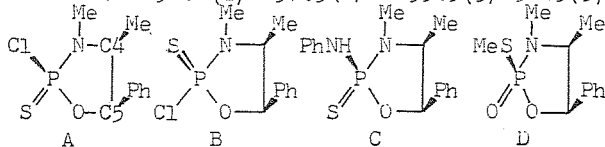


**09.2-42** THE CRYSTAL STRUCTURES AND ABSOLUTE CONFIGURATIONS OF FOUR 1,3,2-OXAZAPHOSPHOLIDINES DERIVED FROM (-)EPHEDRINE. By T.J. Bartczak and Z. Gałdecki, Institute of General Chemistry Technical University, 90-924 Łódź and (in part) M. Rutkowska, Regional Laboratory of Physicochemical Analysis and Structural Research, Jagiellonian University, 30-060 Kraków, Poland and (in part) Yu.T. Struchkov and M.Y. Antipin, Institute of Organoelement Compounds, USSR Academy of Sciences, Moscow 117312, USSR.

The diastereoisomers (2*S*,4*S*,5*R*)- and (2*R*,4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-thiones (A and B) were synthesized from (-)ephedrine i.e. 1*R*,2*S*-2-methylamino-1-phenylpropan-1-ol (Inch and al. *J. Chem. Soc., Perkin 1* 1977, 1969-1980). The <sup>1</sup>H NMR spectra of A and B were not easy to interpret and the configuration at the P atom was assigned as P<sub>R</sub> for A and P<sub>S</sub> for B on the basis of chemical methods. In the course of studies on the synthesis of nucleotide and nucleoside phosphorothioates it was found that dialkyl aryl phosphoroanilidates can be stereospecifically converted into corresponding phosphates and phosphorothioates with retention of configuration at phosphorus. The compounds A and B were used to investigate the stereoselectivity of the conversion when P is incorporated into a five-membered ring (Stec et al. *Z. Naturforschung*, 33b, 782-785, 1978). Again the NMR spectra of A and B as well as (2*R*,4*S*,5*R*)-2-anilido-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-thione (C) and (2*R*,4*S*,5*R*)-2-thiomethyl-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-one (D) were not very helpful for stereochemical analysis. The absolute configuration at the P-atom in A and B was assigned inversely as P<sub>S</sub> and P<sub>R</sub> respectively and was correlated with C and D by chemical methods. Therefore, the compounds were subjected to X-ray analysis to confirm their absolute configurations and to investigate the conformation of oxazaphospholidine rings in the presence of different exocyclic substituents at P. The structural parameters are recorded below. All compounds crystallize in the orthorhombic space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. All the five-membered rings adopt the envelope conformation with C4 deviating 0.50 and -0.53 Å from the l-s plane N-P-O-C5 in A and B respectively. P is deviating by 0.34 Å in C and C5 is deviating by -0.49 Å in D. The analysis confirmed the absolute configuration as assigned by Stec and al., i.e. like in the names given here.

	A	B	C	D
a =	9.630 (1)	10.330 (1)	10.935 (1)	21.744 (6)
b =	10.318 (5)	11.129 (5)	16.757 (5)	8.409 (1)
c =	12.717 (1)	11.151 (1)	9.192 (1)	6.9704 (5)
R =	0.0451	0.0499	0.0682	0.1170
P-Cl	2.049 (1)	2.047 (3)		2.060 (5)
P-S	1.911 (2)	1.890 (2)	1.925 (2)	1.495 (10)
P=O				1.595 (9)
P-Cendo	1.579 (3)	1.578 (4)	1.586 (5)	1.595 (9)
P-Nendo	1.622 (3)	1.624 (5)	1.639 (6)	1.670 (10)
N-P-Cendo	96.8 (2)	97.3 (2)	95.5 (3)	96.9 (5)



**09.2-43** N,N'-DI[2-METHYLDITHIOCARBONYL-1-CYCLOPENTENYL]-1,3-DIAMINOPROPANE, C<sub>17</sub>H<sub>26</sub>S<sub>4</sub>N<sub>2</sub>. By P.B. Sarkar and S.P. Sen Gupta, Department of General Physics and X-rays, Indian Association for the Cultivation of Science, Calcutta - 700032, India.

