

07-Crystallography of Organometallic and Coordination Compounds

199

MS-07.01.06 ORGANIC INCLUSION COMPOUNDS: RELATING STRUCTURE TO THERMAL STABILITY.

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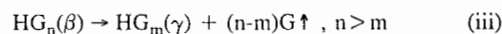
WHEN a suitable host compound H is dissolved in a volatile guest G or is exposed to its vapour, it forms an inclusion compound $HG_n(\beta\text{-phase})$. The latter may decompose in one of several ways. It may lose the guest and the host may revert to its non-porous α -phase:



Alternatively, the host may lose the guest but retain its structural integrity, displaying the empty cage, or β_0 structure:



Thirdly, it may lose only part of the guest and form a new γ phase:

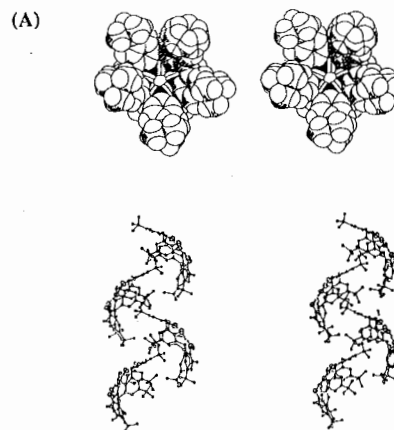


We have synthesised a variety of inclusion compounds of crowded hydroxy hosts which entrap volatile guests, and have elucidated their crystal structures. Their thermal decompositions have been studied using Thermal Gravimetry (TG) and Differential Scanning Calorimetry (DSC). The vapour pressures of these compounds has been measured over a range of temperatures, yielding enthalpy values for the reactions. Phase changes during decomposition have been monitored by X-Ray powder diffraction. The kinetics of inclusion have been measured by subjecting the α -phase of the host to the vapour of the guest and recording the gain in mass under varying conditions of temperature and pressure.

OPS-07.01.07 THE STRUCTURES OF CALIXARENES.

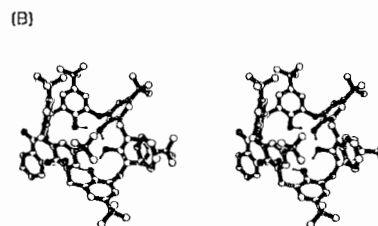
G. Ferguson & J.F. Gallagher, University of Guelph, Ontario, Canada, N1G 2W1, M.A. McKervey, Queens University, Belfast, Northern Ireland and V. Bohmer, Johannes Gutenberg Universitat Mainz, Germany.

We are currently studying the molecular structures of calix[4]-calix[5]- and calix[6]-arenes and their metal complexes. Until recently, there have been few structural studies reported for calix[5]-arenes, mainly due to difficulties with synthesis and purification. Several structures will be described including the following:



(A) $[t\text{-buC}_6\text{H}_2(\text{CH}_2)\text{OH}]_5$, monoclinic, $C2/c$, $a = 34.687(3)$, $b = 13.396(2)$, $c = 25.721(2)$ Å, $\beta = 113.518(7)^\circ$, $V = 10959(2)$ Å³, $Z = 8$, $D_x = 1.01$ gcm⁻³, $R = 0.066$ for 2591 reflections $\geq 3\sigma(I)$.

The open distorted chalice shaped conformation in (A), primarily resulting from O-H...O hydrogen-bonding, facilitates the enclathration of a neighbouring *t*-butyl group in a self-inclusion process that extends through the lattice as a molecular 'zipper'.



(B) $[(t\text{-buC}_6\text{H}_2(\text{CH}_2)\text{OH})_4\{t\text{-buC}_6\text{H}_2(\text{CH}_2)\text{O}\}_2\text{C}_6\text{H}_4(\text{CO})_2]$, monoclinic, $P2_1/n$, $a = 14.555(1)$, $b = 35.380(2)$, $c = 15.016(2)$ Å, $\beta = 99.782(7)^\circ$, $V = 7620(1)$ Å³, $Z = 4$, $D_x = 1.06$ gcm⁻³, $R = 0.075$ for 4028 reflections $\geq 3\sigma(I)$. The molecular cavity in (B) is primarily filled by the phthaloyl residue of another calix[6]arene molecule giving rise to a self-inclusion process. Benzene molecules reside in 'voids' between the calix[6]arenes.

OPS-07.01.08

STRUCTURE AND CONFORMATION OF TWO STEREOISOMERIC C-ALKYLCALIX[4]RESORCINARENES. By Bruno Botta, Giuliano Delle Monache, Domenico Misiti, Antonello Santini, Carlo Pedone and Ettore Benedetti, Centro Chimica dei Recettori C.N.R., Università Cattolica Roma, Istituto di Industrie Agrarie and Dipartimento di Chimica, Università di Napoli, Italy.

Calixarenes represent an interesting family of structures which exhibit characteristic features of cation receptors, carriers, etc. Treatment of (E)-2,4-dimethoxycinnamic acid isopropylesters with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in CHCl_3 at room temperature afforded various C-alkylcalix[4]resorcinarenes (Botta *et al.*, 1992), which differ for their conformation. Crystals of isomer C and D were obtained by slow evaporation of CHCl_3 - CH_3OH mixtures at room temperature. Both isomers are triclinic, space group $P\bar{1}$, with $Z=2$. Isomer C has