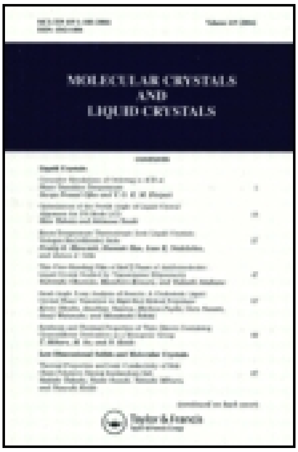

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Solid State Chemistry of Calixarenes and Supramolecular Systems with Calixarenes

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SOLID STATE CHEMISTRY OF CALIXARENES AND SUPRAMOLECULAR SYSTEMS WITH CALIXARENES

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Abstract

Two aspects of the solid state chemistry of calixarenes are presented : in the first part the chlorination of isopropyl and tert-butylcalixarenes is studied, a mechanism is proposed. In the second part the thermal rearrangement of supramolecular systems p-isopropylcalix[4]arene-p-xylene is discussed, the thermal decapsulation of the guest molecules is schematized.

INTRODUCTION

In 1978 GUTSCHE introduced the term "calixarene" to describe the cyclic oligomers produced by condensation of p-substituted phenols with formaldehyde. The name is derived from the Greek calix meaning "vase" or "chalice" and arene which indicates the presence of aryl residues in the macrocyclic array [1,2].

Two aspects of the behaviour of solid state calixarenes are presented in this work.
Firstly, it is shown that isopropyl and tert-butylcalix [4], [6] and [8] arenes can be chlorinated in the solid state by chlorine gas in mild conditions.
Secondly, it is shown that supramolecular systems with calixarenes can be thermally rearranged.

I. SOLID STATE REACTIVITY OF CALIXARENES

The study of calixarene reactivity in the solid state is important for several reasons. Firstly, these substances are only slightly soluble in most common solvents and melt at relatively high temperatures. Secondly, calixarenes are organic molecules of high molecular weight and of the same nature as phenolic resins which are reputed for being inert towards many chemical reactants. Thirdly, many functionalization studies on calixarenes in solution have been carried out in the few solvents which allow sufficient solubilization, but no studies have been published concerning their reactivity in the solid state.

TABLE I Calixarenes studied.

Compound	Empirical formula	Melting point (°C)
p-tert-butylcalix[4]arene	$C_{44}H_{56}O_4$	344
p-isopropylcalix[4]arene	$C_{40}H_{48}O_4$	293
p-tert-butylcalix[6]arene	$C_{66}H_{84}O_6$	380
p-isopropylcalix[6]arene	$C_{60}H_{72}O_6$	350
p-tert-butylcalix[8]arene	$C_{88}H_{112}O_8$	411
p-isopropylcalix[8]arene	$C_{80}H_{96}O_8$	370
calix[6]arene	$C_{42}H_{36}O_6$	>300

Chlorination experiments were carried out in a pyrex reactor at 50°C. The compound to be chlorinated is introduced in a known quantity in the thermoregulated cell maintained at 50°C. The air is evacuated, and nitrogen is passed over the surface. This operation is repeated three times. Chlorine is then introduced at a pressure of 1 bar. After 48 hours reaction time, the chlorine is evacuated using nitrogen and the reactor is maintained under vacuum for 30 mn. The calixarenes remain in the solid state during the whole reaction due to their high melting points. The chlorine content is determined by micronalysis and by weighing. We verified beforehand that the chlorinated compounds did not contain any residual hydrochloric acid, which could modify the analyses. A Karl-Fisher type titration shows that the samples do not contain any water. Among the studied calixarenes, the rather singular behaviour of calix[6]arene has been noted. In the crystallized state[3], it does not react with chlorine, whereas when only partially crystallized it does react.

TABLE II Number of chlorine atom per phenolic moiety.

