

Table 3. Selected dihedral angles ($^{\circ}$) between least-squares planes

Planes: A C1...C6; B C11...C16; C C1, N7, N8; D N7, N8, C10; E N8, C10, C11.

	Me-BMPH	MeO-BMPH
A—B	9.2	4.0
A—C	10.6	7.9
B—E	3.0	3.5
C—D	4.5	0.8
D—E	1.3	1.3

Table 4. Bond lengths (\AA) and angles ($^{\circ}$) for Me-BMPH and MeO-BMPH, with *e.s.d.*'s in parentheses

	Me-BMPH	MeO-BMPH
C(1)...C(6)*	1.376 (5)	1.374 (8)
C(11)...C(16)*	1.383 (4)	1.383 (8)
C(1)—N(7)	1.400 (3)	1.409 (7)
N(7)—N(8)	1.364 (3)	1.363 (7)
N(8)—C(10)	1.279 (4)	1.289 (7)
C(10)—C(11)	1.459 (4)	1.454 (7)
N(7)—C(9)	1.457 (5)	1.427 (10)
C(13)—C(17)	1.508 (6)	
C(15)—O(17)		1.365 (9)
O(17)—C(18)		1.422 (10)
C(1)...C(6)*	120.0 (3)	120.0 (5)
C(11)...C(16)*	120.0 (3)	120.0 (5)
C(1)—N(7)—N(8)	116.3 (2)	116.0 (4)
C(1)—N(7)—C(9)	122.3 (3)	123.4 (5)
N(8)—N(7)—C(9)	121.4 (3)	120.5 (5)
N(7)—N(8)—C(10)	120.5 (2)	120.5 (5)
N(8)—C(10)—C(11)	120.1 (3)	120.0 (5)

* The average for a benzene ring.

crystals. It is concluded that the prominent decrease of the SHG efficiency in Me-BMPH is due to the packing mode of the molecules.

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References

- DEWAR, M. J. S. & STEWART, J. J. P. (1986). *QCPE Bull.* **6**, 24a.
 DEWAR, M. J. S. & THIEL, W. (1977). *J. Am. Chem. Soc.* **99**, 4899.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
 KURTZ, S. K. & PERRY, T. T. (1968). *J. Appl. Phys.* **39**, 3798–3813.
 LYNN, L. L., PIERCE, T. H. & RAYNOLDS, C. H. (1987). *QCPE Bull.* **7**, 37.
 MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). *MULTAN71. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 OUDAR, J. L. & CHEMLA, D. S. (1977). *J. Chem. Phys.* **66**, 2664.
 SAKURAI, T. & KOBAYASHI, K. (1979). *Rep. Inst. Phys. Chem. Res.* **55**, 69–77.
 TOSI, G., CARDELLINI, L. & BOCELLI, G. (1988). *Acta Cryst.* **B44**, 55–63.

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Structure of a Cyclopropaneaziridine Derivative of 1,5-Naphthyridine

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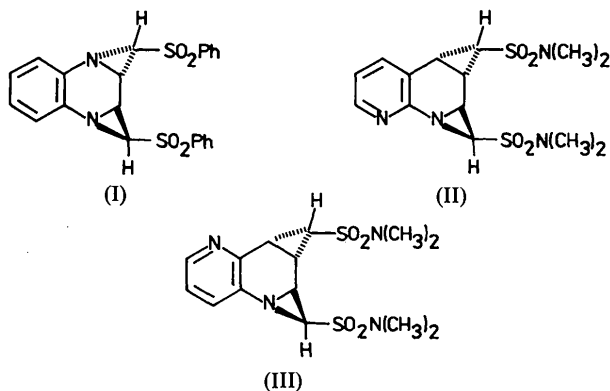
Abstract. 1,2-Bis(dimethylaminosulfonyl)-1,1a,1b,2-tetrahydroaziridino[1,2-*a*]cyclopropano[*c*][1,5]naphthyridine, $C_{14}H_{20}N_4O_4S_2$, $M_r = 372.5$, triclinic, $P\bar{1}$, $a = 8.645$ (2), $b = 10.340$ (1), $c = 12.441$ (1) \AA , $\alpha = 94.65$ (1), $\beta = 106.53$ (2), $\gamma = 119.97$ (2) $^{\circ}$, $V = 889.6$ \AA^3 , $Z = 2$, $D_m = 1.32$, $D_x = 1.390$ g cm^{-3} , $\text{Cu K}\alpha$, $\lambda = 1.54178$ \AA , $\mu = 28.1$ cm^{-1} , $F(000) = 392$, $T = 293$ K, $R = 0.0438$ for 3399 reflections. The structure of the title compound is compared with the

