THE CRYSTAL STRUCTURE OF 4′-FLUOROPYRROLNITRIN

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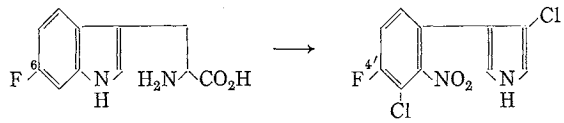
The biosynthetic preparation of an anti-fungal agent assumed to be 4′-fluoropyrrolnitrin from 6-fluorotryptophan by *Pseudomonas aureofaciens* has been previously reported[1,2]. We undertook the



6-Fluorotryptophan 4′-Fluoropyrrolnitrin

determination of the structure by X-ray crystallographic analysis in order to prove the position of the fluorine and to obtain information regarding the relative conformation of the two rings and the effect of substituent crowding in this unusual molecule.

Experimental

Crystals of 4′-fluoropyrrolnitrin were obtained as yellow plates from chloroform[2]. The crystals belong to the centrosymmetric space group $P2_1/C$ with unit cell dimensions $a=7.664\pm0.003$, $b=20.65\pm0.01$, $c=7.811\pm0.003$ Å and $\beta=118.89\pm0.01°$. The observed flotation density is 1.66 g/cm^3 and the density caluculated for four molecules per cell is 1.68 g/cm^3.

The intensities of approximately 1,900 independent reflections were measured using a four-circle automated diffractometer. The position of Cl 16 (see Fig. 1) was located from the three-dimensional PATTERSON function calculated for the corrected intensity data. Although the set of Cl 16–Cl 12 vectors were clear enough, the HARKER vectors for the symmetry related Cl 12 atoms were not as strong as one would expect. This may have been due to the omission of certain strong, low-angle reflections from the calculation of the PATTERSON function. However, a three-dimensional electron density map phased on the position of Cl 16 alone showed clearly the positions of Cl 12 and several other atoms. A second electron density map revealed the positions of all atoms except hydrogen.

Fig. 1. Composite three-dimensional electron density map, excluding hydrogens. Contours drawn at 2, 3, 4, ···e. Å^{-} for all atoms except chlorine where contours are at 2, 4, 6, ···e. Å^{-}.

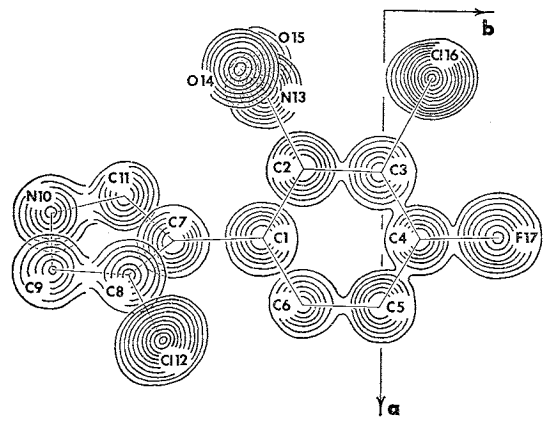
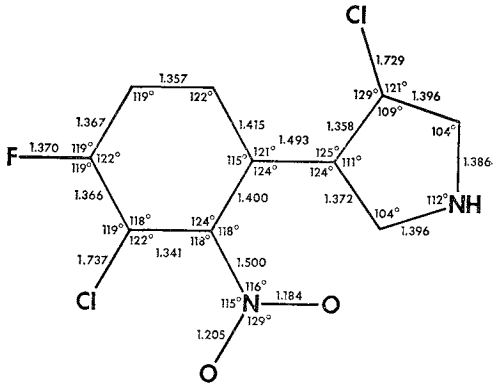


Table 1. Final atomic coordinates with standard deviations ($\times 10^4$) for all atoms except hydrogen.
Atoms are numbered as in Fig. 1.

