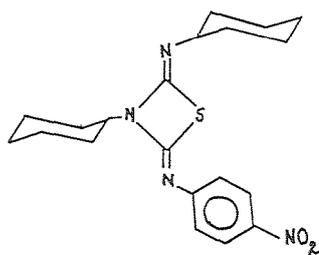
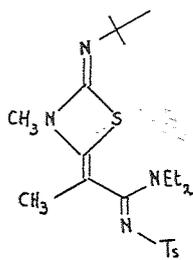


$\beta = 108.31(4)^\circ$, $U = 2401(2) \text{ \AA}^3$, space group $P2_1/n$,
 $D_m = 1.20 \text{ g cm}^{-3}$, $D_c (Z = 4) = 1.21 \text{ g cm}^{-3}$.



(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:

4CN-K($C_4H_2N_3O_3SK \cdot H_2O$): $a=9.811(1)$; $b=7.296(1)$; $c=5.858(1) \text{ \AA}$
 $\alpha=103.06(1)$; $\beta=94.56(2)$; $\gamma=100.51(2)^\circ$; $Z=2$; $P\bar{1}$; n° reflex. in refinement 2835.

4NO2-K($C_3H_2N_3O_5SK \cdot H_2O$): $a=6.0744(4)$; $b=18.583(2) \text{ \AA}$
 $c=7.497(1) \text{ \AA}$; $\beta=91.68(1)^\circ$; $Z=4$; $P2_1/c$; n° reflex. in refinement 2006.

Both structures have been solved by using single crystal data and MoK α 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

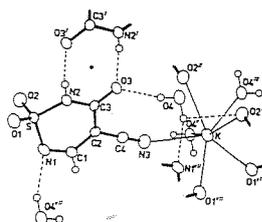


Fig.1

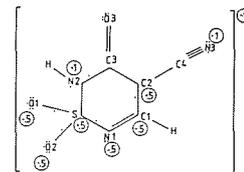


Fig.3

4NO2-K

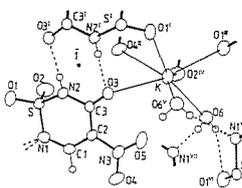


Fig.2

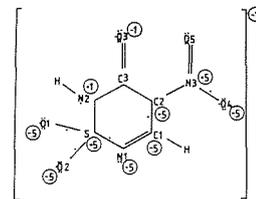
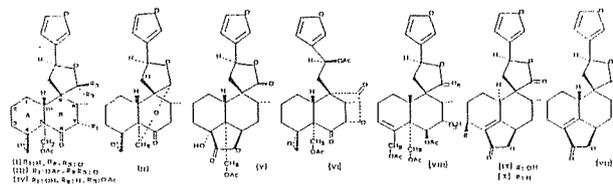


Fig.4

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), θ ($^\circ$), ϕ ($^\circ$) and Q (Å). Chairs occur for $\theta=0, 180^\circ$, and boat or twist for $\theta=90^\circ$. ϕ 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. τ_A is the internal torsion C1-C10-C5-C4 and τ_B is C6-C5-C10-C9. It is observed that $\langle \tau_A + \tau_B \rangle$ is nearly constant: 108° for sp^3-sp^3 bonds and 53° for sp^2-sp^3 bonds. The 108° 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 θ_i to reach a maximum at $\theta_i \sim 90^\circ$ and decreases again towards $\theta_i \sim 180^\circ$,

although for chairs Q_A remains almost constant.

Com pound	θ_A	ϕ_A	Q_A	τ_A	$\tau_A + \tau_B$	τ_B	Q_B	ϕ_B	θ_B
I	6	222	.60	-57.8	102.9	45.1	.50	223	6
II	7	350	.57	-55.2	107.2	52.0	.80	39	80
III	9	251	.61	-62.5	109.4	46.9	.76	71	98
IV	16	293	.62	-65.9	103.2	37.3	.74	72	104
V	18	309	.59	-64.2	114.4	50.2	.51	1	4
VI	18	259	.62	-68.8	102.3	32.5	.67	293	30
VII	47	359	.56	-34.7	60.2	25.5	.84	28	94
VIII	51	304	.55	-60.2	108.0	47.8	.51	192	8
IX	125	229	.50	1.1	49.3	-48.2	.57	118	166
X	123	226	.50	-0.6	50.4	-49.8	.57	128	169

- Compounds with ring A being cyclohexane. Ring A takes a chair conformation only distorted by the ring B. Ring B is in a chair conformation when no substituent is present in C7 and boat otherwise. In II, ring B is in a twist conformation due to the influence of the twist pyranoid ring. In VI, due to the lactonic bridge, ring B is a chair slightly distorted to boat.

- Compounds with ring A being cyclohexene. Rings A are envelopes with the flap at the atoms as predicted by Bucourt (Bucourt and Hainaut. Bull. Soc. Chim. Fr. (1975) 2, 1366-78) for cyclohexenes. In VII, ring B is forced to boat by the α, β -unsaturated γ -lactone ring; there is some deformation to twist induced by the C6-C9 substituent interaction; envelope A has the flap at C1. In VIII, ring B is chair by the interaction between C4-C6 substituents, there is also an α H-bond O3-H...O8; the τ_A angle induced for τ_B , produces envelope A with the flap at C10. The compounds IX and X with α H10 have rings B with no 1,3 axial interaction, being in a chair conformation; the high value of τ_B induces τ_A to be zero defining the envelope A with the flap at C2.

