

SHORT STRUCTURAL PAPERS

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Acta Cryst. (1977). B33, 3866–3868

4,5-Dichloro-1,3,6,8-tetrafluoro-2,7-naphthyridine

BY D. M. W. VAN DEN HAM AND G. J. VAN HUMMEL

Chemical Physics Laboratory, Twente University of Technology, PO Box 217, Enschede, The Netherlands

(Received 20 May 1977; accepted 26 June 1977)

Abstract. $C_8N_2Cl_2F_4$, FW 271.0; monoclinic, $P2_1$, $a = 11.925$ (2), $b = 5.523$ (1), $c = 6.785$ (1) Å, $\beta = 95.09$ (2)° (20°C). $Z = 2$, $D_x = 2.02$ g cm⁻³. The final R index was 5.2% (weighted R 4.0%). No absorption correction was applied ($\mu = 7.84$ cm⁻¹). Substantial deformation of the parent 2,7-naphthyridine skeleton results because of the short Cl–Cl distance (2.307 Å).

Introduction. Conversion of hexachloro-2,7-naphthyridine with dry KF yields a product of composition corresponding to the formula $C_8Cl_2F_4N_2$ (van den Ham, 1975).

From ¹⁹F NMR experiments it followed that the product had to be one of three possible symmetric isomers. Moreover, both F resonance peaks showed considerable line broadening. When the F atoms are placed *ortho* to the N atoms, this line broadening can be explained as the result of the incomplete ¹⁴N quadrupolar relaxation (Lehn & Kintzinger, 1973). Therefore, we tentatively assigned the structure of the title compound to the obtained product.

To check whether this line-broadening effect can be a reliable guide in the analysis of ¹⁹F NMR spectra, we wanted to characterize the structure of the compound by means of a different technique.

The specimen used for data collection was a clear, thin needle, mounted in a capillary of Lindemann glass (size: 0.17 × 0.10 × 0.64 mm). Intensity data were collected on a computer-controlled single-crystal diffractometer (Philips PW 1100) with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å).

The θ – 2θ scan mode was applied. The scan speed was 0.04° s⁻¹, scan width 1.6°. θ values ranged from 2 to 30°. The stationary background was counted during half the scan time on both sides of the peak. The data set contained 1519 reflexions of which 1229 had intensities greater than the standard deviation as estimated from counting statistics. These reflexions were used for the refinement.

The structure was solved with the aid of the program *MULTAN* (Germain, Main & Woolfson, 1971). The

E map showed the positions of all atoms. The refinement was carried out with a local version of the program *ORFLS* (Busing, Martin & Levy, 1962). Parameters refined were: positional and anisotropic thermal parameters of all atoms, isotropic extinction factor (Larson, 1969) and a scaling factor. The final R index was 5.2% (weighted 4.0%). The function minimized was $\Sigma w(|F_o| - k|F_c|)^2$. w was taken as $1/\sigma^2$ for each reflexion; $\sigma = 2s + 0.01|F_o|$; s denotes the standard deviation from counting statistics and k is the scaling factor. Atomic scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The analysis confirms the ¹⁹F NMR results. Final atomic coordinates are given in Table 1.* Inter-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32810 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic positional parameters ($\times 10^4$)

Standard deviations are shown in parentheses and refer to the last digits.

	X/a	Y/b	Z/c
C(1)	1636 (4)	3116 (14)	–3334 (6)
N(2)	955 (3)	1325 (13)	–3260 (6)
C(3)	1018 (4)	0	–1642 (8)
C(4)	1773 (3)	409 (12)	6 (6)
C(5)	3418 (3)	3018 (12)	1419 (5)
C(6)	4042 (3)	5005 (13)	1060 (6)
N(7)	3970 (2)	6370 (12)	–545 (5)
C(8)	3213 (3)	5741 (12)	–1921 (6)
C(9)	2472 (3)	3741 (12)	–1823 (5)
C(10)	2556 (3)	2341 (12)	58 (5)
H(11)	1536 (2)	4380 (11)	4924 (4)
F(12)	314 (2)	1748 (11)	–1600 (4)
Cl(13)	1660 (1)	–1453 (9)	2002 (2)
Cl(14)	3772 (1)	1490 (9)	3593 (1)
F(15)	4839 (2)	5732 (10)	2434 (3)
F(16)	3145 (2)	7083 (10)	–3537 (3)