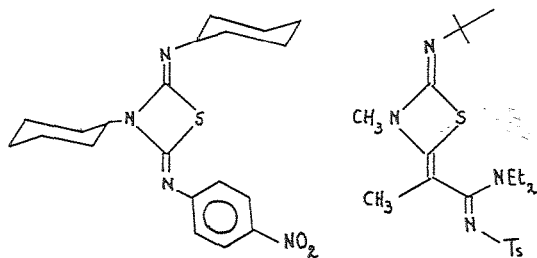
The title compound is a condensation product of 1,3-diaminopropane and the methylester of 2-aminocyclopentene-1-dithiocarboxylic acid (Bordas et al., *J. Org. Chem.* (1972) 37, 1727). The compound crystallized in the space group P2<sub>1</sub>/n, with the following cell dimensions: a<sup>+</sup> = 6.802(3), b = 24.242(14), c = 11.953(4) Å, β = 100.90(3)°, Z = 4. Altogether, 3391 reflexions were collected on the single crystal diffractometer (CAD-4) of which 1607 with F<sub>o</sub> > 4σ(F<sub>o</sub>) were considered for the final refinement which gave R = 0.08. Using Multan-78, the structure was solved for all the non-hydrogen and 24 hydrogen atoms.

**09.2-44** CRYSTAL STRUCTURE OF BIS(IMINO)THIAZETIDINES. By G.S.D. King and L. Van Meervelt, Lab. voor kristallografie, K.U. Leuven, Celestijnenlaan 200 C, B-3030 Heverlee, Belgium.

Bis(imino)thiazetidines are formed by the reaction of carbodiimides with isothiocyanates. The stereochemistry of the C=N functions is important for the elucidation of the reaction mechanism, and is shown for 2-cyclohexylimino-3-cyclohexyl-4-(p-nitrophenylimino)-1,3-thiazetidine (1) to be Z,Z. Crystal data for C<sub>20</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub>S (M = 386) are : a = 9.519(9), b = 19.088(9), c = 5.965(2) Å, α = 86.10(3), β = 77.80(6), γ = 83.10(6)°, U = 1051(1) Å<sup>3</sup>, space group P $\bar{1}$ , D<sub>m</sub> = 1.22 g cm<sup>-3</sup>, D<sub>c</sub> (Z = 2) = 1.22 g cm<sup>-3</sup>. Structure solved by direct methods. At present stage of refinement R = 0.10. The crystal structure of 2-(t-butylimino)-3-methyl-4-[N,N-diethylamino-N'-tosyl-propioneamidino-2-ylidene]-1,3-thiazetidino (2), one of the products of the reaction of a bis(imino)thiazetidino with diethylamino-propyne has also been determined by direct methods and refined to R = 0.097 (the t-butyl group shows some rotational disorder). Crystal data for C<sub>21</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub> (M = 436) are :

a = 15.304(10), b = 8.263(3) = 20.002(9) Å,

$\beta = 108.31(4)^\circ$ ,  $U = 2401(2) \text{ \AA}^3$ , space group  $P2_1/n$ ,  
 $D_m = 1.20 \text{ g cm}^{-3}$ ,  $D_c (Z = 4) = 1.21 \text{ g cm}^{-3}$ .



(1)

(2)

These thiazetidine rings are planar and more symmetrical than other published thiazetidine rings because both carbon atoms of the ring have external double bonds (C-S : 1.81 - 1.88 Å and C-N : 1.37 - 1.40 Å).

**09.2-45** MONOPOTASSIUM SALTS OF 4-CYANO AND 4-NITRO-3-HYDROXY-6H-1,2,6-THIADIAZINE 1,1-DIOXIDE.MONOHYDRATE. By C. Esteban-Calderón, M. Martínez-Ripoll and S. García-Blanco, X-Ray Department, Institute "Rocasolano", Serrano 119, Madrid-6, Spain.

Both compounds have been synthesized by Goya and Stud (J. Heterocyclic Chem. (1978) 15, 253-256), as a part of a research project aimed at obtaining substances with biological activity.

Crystal data are:

$4\text{CN-K}(\text{C}_4\text{H}_2\text{N}_3\text{O}_3\text{SK}\cdot\text{H}_2\text{O})$ :  $a=9.811(1)$ ;  $b=7.296(1)$ ;  $c=5.858(1) \text{ \AA}$   
 $\alpha=103.06(1)$ ;  $\beta=94.56(2)$ ;  $\gamma=100.51(2)^\circ$ ;  $Z=2$ ;  $P\bar{1}$ ;  $n^\circ$  reflex. in refinement 2835.

$4\text{NO}_2\text{-K}(\text{C}_3\text{H}_2\text{N}_3\text{O}_5\text{SK}\cdot\text{H}_2\text{O})$ :  $a=6.0744(4)$ ;  $b=18.583(2) \text{ \AA}$   
 $c=7.497(1) \text{ \AA}$ ;  $\beta=91.68(1)^\circ$ ;  $Z=4$ ;  $P2_1/c$ ;  $n^\circ$  reflex. in refinement 2006.

