

although for chairs  $Q_1$  remains almost constant.

Com pound	$\theta_A$	$\phi_A$	$Q_A$	$\tau_A$	$\tau_A + \tau_B$	$\tau_B$	$Q_B$	$\phi_B$	$\theta_B$
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  $\alpha, \beta$ -unsaturated  $\gamma$ -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  $\alpha$  H-bond O3-H...O8; the  $\tau_A$  angle induced for  $\tau_B$ , produces envelope A with the flap at C10. The compounds IX and X with  $\alpha$  H10 have rings B with no 1,3 axial interaction, being in a chair conformation; the high value of  $\tau_B$  induces  $\tau_A$  to be zero defining the envelope A with the flap at C2.

- Five membered rings. All  $\gamma$ -lactone rings, are envelopes with  $\tau=0$  in the lactonic group, except for VII. The  $\alpha, \beta$  unsaturated  $\gamma$ -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  $D_c=1.14\text{g cm}^{-3}$  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,  $\beta=92.51(2)^\circ$ ,  $D_c=1.11\text{g cm}^{-3}$ ,  $Z=4$  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,  $\alpha=105.56(3)$ ,  $\beta=94.52(2)$ ,  $\gamma=83.98(2)^\circ$ ,  $D_c=1.09\text{g cm}^{-3}$ ,  $Z=2$  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.

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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,  $(Ph_3Si)_2O \cdot 1/2C_6H_6$  (VII, SiOSi bond angle of  $180^\circ$ ) 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  $\{[MeVinSi(OPh_2SiO)_2SiO](Ph_2SiO)\}_2$  (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.