysis of a few low-angle reflections indicated that an ω–$\frac{4}{3}\theta$ scan method was the most appropriate for data collection. The intensities of three standard reflections diminished by about 21% during the data collection and a correction was made. The absorption effect was neglected and the final data set consisted of 1962 independent reflections of which 1485 with $I > 3\sigma(I)$ were used in the refinements.

The structure was solved in the centrosymmetric space group $P\bar{1}$ using direct methods, Fourier and least-squares refinement techniques. Scattering factors for neutral atoms were taken from Doyle & Turner

(1968). All the non-hydrogen atoms were revealed by the Fourier step of *MULTAN* (Main, Woolfson & Germain, 1971); refinements of these positions and isotropic temperature parameters gave a conventional R factor of 0.14. Refinements were conducted using the full-matrix least-squares technique, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2_{count}(F)^2/4(F)^2 + (0.02F)^2$. In the earlier stages of refinement, it was not possible to distinguish the F atoms from the O atoms in the fluorosulfate anions, so these positions were refined using O atom scattering factors; the refinement was then continued using anisotropic temperature factors for all the non-hydrogen atoms. At this stage, calculations of interatomic distances in the anions suggested some disorder. The distances between S and O or F atoms in both anions fall into groups of two short and two longer distances (mean values of 1.41 and 1.46 Å) compared to expected distances for S—O and S—F bonds of about 1.43 and 1.56 Å (Kvick, Jönsson & Olovsson, 1969); it was concluded, therefore, that in both anions, F and O atoms were disordered between at least two sites. Some attempts were made to refine these disordered F and O atoms separately using partial occupancy factors, but this was not satisfactory; the results were better when these positions were refined using an (O/F) averaged scattering factor. In the last stages the H atoms were refined using an isotropic thermal parameter of 5 Å^2. The final agreement factors were $R(F) = 0.063$ and $R_w(F) = 0.081$; the goodness-of-fit, defined as $[\sum w(|F_o| - |F_c|)^2/(N - M)]^{1/2}$ where N is the number of observations (1485) and M the number of parameters varied (229), was 1.33. In the final cycle of refinement, the shift/e.s.d. values in the non-hydrogen atoms were <0.1 in positions and temperature factors, while the changes for H atoms were <0.6; the final electron density difference map was flat, except for a very few areas with a background <0.4 e Å^{-3}. The crystallographic programs used were *MULTAN* (Main, Woolfson & Germain, 1971), *DRF* (a modification of A. Zalkin's Fourier program), *ORFLS* (Busing, Martin & Levy, 1962) for least-squares refinements, *ORFFE* (Busing, Martin & Levy, 1964) for molecular geometry and error functions, and *ORTEP* II (Johnson, 1971) as the thermal-ellipsoid program for molecular plots.

Discussion. Final atomic parameters with their estimated standard deviations are listed in Table 1.* Bond distances and angles for the molecule are given in Table 2. Fig. 1 shows a *transoid* diprotonated bipyridinium

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Table 1. *Final positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and temperature factors*

	x	y	z	B_{eq} (Å^2)*
N(2)A	2622 (6)	2430 (5)	−802 (4)	3·0 (1)
C(1)A	2608 (6)	2866 (6)	−1946 (4)	2·4 (1)
C(6)A	2534 (7)	4394 (6)	−2057 (5)	3·2 (2)
C(5)A	2480 (8)	5385 (7)	−998 (5)	3·7 (2)
C(4)A	2471 (9)	4863 (7)	136 (5)	3·9 (2)
C(3)A	2529 (9)	3391 (7)	220 (5)	3·9 (2)
N(2)B	3418 (6)	2280 (5)	−3942 (4)	3·2 (1)
C(1)B	2603 (6)	1719 (6)	−3023 (4)	2·6 (1)
C(6)B	1777 (8)	78 (6)	−3150 (5)	3·2 (2)
C(5)B	1818 (8)	9108 (7)	−4235 (5)	3·5 (2)
C(4)B	2603 (8)	9757 (7)	−5163 (5)	3·8 (2)
C(3)B	3424 (9)	1376 (7)	−5016 (5)	3·7 (2)
SA	3101 (2)	9584 (2)	1225 (1)	3·59 (4)
SB	7877 (2)	5294 (2)	−3659 (1)	3·28 (4)
O(1)A	2547 (7)	9600 (5)	−80 (4)	5·3 (1)
O(2)A	4039 (7)	8480 (5)	1465 (5)	6·3 (1)
O/F(3)A	1444 (7)	9156 (10)	1746 (5)	12·1 (2)
O/F(4)A	4240 (9)	1157 (6)	1931 (5)	8·8 (2)
O(1)B	6146 (6)	5247 (5)	−3382 (4)	5·3 (1)
O(2)B	8045 (7)	5461 (8)	−4911 (4)	7·7 (2)
O/F(3)B	9397 (6)	6504 (5)	−2760 (4)	7·0 (1)
O/F(4)B	8173 (7)	3782 (5)	−3438 (5)	7·5 (2)
H(2)A	262 (8)	128 (7)	−66 (5)	
H(3)A	245 (8)	299 (7)	84 (6)	
H(4)A	233 (8)	559 (7)	81 (6)	
H(5)A	240 (8)	633 (7)	−100 (6)	
H(6)A	256 (8)	470 (7)	−293 (6)	
H(6)B	117 (8)	953 (7)	−251 (5)	
H(5)B	123 (9)	812 (7)	−436 (6)	
H(4)B	277 (8)	906 (7)	−587 (6)	
H(3)B	402 (8)	200 (7)	−554 (6)	
H(2)B	404 (9)	307 (7)	−396 (6)	