previously described 1,8 isomer. The two isomers have different conformations for the sulfonamide groups.

Introduction. Aziridine derivatives have attracted attention because of their antitumor (Dermer & Ham, 1969), antibiotic (Athar, Begleiter, Jonson, Lown, McLaughlin & Sim, 1975), and insect chemosterilant properties (Haynes, Mattix, Mitlin,

Borkovec & Linding, 1976). The antitumor activity displayed by the compounds having aziridine rings condensed with other heterocyclic systems, such as mitomycins, results from their ability to act as alkylating agents which modify (crosslink) DNA (Lown & Weir 1978)

The structure determinations of diazanaphthalene derivatives (I) and (II), condensed with aziridine and cyclopropane rings, respectively, have been undertaken previously (Pniewska & Anulewicz, 1986, 1987) as part of our studies of the structure-biological activity relationships of annulated aziridine derivatives with potential antitumor and antiviral properties. In this paper the structure of compound (III) is investigated and the results are compared with those for compound (II). Compound (III) was prepared according to the method previously reported by Goliński, Makosza & Rykowski (1983).



Experimental. Colourless crystal recrystallized from methanol by slow evaporation. D_m determined by flotation from KI solution. Crystal dimensions 0.30 × 0.17 × 0.13 mm. Enraf-Nonius CAD-4 diffractometer, Cu $K\alpha$ radiation, graphite monochromator, no absorption correction. Cell dimensions from refinement of 25 reflections in the range $4 < 2\theta < 24^\circ$, 4564 reflections scanned by ω - 2θ scans up to $\theta_{\max} = 78^\circ$, 3678 reflections considered observed [$I > \sigma(I)$], index range $-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $0 \leq l \leq 15$. Two standard reflections ($\bar{1}22$ and $\bar{1}14$) measured every 1 h; no significant intensity variations. 3438 unique reflections ($R_{\text{int}} = 0.0145$), 3399 with $F > 3\sigma(F)$ used in the refinement. Structure solved by direct methods with MULTAN80 (Main *et al.*, 1980). Least-squares refinement on F with SHELX76 (Sheldrick, 1976). All non-H atoms were refined anisotropically; atoms H(7), H(8), H(9) and H(10) were located from a difference map and refined isotropically. All other H atoms were included at calculated positions, C—H = 1.08 Å, and allowed to ride on their parent atoms. Final $R = 0.0438$, unit weights, 252 refined parameters, $(\Delta/\sigma)_{\max} = 0.045$; residual

Table 1. Atomic fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2)

