

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 (2S,4S,5R)- and (2R,4S,5R)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-thione (A and B) were synthesized from (-)ephedrine i.e. 1R,2S-2-methylamino-1-phenylpropan-1-ol (Inch and al. J. Chem. Soc., Perkin 1 1977, 1969-1980). The ¹H NMR spectra of A and B were not easy to interpret and the configuration at the P atom was assigned as P_R for A and P_S 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 (2R,4S,5R)-2-anilido-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine-2-thione (C) and (2R,4S,5R)-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_S and P_R 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 P2₁2₁2₁. 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, C₁₇H₂₆S₄N₂. 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 P2₁/n, with the following cell dimensions: a = 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_o > 4σ(F_o) 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-thiazetidines (1) to be Z,Z. Crystal data for C₂₀H₂₆N₄O₂S (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) Å³, space group P $\bar{1}$, D_m = 1.22 g cm⁻³, D_c (Z = 2) = 1.22 g cm⁻³. 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-thiazetidines (2), one of the products of the reaction of a bis(imino)thiazetidines 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 C₂₁H₃₂N₄O₂S₂ (M = 436) are :

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