- Five membered rings. All γ -lactone rings, are envelopes with $\tau=0$ in the lactonic group, except for VII. The α, β unsaturated γ -lactone rings are almost planar.

09.3-01 STRUCTURAL INVESTIGATIONS OF LIQUID CLATHRATE PARENT COMPLEXES: THE CRYSTAL AND MOLECULAR STRUCTURES OF $K_2[Al_4Me_{12}SO_4]$, $K_2[Al_4Me_{12}SO_4] \cdot 0.5 p\text{-Me}_2\text{C}_6\text{H}_4$, and $K[Al_7O_6C_{16}H_{48}] \cdot C_6H_6$. R. D. Rogers, D. C. Hrcir, and J. L. Atwood, Department of Chemistry, University of Alabama, University, Alabama, 35486.

The interaction of tri-alkyl aluminum with metal halides and pseudo halides to form complexes of the type $M[Al_2R_6X]$ has been of interest for quite some time. Our primary goal has been to find those complexes which trap aromatic molecules in either the liquid or solid state. Expansion of the metal salts capable of forming liquid clathrates has led away from compounds restricted to the general formulation above. We have recently completed two structural studies on $K_2[Al_4Me_{12}SO_4]$. One was crystallized from benzene and contained no solvent molecules, while the same compound taken from para-xylene resulted in 0.5 mole of p-xylene of crystallization. $K_2[Al_4Me_{12}SO_4]$ crystallizes in the monoclinic space group $P2_1/c$ with $a=10.223(4)$, $b=20.225(5)$, $c=14.039(4)$ Å, $\beta=112.20(2)^\circ$ and $D_c=1.14$ g cm $^{-3}$ for $Z=4$. This compound was refined to a final R value of 0.095 for 1576 independent observed reflections. $K_2[Al_4Me_{12}SO_4] \cdot 0.5 p\text{-Me}_2\text{C}_6\text{H}_4$ was also monoclinic, $P2_1/c$, with $a=9.773(3)$, $b=15.497(4)$, $c=20.442(4)$ Å, $\beta=92.51(2)^\circ$, $D_c=1.11$ g cm $^{-3}$, $Z=4$ and $R_{\text{final}}=0.055$ for 1300 reflections. The third compound, $K[Al_7O_6C_{16}H_{48}] \cdot C_6H_6$, was prepared by the reaction of KO_2 with trimethylaluminum, and crystallizes in the triclinic space group $P\bar{1}$ with $a=12.095(4)$, $b=12.222(4)$, $c=13.893(4)$ Å, $\alpha=105.56(3)$, $\beta=94.52(2)$, $\gamma=83.98(2)^\circ$, $D_c=1.09$ g cm $^{-3}$, $Z=2$ and $R_{\text{final}}=0.042$ for 2509 observed reflections. Comparisons between structural characteristics and liquid clathrate behavior will be discussed.

09.3-02 THE X-RAY STUDY OF ORGANOSILOXANES.

By V.E. Shklover, I.L. Dubchak, T.V. Timofeeva and Yu.T. Struchkov, Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences Moscow, USSR.

Crystal structure investigation provides valuable information for better understanding of physico-chemical properties of monomeric organosiloxanes (OS) and corresponding polymers. In this report we describe some specific features of crystal structures of OS belonging to different structural types. Crystals of ionic OS which are important in silicon chemistry, viz. $Na(Me_3SiO) \cdot 3H_2O$ (I), $Na_2[(Me_2SiO)_2O] \cdot 4H_2O$ (II) and $Na_3[PhSi(O)O]_3 \cdot 8H_2O$ (III), are built of alternating hydrophobic (organic radicals) and hydrophilic layers (H-bonds of a moderate strength with participation of water molecules and ionic interactions $Na^+ \dots O^-$). In contrast to I-III in crystals of cis- $\{[MeSi(OH)O](Ph_2SiO)\}_2$ (IV) trans- $\{[Me_2Si(OH)O](Ph_2SiO)\}_2$ (V) and trans- $\{[(HO)_2SiO](Ph_2SiO)\}_2 \cdot 2Py$ (VI) H-bonds are formed by SiOH-groups. In VI solvating Py molecules also participate in H-bonds. The porous packing and inclusion of solvent are observed in crystals of simple OS I, $(Ph_2Si)_2O \cdot 1/2C_6H_6$ (VII, SiOSi bond angle of 180°) and OS with framework structure $(PhSiO_{1.5})_8 \cdot C_6H_6$ (VIII) and $[O(Ph_2SiO)_2Si](NH)_3 \cdot C_6H_6$ (IX). The flexibility of SiO patterns of OS (variation of SiOSi bond angles within the range of $130-180^\circ$, and of Si-O distances within the range of 1.57-1.65 Å) explains the frequent occurrence of disorder of surrounding hydrocarbon radicals (in IX and spiro-OS $\{[MeVnSi(OPh_2SiO)_2SiO](Ph_2SiO)\}_2$ (X) and of the SiO-framework itself (cycloliner OS $\{[(Me_2SiO)_2O] \cdot (SiO)_2\}_2O_2$ (XI) and also looseness of packing in OS crystals. To characterize this looseness an analysis of molecular environment was carried out which showed molecules of flexible OS to occupy larger volume than that expected on the ground of standard values of van der Waals radii. On the basis of the analysis of molecular packing possibility of polymerisation in crystals of cis- (XII) and trans- $(MePhSiO)_3$ (XIII), and also $[O(Ph_2SiO)_3 \cdot (CH=CHSi)_2]$ (XIV) is considered.