Calixarene	Number of chlorine atoms per moiety	
	Weighing	Microanalysis
P-TBU-4-Cl	2.5	3
P-ISO-4-Cl	2.7	2.5
P-TBU-6-Cl	2.8	3
P-ISO-6-Cl	2	2.3
P-TBU-8-Cl	2.8	2.8
P-ISO-8-Cl	2.5	2.6
P-H-6-Cl	2.6	2.5

Both methods are in excellent agreement and show that all the calixarenes have reacted, the number of chlorine atoms introduced varying on average between 2 and 3.

Gas chromatography analysis shows the absence of small molecules in the reaction product. Mass spectrometry analysis using the FAB positive ionization method confirms that the chlorination reaction does not degrade the calixarene molecules and leads to compounds which conserve their cyclic nature. In this way, for compound P-ISO-4-Cl we observe the mass distributions, the highest of which corresponds to a derivative containing 13 chlorine atoms.

Microanalysis of P-ISO-4-Cl establishes the presence of 10 chlorine atoms in the compound, which allows us to state that P-ISO-4-Cl is constitued of calixarenes which are chlorinated to a greater or lesser extent : the number of chlorine atoms estimated by microanalysis is only a mean value.

In order to determine the nature of the products formed, we have undertaken a study using ultraviolet and infrared spectrometries. NMR ^{13}C is also taken into account and confirms the results provide by UV and IR studies. These three methods allowed us to determine the different possible structures of the formed compounds.

As calixarenes are constitued of phenolic moieties, their reaction with chlorine can form compounds such as chlorophenols, chlorocyclohexadienones and chlorocyclohexanones [4].

TABLE III UV absorption of chlorinated calixarenes.

Compound	Wavelength (nm)	Concentration (mg/l)
P-TBU-4-Cl	296 233 <210	25.95
P-ISO-4-Cl	239.4 <210	23.60
P-TBU-6-Cl	295 241.5 <210	24.90
P-ISO-6-Cl	242.1 <210	25.90
P-TBU-8-Cl	295 241.5 <210	41.75
P-ISO-8-Cl	242.9 <210	29.9
P-H-6-Cl	290 250 225 200	45.00 (partially soluble)

According to the above table, the absorption band in the vicinity of 240 nm is common to all the compounds and it is also intense. This band is attributed to the presence of paracyclohexadienone. We noted the absence of orthocyclohexadienone as no band can be found in the region 290-350 nm. The weak band at 295 nm is only observed for derivatives containing the tertiobutyl group. It is therefore not due to the R band of paracylohexadienone, but to residual phenolic moieties in the formed compounds. Finally, the absorption band in the vicinity of 200 nm is attributed to a chromophore, double bond or carbonyl group containing an auxochrome substituent (chlorine, alkyl, etc...). The spectra of tert-butyl derivatives differ from those of isopropyl derivatives by the presence of an absorption band at 295 nm. The spectrum of compound P-H-6-Cl is different from the spectra of the other compounds, the intensity of the band at 200 nm being much greater than that of the bands at 250 and 290 nm. This shows that the nature of the formed products depends on the alkyl group.

In infrared studies, the stretching vibration band ν OH of the calixarene absorbing in the vicinity of 3150 cm-1 has disappeared, which implies that the solid state chlorination reaction is complete in all cases. In the region 1750-1640 cm^{-1}, the spectra show the appearance of 4 bands at 1745, 1700, 1670 and 1648 cm^{-1}. The first three are attributed to the stretching vibration ν C = O of the carbonyl group, whereas the intense band at 1648 cm^{-1} is associated to the stretching vibration of the C = C bond conjugated with the carbonyl group. The absorption at 1670 cm^{-1} which is associated to it, is at least of the same intensity if not stronger. This value at 1648 cm-1 is characteristic of paracyclohexadienone with large substituents, such as a tertbutyl group in the ortho position. The two bands ν C = 0 observed at 1700 cm^{-1} and 1745 cm^{-1} arise from a mono or disubstituted carbonyl group in the α or α' position by one or two atoms of chlorine 5. In all the spectra, for the range 1500-1350 cm^{-1}, it can be noted that the band at 1480 cm^{-1}, attributed to vibrations in the plane of the aromatic skeleton, has disappeared. Furthermore, we observe that the absorption bands of the tert-butyl and isopropyl groups are not modified ; the chlorination has therefore taken place on the aromatic nucleus.