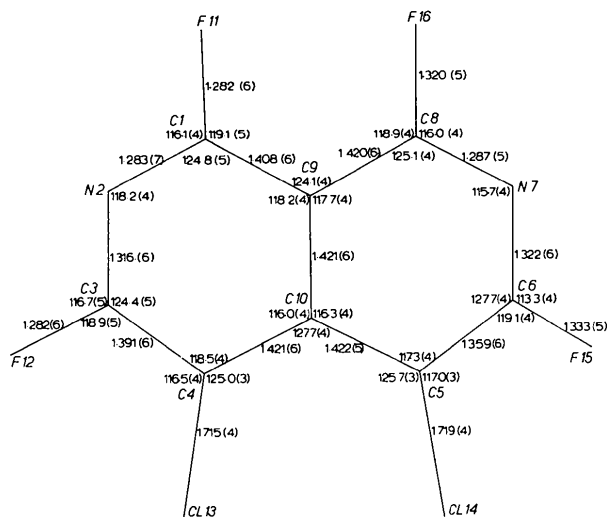


Fig. 1. Bond lengths (Å) and bond angles (°). Standard deviations are shown in parentheses and refer to the last digit.

Table 2. Atomic deviations (Å) from the best plane through the carbon and nitrogen atoms with the exception of C(4) and C(5)

Interception equation: $6.0879x - 2.4319y - 2.267z = 1.0$.

C(1)	-0.003 (10)*	C(9)	0.015 (9)
N(2)	0.003 (10)	C(10)	0.001 (10)
C(3)	-0.008 (10)	F(11)	-0.011 (8)
C(4)	-0.028 (10)	F(12)	-0.026 (8)
C(5)	0.034 (10)	Cl(13)	-0.125 (6)
C(6)	0.004 (10)	Cl(14)	0.159 (6)
N(7)	-0.010 (9)	F(15)	-0.002 (7)
C(8)	-0.002 (10)	F(16)	-0.002 (7)

* Errors quoted refer to twice the radius of the error sphere.

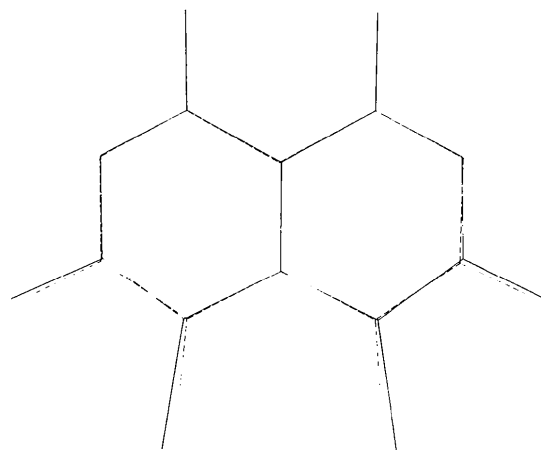


Fig. 3. Structure of 2,7-naphthyridine (dashed lines) and of the title compound (full lines).

atomic distances and angles have been calculated by means of the program *ORFFE* (Busing, Martin & Levy, 1964) taking into account the covariances of the different parameters. A pictorial representation of these values is given in Fig. 1.

A stereoview of the molecular packing (*ORTEP*, Johnson, 1965) is shown in Fig. 2. Atomic deviations from the best plane through the C and N atoms are given in Table 2.

As the Cl-Cl distance (2.307 Å) is much smaller than twice the van der Waals radius (2×1.80 Å) one can expect substantial deformation of the parent 2,7-naphthyridine skeleton (Huiszoon, van Hummel & van den Ham, 1977). We tried to visualize this deformation in Fig. 3, where both molecules have been placed on top of each other so that the C(9)-C(10) bonds coincide. Deviations of bond lengths and angles from C_2 symmetry are also significant (see Fig. 1).