$$B_{\text{eq}} = 8\pi^2(U_{11}U_{22}U_{33})^{1/3}.$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
S(1)	6326 (1)	1590 (1)	6748 (1)	2.93 (2)
S(2)	6560 (1)	3801 (1)	1728 (1)	3.62 (3)
O(11)	7444 (3)	912 (2)	6845 (2)	3.97 (7)
O(21)	6784 (3)	5145 (2)	1371 (2)	4.68 (9)
O(12)	4275 (3)	622 (2)	6156 (2)	4.31 (5)
O(22)	7986 (4)	3442 (3)	1808 (2)	5.17 (2)
N(11)	6755 (4)	2387 (3)	8055 (2)	3.91 (7)
N(22)	4487 (4)	2324 (3)	838 (2)	4.39 (7)
N(1)	7560 (3)	6533 (2)	6593 (2)	3.33 (6)
N(2)	8246 (3)	4962 (2)	4091 (2)	2.89 (7)
C(1)	7408 (3)	5535 (3)	5750 (2)	2.64 (6)
C(2)	8317 (3)	6005 (3)	4964 (2)	2.22 (7)
C(3)	9428 (4)	7584 (3)	5056 (2)	3.46 (9)
C(4)	9590 (4)	8610 (3)	5922 (3)	4.02 (8)
C(5)	8644 (4)	8052 (3)	6667 (3)	3.91 (8)
C(6)	6179 (3)	3862 (3)	5673 (2)	2.63 (7)
C(7)	7220 (3)	3046 (3)	6038 (2)	2.58 (7)
C(8)	6039 (3)	2712 (3)	4777 (2)	2.65 (6)
C(9)	7055 (3)	3279 (3)	3969 (2)	2.82 (7)
C(10)	6374 (4)	3971 (3)	3102 (2)	3.00 (8)
C(21)	3961 (7)	780 (4)	973 (4)	6.71 (16)
C(22)	2870 (5)	2530 (5)	425 (3)	5.96 (10)
C(11)	8746 (6)	3266 (5)	8870 (3)	6.29 (9)
C(12)	5599 (10)	3007 (7)	8202 (4)	7.07 (7)

electron density in final difference map within +0.42 and -0.46 e \AA^{-3} ; atomic scattering factors as supplied with the program.

Discussion. Final atomic parameters are listed in Table 1,* bond lengths and angles in Table 2, and the atomic numbering scheme and Newman projections are shown in Figs. 1 and 2, respectively.

Compounds (II) and (III) differ by rotation of the sulfonamide groups around the C—S bonds (Figs. 2*c-f*). In both compounds, the position of one of the two S—O bonds with respect to the cyclopropane and aziridine rings is similar, but the sulfonamide groups are rotated in different directions around the C—S bonds. This difference is most probably due to crystal-packing forces.

The geometries of the sulfonamide groups in both compounds agree well with those found for N-substituted arylsulfonamides (Kálmán, Czugler & Argay, 1981). The C—S—N—C torsion angles (Figs. 2*a,b*) have values in the range of $|\epsilon_2| = 60$ – 90° and X—C—S—N [$X = \text{C}(6), \text{C}(9)$ or $\text{C}(8)$ N(2)] (Figs. 2*c-f*) in the range $|\epsilon_1| = 70$ – 120° . The S(1)—N(11) bonds of 1.610 (3) Å for (III) and 1.616 (2) Å for (II), and the S(2)—N(22) bonds of 1.623 (2) Å for (III) and 1.614 (2) Å for (II), respectively, are very close to the mean values of 1.63–1.69 Å found in the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52180 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