NMR ^{13}C analysis provides complementary information concerning the previously supposed structures. The carbon atoms are identified by the DEPT method. It is shown that the methylenic carbon atoms are substitued in the α or α' position by a chlorine atom and that there is no gemdihalogenated carbon.

Chlorination of calixarenes in the solid state therefore leads, in parts, to the formation of structures of a dienone type. The following reaction diagram (Figure 1) shows the different structures containing one to five chlorine atoms that we believe to exist in the form of macrocycles defined by 4, 6 or 8 of these structural units.

We have introduced an orthocyclohexadienone into the reaction diagram according to pathway A. Although theoretically possible, the formation of this intermediate has not been observed among the final products, no doubt due to the fact that 2-5 dienones are more stable than their 2-4 isomers .

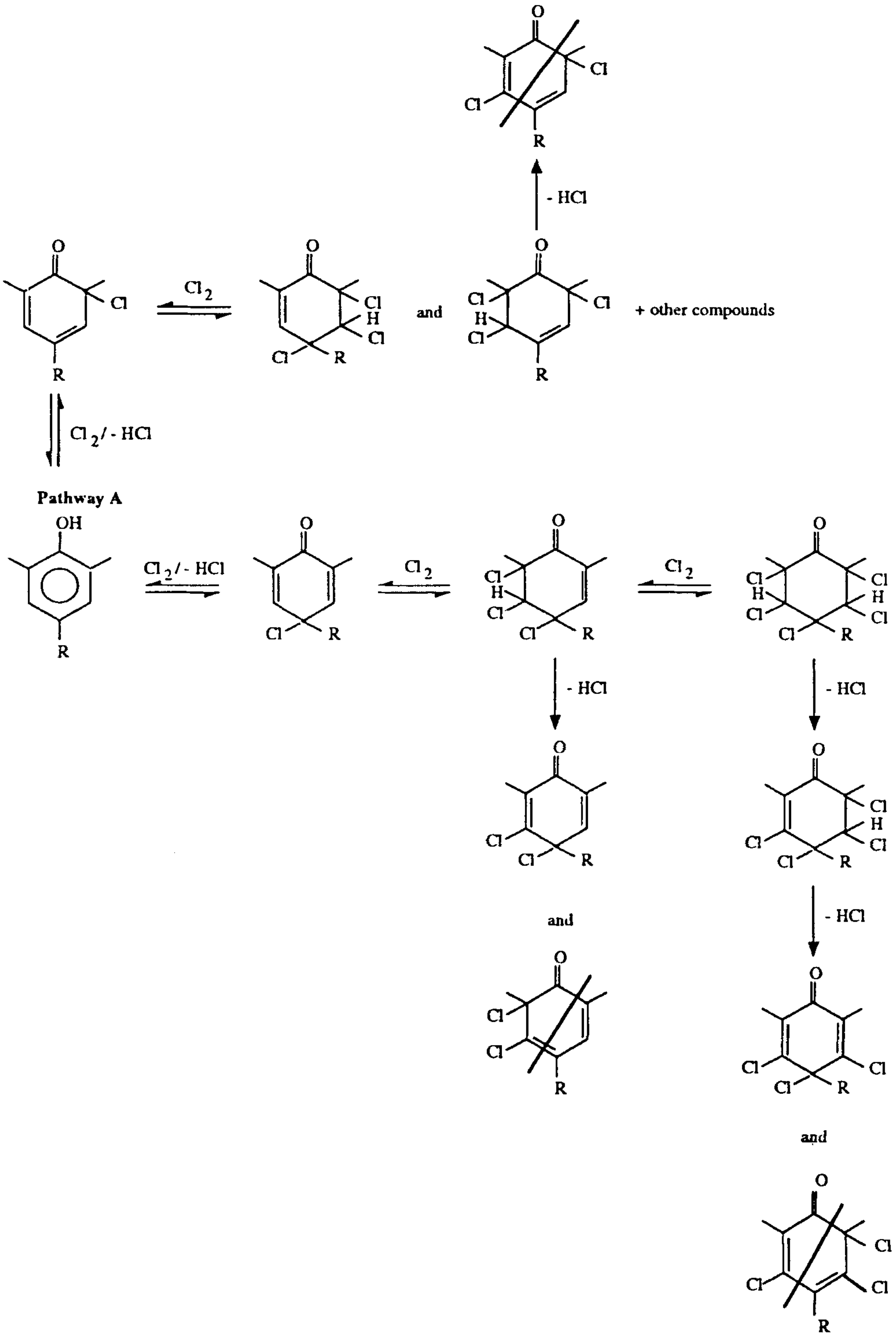

FIGURE 1 Reaction diagram showing the different chlorinated structures.

II. COMPLEXATION - SOLID STATE REARRANGEMENT

Many of the calixarenes form complexes in the solid state. According to the cavity topology, size and substituent distribution, the complexing properties of calixarenes vary as also the tenacity with which the guest molecule is held by the calixarene. We observe that cyclic octamer loses the guest molecule in few minutes whereas the cyclic tetramer retains the solvent for many hours at room temperature.