* $B_{eq} = 8\pi^2 U_{eq}$ (Willis & Pryor, 1975).

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

SA−O(1)	1·414 (4)	SB−O(1)	1·415 (4)
SA−O(2)	1·422 (4)	SB−O(2)	1·405 (4)
SA−O/F(3)	1·451 (5)	SB−O/F(3)	1·450 (4)
SA−O/F(4)	1·451 (5)	SB−O/F(4)	1·482 (4)

Ring A

C(1)−N(2)	1·343 (6)	N(2)−H(2)	1·06 (6)
N(2)−C(3)	1·345 (7)	C(3)−H(3)	0·80 (6)
C(3)−C(4)	1·346 (8)	C(4)−H(4)	0·96 (6)
C(4)−C(5)	1·368 (8)	C(5)−H(5)	0·86 (6)
C(5)−C(6)	1·378 (8)	C(6)−H(6)	1·01 (6)
C(6)−C(1)	1·406 (7)		
C(1)A−C(1)B	1·457 (7)		

C(1)−N(2)−C(3)	122·2 (5)	C(5)−C(6)−C(1)	119·2 (5)
N(2)−C(3)−C(4)	120·5 (5)	C(6)−C(1)−N(2)	118·3 (4)
C(3)−C(4)−C(5)	120·1 (5)	N(2)A−C(1)A−C(1)B	118·7 (4)
C(4)−C(5)−C(6)	119·7 (5)	C(6)A−C(1)A−C(1)B	123·0 (4)

Ring B

C(1)−N(2)	1·333 (6)	N(2)−H(2)	0·73 (6)
N(2)−C(3)	1·336 (7)	C(3)−H(3)	0·93 (6)
C(3)−C(4)	1·370 (8)	C(4)−H(4)	0·98 (6)
C(4)−C(5)	1·358 (8)	C(5)−H(5)	0·84 (6).
C(5)−C(6)	1·386 (7)	C(6)−H(6)	0·99 (6)
C(6)−C(1)	1·389 (7)		

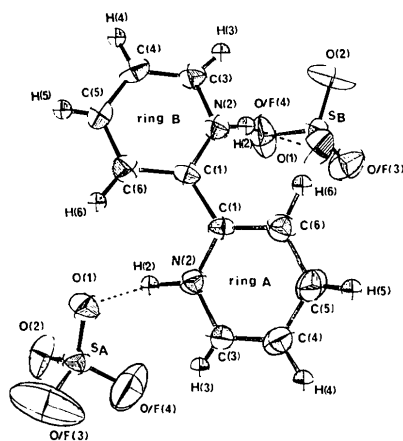|			
C(1)−N(2)−C(3)	124·4 (5)	C(5)−C(6)−C(1)	118·4 (5)
N(2)−C(3)−C(4)	118·1 (5)	C(6)−C(1)−N(2)	118·4 (5)
C(3)−C(4)−C(5)	120·3 (6)	N(2)B−C(1)B−C(1)A	118·0 (4)
C(4)−C(5)−C(6)	120·4 (5)	C(6)B−C(1)B−C(1)A	123·6 (5)

Fig. 1. 2,2'-Bipyridinium bis(fluorosulfate). *ORTEP* drawing showing thermal ellipsoids of the non-hydrogen atoms at the 50% probability level, and those of H atoms ($B_{iso} = 5$ Å^2) at the 20% probability level. Positions labelled O/F refer to disordered O and F atoms sharing the same sites.

cation involved in hydrogen bonding with two surrounding fluorosulfate anions.