O(11)—S(1)	1.437 (3)	C(2)—N(2)	1.433 (4)
O(12)—S(1)	1.433 (2)	C(9)—N(2)	1.480 (3)
N(11)—S(1)	1.611 (3)	C(10)—N(2)	1.479 (3)
C(7)—S(1)	1.757 (3)	C(2)—C(1)	1.394 (4)
O(21)—S(2)	1.430 (3)	C(6)—C(1)	1.486 (4)
O(22)—S(2)	1.436 (4)	C(3)—C(2)	1.393 (4)
N(22)—S(2)	1.622 (2)	C(4)—C(3)	1.373 (5)
C(10)—S(2)	1.765 (3)	C(5)—C(4)	1.381 (5)
C(11)—N(11)	1.453 (4)	C(7)—C(6)	1.522 (5)
C(12)—N(11)	1.472 (11)	C(8)—C(6)	1.495 (4)
C(21)—N(22)	1.465 (5)	C(8)—C(7)	1.507 (3)
C(22)—N(22)	1.473 (6)	C(9)—C(8)	1.486 (4)
C(1)—N(1)	1.339 (4)	C(10)—C(9)	1.485 (4)
C(5)—N(1)	1.346 (3)		
O(11)—S(1)—O(12)	119.3 (1)	N(1)—C(1)—C(6)	116.5 (2)
O(11)—S(1)—N(11)	106.7 (2)	C(1)—N(1)—C(5)	117.4 (3)
O(11)—S(1)—C(7)	106.6 (2)	N(1)—C(5)—C(4)	123.1 (3)
O(12)—S(1)—N(11)	107.3 (2)	N(2)—C(2)—C(1)	123.8 (2)
O(12)—S(1)—C(7)	107.9 (1)	N(2)—C(2)—C(3)	117.6 (2)
S(1)—N(11)—C(11)	117.2 (3)	C(2)—N(2)—C(9)	118.4 (2)
S(1)—N(11)—C(12)	117.5 (3)	C(2)—N(2)—C(10)	115.7 (3)
N(11)—S(1)—C(7)	108.8 (1)	N(2)—C(9)—C(8)	119.9 (3)
S(1)—C(7)—C(6)	119.5 (2)	N(2)—C(9)—C(10)	59.9 (2)
S(1)—C(7)—C(8)	117.8 (1)	C(9)—N(2)—C(10)	60.3 (2)
O(21)—S(2)—O(22)	119.6 (2)	N(2)—C(10)—C(9)	59.9 (2)
O(21)—S(2)—N(22)	107.1 (2)	C(1)—C(2)—C(3)	118.6 (3)
O(21)—S(2)—C(10)	107.3 (2)	C(2)—C(1)—C(6)	120.5 (3)
O(22)—S(2)—N(22)	108.2 (2)	C(1)—C(6)—C(7)	116.5 (2)
O(22)—S(2)—C(10)	107.8 (2)	C(1)—C(6)—C(8)	118.2 (2)
S(2)—N(22)—C(21)	117.9 (3)	C(2)—C(3)—C(4)	118.6 (3)
S(2)—N(22)—C(22)	118.1 (3)	C(3)—C(4)—C(5)	119.4 (3)
N(22)—S(2)—C(10)	106.0 (1)	C(6)—C(7)—C(8)	59.2 (2)
S(2)—C(10)—N(2)	114.3 (2)	C(7)—C(6)—C(8)	59.9 (2)
S(2)—C(10)—C(9)	121.3 (3)	C(6)—C(8)—C(7)	60.9 (2)
C(11)—N(11)—C(12)	115.4 (4)	C(6)—C(8)—C(9)	118.9 (2)
C(21)—N(22)—C(22)	115.4 (3)	C(7)—C(8)—C(9)	118.7 (2)
N(1)—C(1)—C(2)	123.0 (2)	C(8)—C(9)—C(10)	118.6 (3)

work of Kálmán; the S(1)—C(7) and S(2)—C(10) distances of 1.757 (3), 1.764 (3) Å for (III) and 1.764 (2), 1.767 (2) Å for (II), respectively, also agree well with the mean values of 1.76 Å for S—C_{sp}² bonds. These data indicate an electron delocalization from both substituents to π -accepting sulfone groups (Kálmán *et al.*, 1981).

There are no appreciable differences in the bond lengths and valency angles for compounds (II) and (III).

The naphthyridine rings are planar in both compounds to within 0.027 (3) Å for (III) and 0.030 (3) Å for (II). Deviations from the least-squares plane [-0.017 (3) for N(1) and -0.020 (3) Å for N(2)] are comparable with those found in (II). The C(7) and C(10) atoms deviate from this plane by -1.247 (3) and 1.216 (3) Å, while these distances are -1.254 (3) and 1.247 (3) Å, respectively, in (II).

The small rings are bent in opposite directions with respect to the naphthyridine plane making dihedral angles with the plane of 107.6 (2)° for the cyclopropane ring and 72.9 (2)° for the aziridine ring, with the angle between three-membered rings being 123.5 (2)°. The corresponding angles for (II) were 108.2 (2), 75.7 (2) and 123.1 (2)°.