Both structures have been solved by using single crystal data and MoK $\alpha$  radiation, and refined by least-squares analysis to the values of 0.042 ( $R_w=0.049$ ) and 0.039 ( $R_w=0.050$ ), respectively.

Major electron distributions are proposed (Fig.3 and 4), according to Linnett's model (Linnett, J.W. (1966). The Electron Structure of Molecules. A New Approach. London. Methuen)

Two facts are relevant in these salt crystal structures, when compared with the structures of both free compounds (C. Esteban-Calderón, M. Martínez-Ripoll and S. García-Blanco, Acta Cryst. (1979), B35, 2795-2797) and (C. Esteban-Calderón, M. Martínez-Ripoll, to be published elsewhere):

- 1) Strong electron modifications occur within the thiazetidine ring, the main alterations being around O(3), C(3), N(2), S and N(1).

- 2) The different location of the H atom, attached to N(2) in these structures, in comparison with the free compounds (where H is attached to N(1)), explains the different behaviour of both free and salt compounds, versus

alkylating reagents.

Other interesting fact is the lower stability of these K-salts versus the Na-salts (C. Esteban-Calderón, M. Martínez-Ripoll, to be published elsewhere): The free compounds behave as sequestering agents for Na ions.

4CN-K

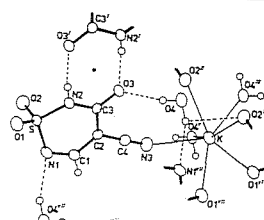


Fig.1

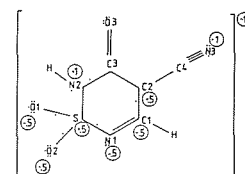


Fig.3

4NO2-K

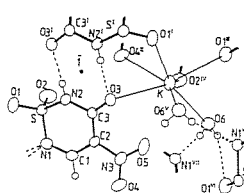


Fig.2

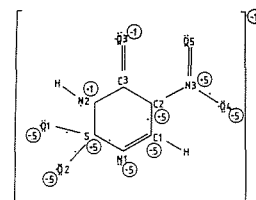
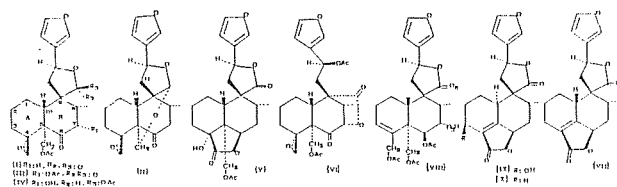


Fig.4

**09.2-46** CONFORMATIONAL AND STRUCTURAL RELATIONSHIPS BETWEEN TEN DITERPENOIDS FROM TEUCRIUM SPECIES. By L. Eguren, J. Fayos and A. Perales, X-Ray Department, Instituto "Rocasolano", C.S.I.C., Serrano 119, Madrid-6, Spain.

The chemistry of diterpenoids occurring in the genus Teucrium, is described in a recent general review (Piozzi, Heterocycles. (1981) in press). The structures of ten of these compounds shown below have been determined by X-Ray diffraction.



The purpose of this study is to classify these compounds according to the conformation of their rings. Special attention has been devoted to the decaline group. Parameters definition: for this study Cremer's parameters have been used (Cremer and Pople, J. Am. Chem. Soc. (1975) 97(6), 1354-58),  $\theta$  ( $^\circ$ ),  $\phi$  ( $^\circ$ ) and  $Q$  (Å). Chairs occur for  $\theta=0, 180^\circ$ , and boat or twist for  $\theta=90^\circ$ .  $\phi$  describes the boat form ( $\phi=0, 60, 120, \dots$ ) and twist form ( $\phi=30, 90, 150, \dots$ ), and  $Q$  the puckering. The table shows the experimental X-Ray values for the decaline moieties.  $\tau_A$  is the internal torsion C1-C10-C5-C4 and  $\tau_B$  is C6-C5-C10-C9. It is observed that  $\langle \tau_A + \tau_B \rangle$  is nearly constant:  $108^\circ$  for  $sp^3-sp^3$  bonds and  $53^\circ$  for  $sp^2-sp^3$  bonds. The  $108^\circ$  value is diminished by the C5-C9 axial interaction and the oxo substituted C6 in compounds I, IV and VI. For saturated cyclohexane rings  $Q_i$  increases with  $\theta_i$  to reach a maximum at  $\theta_i \sim 90^\circ$  and decreases again towards  $\theta_i \sim 180^\circ$ ,