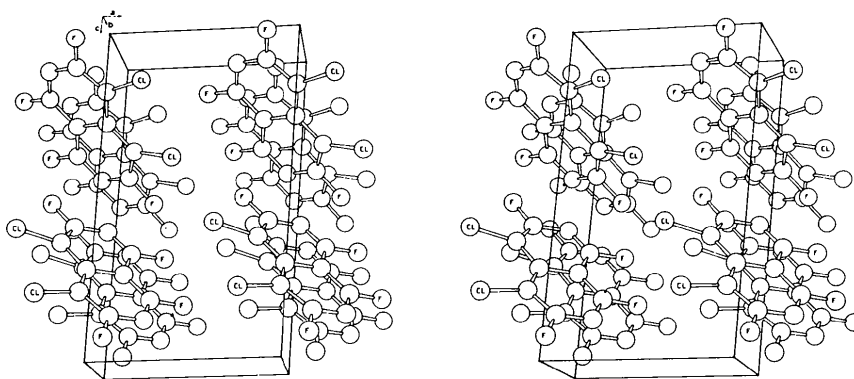


Fig. 2. Stereoscopic pair showing the molecular packing.

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Acta Cryst. (1977). **B33**, 3868–3871

Céphapyrine

PAR J. P. DECLERCQ, G. GERMAIN, C. MOREAUX ET M. VAN MEERSSCHE

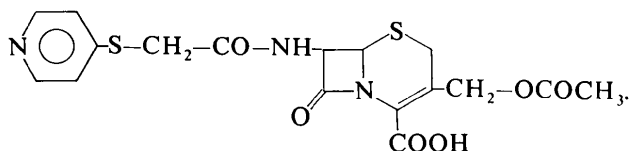
Laboratoire de Chimie Physique et de Cristallographie de l'Université de Louvain, Bâtiment Lavoisier, 1 place Louis Pasteur, B-1348 Louvain-la-Neuve, Belgique

(Reçu le 20 juin 1977, accepté le 1 juillet 1977)

Abstract. $C_{17}H_{17}N_3O_6S_2 \cdot H_2SO_4$, triclinic, $P1$, $a = 4.632$ (1), $b = 11.515$ (4), $c = 11.293$ (4) Å, $\alpha = 65.95$ (2), $\beta = 96.00$ (3), $\gamma = 99.04$ (3)°, $Z = 1$. The structure was solved by direct methods and refined by least squares to an R value of 0.045 for 1179 reflexions. The structure can be considered as consisting of $C_{17}H_{18}N_3O_6S_2^+$ and HSO_4^- ions.

Introduction. Dans le cadre de notre étude sur une éventuelle corrélation entre l'activité potentielle des céphalosporines et la conformation de la molécule, principalement au niveau du cycle β -lactame, nous avons entrepris la détermination de la structure de la céphapyrine. Ce travail fait suite à une détermination portant sur un dérivé de l'acide désacétylcéphalosporanique (Dereppe, Declercq, Germain & Van Meerssche, 1977).

La céphapyrine est un dérivé pyridylthioacétamido de l'acide céphalosporanique correspondant à la formule suivante:



Il est apparu en cours d'analyse que le composé en question cristallise avec une molécule d'acide sulfurique, provenant d'impuretés, soit des produits de départ, soit des solvants de cristallisation. La présence d'acide

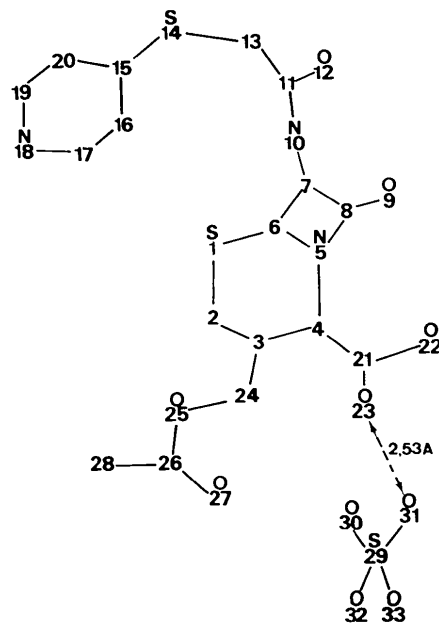


Fig. 1. Numérotation des atomes.

Tableau 1. Conditions expérimentales

Instrument: diffractomètre automatique à quatre cercles Syntax $P2$,
 Source: $Mo K\alpha$, $\lambda = 0.7107$ Å; monochromateur graphite
 Balayage $\omega-2\theta$; $2\theta_{max} = 45^\circ$
 Nombre de réflexions indépendantes mesurées: 1406
 Nombre de réflexions observées: 1179
 Condition de rejet: $I < 2.5\sigma(I)$