Corresponding C−C and C−N distances in the two pyridinium rings are not significantly different (within the 3σ limit). The C−H bond lengths average 0·92 (6) and the N−H lengths 0·89 (6) Å. The mean planes through the C and N atoms in the pyridine rings are described by the equations $-6·8444X + 3·7784Y - 3·4674Z = 3·6826$ for ring A and $7·0981X + 0·3518Y + 0·1389Z = 2·2801$ for ring B. The distortion from the *trans* configuration for the bipyridinium rings is 31·5°.

The fluorosulfate anions exhibit the expected tetrahedral geometry; however, the temperature factors are relatively large owing to vibrational thermal motion and orientational disorder. In fact, the O(1)A and O(1)B atoms, which are involved in hydrogen bonding to the N atoms of the bipyridinium rings, possess the smallest temperature factors, and in both anions, the two (O/F) sites which are involved in orientational disorder between the O and F atoms display relatively high temperature factors. The hydrogen bonds which occur between O(1)A, O(1)B and the N atoms have distances of 2·728 (6) [N(2)A−O(1)A] and 2·764 (6) Å [N(2)B−O(1)B]; they are nearly linear [166 (5) and 161 (7)° respectively] and are responsible for the distortion of the cation from the ideal *trans* configuration.

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Structure de la Géogénine, Nouvelle Quinone Lactone Isolée de *Hohenbuehelia geogenius*

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Abstract. $C_{21}H_{22}O_5$, $M_r = 356.42$, orthorhombic, $P2_12_12_1$, $a = 23.650$ (9), $b = 9.390$ (7), $c = 7.682$ (4) Å, $Z = 4$, $d_x = 1.39$ Mg m^{-3}; $R = 0.045$ for 1378 reflexions. This new molecule, extracted from *Hohenbuehelia geogenius* (DC ex Fr.) Sing, is an antitumor agent. The X-ray structure determination revealed a six-ring molecule with lactone and quinone units which may be responsible for the pharmacological activity.

Introduction. Un principe actif antitumoral, la géogénine, a été isolé du filtrat de culture du mycélium de *Hohenbuehelia geogenius* (Basidiomycète) par extraction chloroformique suivie d'une chromatographie sur colonne de gel de silice. La procédure d'isolement de la géogénine et son activité biologique ont été décrites par ailleurs (Riondel, 1979; Riondel, Beriel, Dardas, Carraz & Oddoux, 1981). Le principe actif est recristallisé à partir d'une solution méthanolique à 277 K.

Les intensités diffractées par un cristal de 0,5 × 0,3 × 0,25 mm ont été collectées avec un diffractomètre automatique Siemens, selon la méthode des cinq points avec un balayage en ω, à la longueur d'onde $K\alpha$ du cuivre (Troughton, 1969).* La structure a été résolue par méthode directe à l'aide du programme *MULTAN* (Germain, Main & Woolfson, 1971). Les paramètres cristallographiques ont été affinés par une méthode de moindres carrés utilisant le programme *ORXFLS*3 (Busing *et al.*, 1962).

Un affinement, portant sur 1378 réflexions significatives [$I > 3\sigma(I)$], a été effectué dans les conditions suivantes: coordonnées et facteurs de température anisotrope variables pour les atomes lourds, coordonnées et facteurs de température isotropes fixes pour les atomes d'hydrogène dont les positions ont été calculées. L'étude de la courbe $w(F_o - |F_c|)^2$ en fonction de F_o détermine la pondération (Rollett, 1965).

L'indice résiduel vaut $R_w = [\sum w(F_o - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0,045$. Les coordonnées cristallographiques des atomes sont données dans le Tableau 1; les écarts types figurent entre parenthèses.*

Discussion. Cette étude a permis de révéler la formule développée et la stéréochimie relative de cette molécule inconnue. La Fig. 1 représente la formule chimique, la

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* Les mesures ont été effectuées à l'Institut Laue–Langevin, Grenoble, France.

* Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope et des coordonnées calculées des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 35795: 17 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.