In the case of p-isopropylcalix[4]arene we obtain easily from a saturated solution in p-xylene at room temperature a 1 : 1 complex. The crystal structure shows where the solvent molecules are located in the crystals (Figure 2). The p-xylene molecule is inside the macrocycle giving a supramolecule with CH$_3\Pi$ interactions between the methyl carbon atoms of p-xylene and the aromatic rings of calixarene. The packing of the 1 : 1 complex can be described as slices of macrocycles with the aperture alternatively up and down.

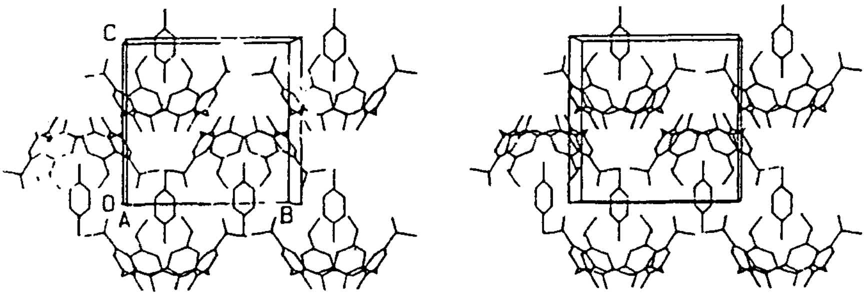

FIGURE 2 Stereoscopic views along [100] of the packing for the 1 : 1 complex.

On heating the 1 : 1 complex is transformed by loss of p-xylene[6]. The differential scanning calorimetry curve (Figure 3) recorded at 20°C min^{-1} shows three endothermic peaks : the initial endotherm with a maximum at 78°C corresponds to the release of some guest molecules (ΔH = 10.94 kJ mol^{-1}), the second endotherm at 170°C, (ΔH = 17.52 kJ mol^{-1}) corresponds to the release of the remaining p-xylene molecules. This is followed by a final endotherm peak between 270 and 310°C (ΔH = 68.77 kJ mol^{-1}). The thermogravimetric curve (Figure 4) shows a total mass loss of 15.09 %, when the theoretical value is 15.19 % for the 1 : 1 complex. Therefore with heat, between 52 and 83°C, the 1 : 1 complex releases one of the two xylene molecules and gives rise to a 2 : 1 complex. Then by increasing the temperature, between 157 and 212°C the remaining xylene molecules are released and the empty calixarene appeared.