Atom	x	y	z
C 1	6,276(14)	−1,037(5)	2,686(14)
C 2	4,648(13)	− 669(5)	2,470(15)
C 3	4,572(14)	− 21(5)	2,349(14)
C 4	6,163(16)	301(5)	2,428(15)
C 5	7,828(14)	− 14(6)	2,649(16)
C 6	7,888(14)	− 670(6)	2,800(16)
C 7	6,372(14)	−1,759(5)	2,787(14)
C 8	7,927(15)	−2,108(6)	4,146(15)
C 9	7,491(18)	−2,768(6)	3,817(19)
N 10	5,637(15)	−2,780(5)	2,155(14)
C 11	4,884(18)	−2,159(6)	1,492(18)
Cl 12	10,113(4)	−1,838(2)	6,121(5)
N 13	2,866(11)	−1,019(4)	2,332(13)
O 14	3,012(10)	−1,177(4)	3,879(12)
O 15	1,532(10)	−1,107(4)	737(11)
Cl 16	2,534(4)	418(2)	2,120(5)
F 17	6,051(10)	961(4)	2,197(11)

Least-squares refinement using first isotropic and then anisotropic temperature factors and hydrogen atoms at assumed positions gave a final R factor of 0.13 for the 1,745 reflections included in the calculation. Table 1 gives the refined coordinates for all atoms except hydrogen. The final three-dimensional electron density map for the refined structure is shown in Fig. 1.

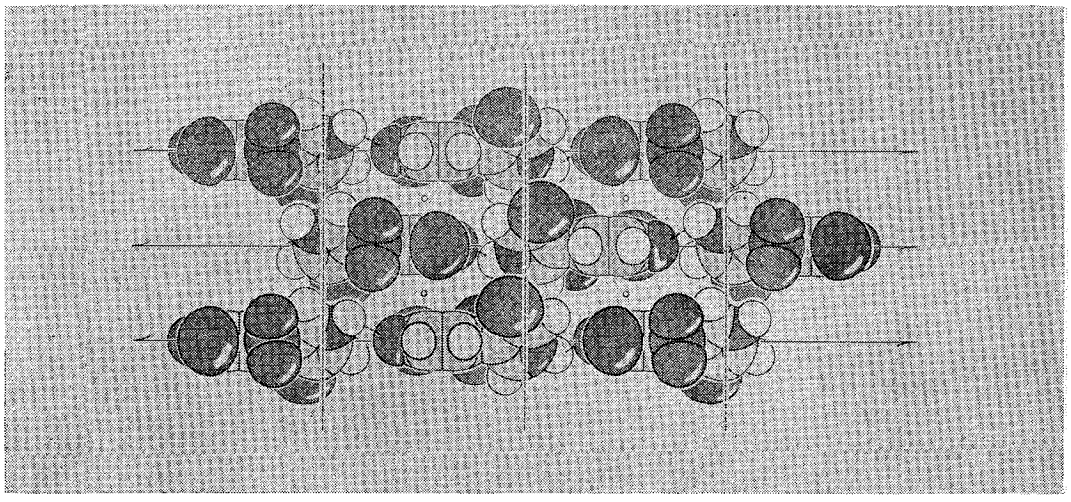
Fig. 2. Bond lengths and angles.



Discussion of Results

The bond distances and angles for 4′-fluoropyrrolnitrin are shown in Fig. 2. The standard deviation for a carbon-carbon bond is apporximately 0.017 Å and for a carbon-chlorine bond, 0.012 Å. The dihedral angle between the planes of the phenyl and the pyrrole rings is 49°, while between the phenyl and nitro groups the angle is 82°. These angles may be compared with the values 52° and 88°, respectively, found recently by MORIMOTO, HASHIMOTO and HATTORI[3] for pyrrolnitrin. The bond angles

Fig. 3. Molecular packing as viewed down a-axis. Arrows indicate screw axes, vertical dotted lines glide planes and small circles centers of symmetry. The VAN DER WAAL'S distances are slightly exaggerated for clarity.



would seem to indicate that both substituents *ortho* to the nitro group (the pyrrole ring and the chlorine atom) are bent away slightly to relieve steric interaction. Similarly, the chlorine atom on the pyrrole ring is bent away from the *ortho* phenyl ring.

The packing of the molecules to form the crystal structure is shown in Fig. 3. It may be described as consisting of chains of molecules arranged "head to tail" with weak N-H···F hydrogen bonds (distance 3.054 ± 0.014 Å) joining molecules. Although all molecules in any one chain have the same handedness with respect to hindered rotational asymmetry, adjacent parallel chains are related by centers of symmetry and are, therefore, headed in opposite directions and have opposite handedness.

References

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