There are two short intermolecular distances: C(10)⋯N(1) 3.279 (3), H(10)⋯N(1) 2.32 (4) Å, C(10)—H(10)—N(1) (1-x, 1-y, 1-z) 157 (2)°; C(8)⋯O(11) 3.350 (3), H(8)⋯O(11) 2.47 (2) Å, C(8)—H(8)—O(11) (1-x, -y, 1-z) 154 (3)°. The volume of the unit cell in (III) is 42.4 Å³ larger than that in (II).

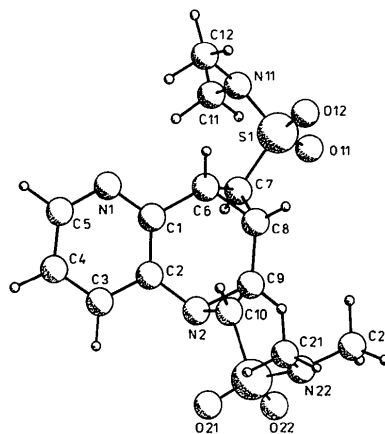
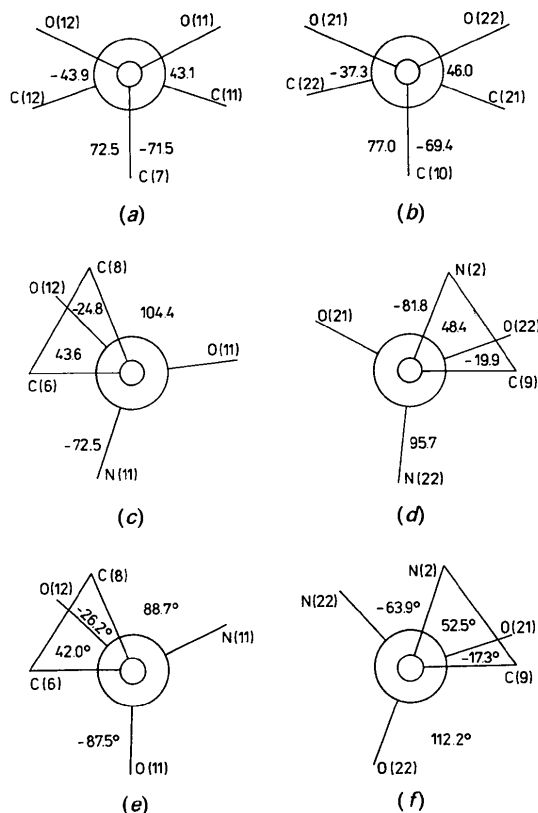


Fig. 1. A view of the molecule with the numbering of the atoms.

Fig. 2. Newman projections along the bonds: (a) S(1)—N(11), (b) S(2)—N(22), (c) C(7)—S(1), (d) C(10)—S(2) for compound (III), (e) C(7)—S(1), (f) C(10)—S(2) for compound (II). *E.s.d.*'s are 0.2–0.3°.

The intensities were measured in the Regional Laboratory of Physicochemical Analysis and Structure Research, Jagiellonian University, Krakow. This work was supported by project R.P.II.10 from the MEN.

References

- ATHAR, M. H., BEGLEITER, A., JONSON, D., LOWN, J. W., MCLAUGHLIN, L. & SIM, S. K. (1975). *Can. J. Chem.* **53**, 2891–2905.
- DERMER, O. C. & HAM, G. E. (1969). *Ethylenimine and Other Aziridines*, p.403. New York: Academic Press.
- GOLIŃSKI, J., MAKOSZA, M. & RYKOWSKI, A. (1983). *Tetrahedron Lett.* **24**, 3279–3280.
- HAYNES, J. W., MATTEK, E., MITLIN, N., BORKOVEC, A. B. & LINDING, O. H. (1976). *US Agric. Res. Serv. South Reg. Rep.* pp. 30–32.
- KÁLMÁN, A., CZUGLER, M. & ARGAY, GY. (1981). *Acta Cryst.* **B37**, 868–877.
- LOWN, J. W. & WEIR, G. (1978). *Can. J. Biochem.* **56**, 296–304.
- MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- PNIEWSKA, B. & ANULEWICZ, R. (1986). *Acta Cryst.* **C42**, 1627–1630.
- PNIEWSKA, B. & ANULEWICZ, R. (1987). *Acta Cryst.* **C43**, 2198–2200.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Structure du Tris(éthylènediammonium) Bis(monohydrogénodiphosphate) Dihydrate

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Abstract. 3C₂H₁₀N₂²⁺·2HO₇P₂³⁻·2H₂O, *M_r* = 572.2, monoclinic, *P*₂₁/*n*, *a* = 11.860 (2), *b* = 6.463 (1), *c* = 14.997 (3) Å, β = 112.36 (1)°, *V* = 1063 (1) Å³, *Z* = 2, *D_m* = 1.716, *D_x* = 1.788 Mg m⁻³, λ(Ag Kα) = 0.5608 Å, μ = 0.228 mm⁻¹, *F*(000) = 604, *T* = 298 K, final *R* = 0.053 for 1797 unique reflexions. The P—O(*L*) bridge is unsymmetrical with P—O(*L*) distances of 1.584 (3) and 1.623 (3) Å, and a P—O—P angle of 132.2 (2)°. There is a short O—H⋯O hydrogen bond (2.493 Å) linking diphosphate groups into infinite chains. The ethylenediammonium groups are located in the channels delimited by monohydrogendiphosphate chains. N—H⋯O hydrogen bonding ensures the three-dimensional cohesion of the atomic arrangement.

Introduction. L'étude de [NH₃(CH₂)₂NH₃]₃[HP₂O₇]₂·2H₂O s'inscrit dans le cadre d'une étude systématique de l'interaction entre l'acide diphosphorique, H₄P₂O₇, avec l'éthylènediamine. Peu de travaux, dans ce domaine, sont signalés dans la littérature; on ne peut guère citer, pour les amines aliphatiques, que [C(NH₃)₃]₃HP₂O₇ (Adams & Ramdas, 1976) et [C(NH₃)₃]₄P₂O₇·H₂O (Adams & Ramdas, 1977). Dans le présent travail, nous décrivons la structure

crystalline du tris(éthylènediammonium) bis(monohydrogénodiphosphate) dihydrate.

Partie expérimentale. Dimensions du cristal: 0,12 × 0,15 × 0,17 mm; Philips PW1100; monochromateur: graphite; paramètres cristallins obtenus avec 25 réflexions (11 < θ < 14°); *D_m* par pycnométrie (bromobenzène). Domaine de mesure 3 à 30° (θ); type de balayage: ω; domaine de balayage: (1,2 + 0,2tgθ)°; vitesse de balayage 0,03° s⁻¹; réflexions de référence: 510, 510, 510, variation négligeable; temps total de mesure du fond continu: 10 s; nombre de réflexions mesurées: 3636 (± *h*, ± *k*, *l*), *h*_{max} = 20, *k*_{max} = 12, *l*_{max} = 25; correction de Lorentz-polarisation sur les 2170 réflexions indépendantes; aucune correction d'absorption. La structure a été déterminée par exploitation de la fonction de Patterson et synthèses de Fourier successives; ∑*w*[|*F_o*| - |*F_c*|]² minimisée; *w* = [σ(*I*)² + (*pI*)²]^{-1/2} avec *p* = 0,05 pour rendre ∑*w*Δ*F*² uniformément distribuée dans |*F_o*|. Les derniers cycles d'affinements par moindres carrées à matrices complètes sont effectués à l'aide de 1797 raies retenues correspondant à *F_o* > 3σ(*F*) et élimination de 15 raies fortes et mal mesurées telle que |*F_o* - *F_c*| > 10 dans une échelle de 0 à 1304; facteurs