In order to investigate the thermal transformation the 2 : 1 complex and the empty form were prepared and their crystal structures carried out (Figure 5). The 2 : 1 complex is obtained from evaporation at 85°C of a saturated solution of calixarene in p-xylene. The empty calixarene is obtained from evaporation at 65°C of a solution in molten menthol. The crystal structure of the 2 : 1 complex shows that two macrocycles encapsulate the p-xylene molecule.

The two methyl carbon atoms of p-xylene lie at 3.70 Å from the aromatic ring plane. The empty form shows that two macrocycles related by a center of symmetry are in position such that a methyl group of the isopropyl substituent lies inside the cavity. These dimers are repeated in the crystal with Van Der Waals interactions.

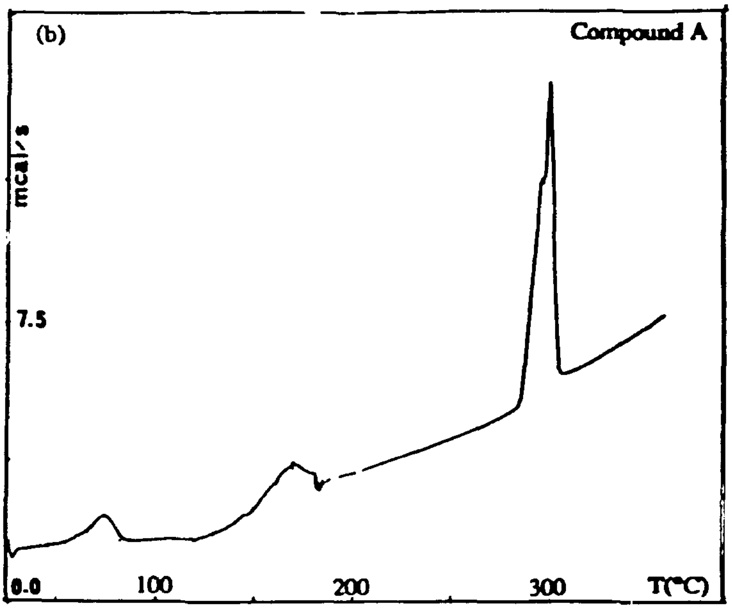

FIGURE 3 Thermal analysis curve of the 1 : 1 complex.

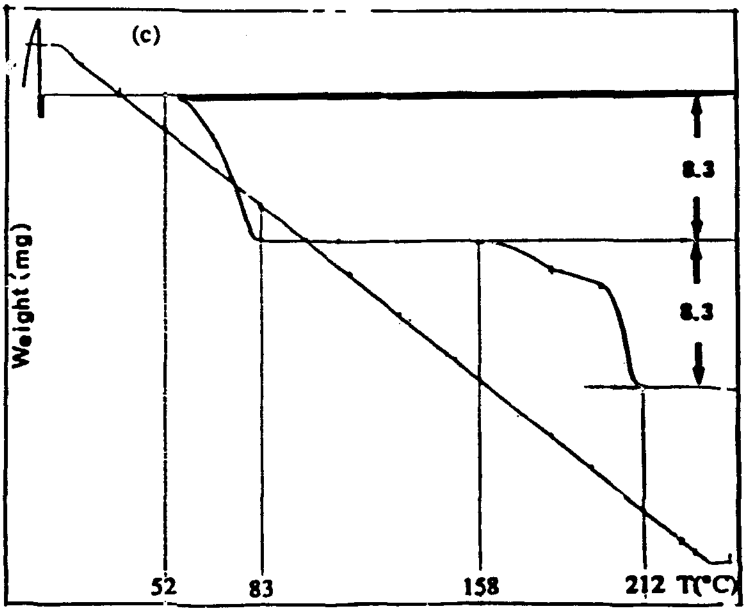

FIGURE 4 Thermogravimetric curve of the 1 : 1 complex.

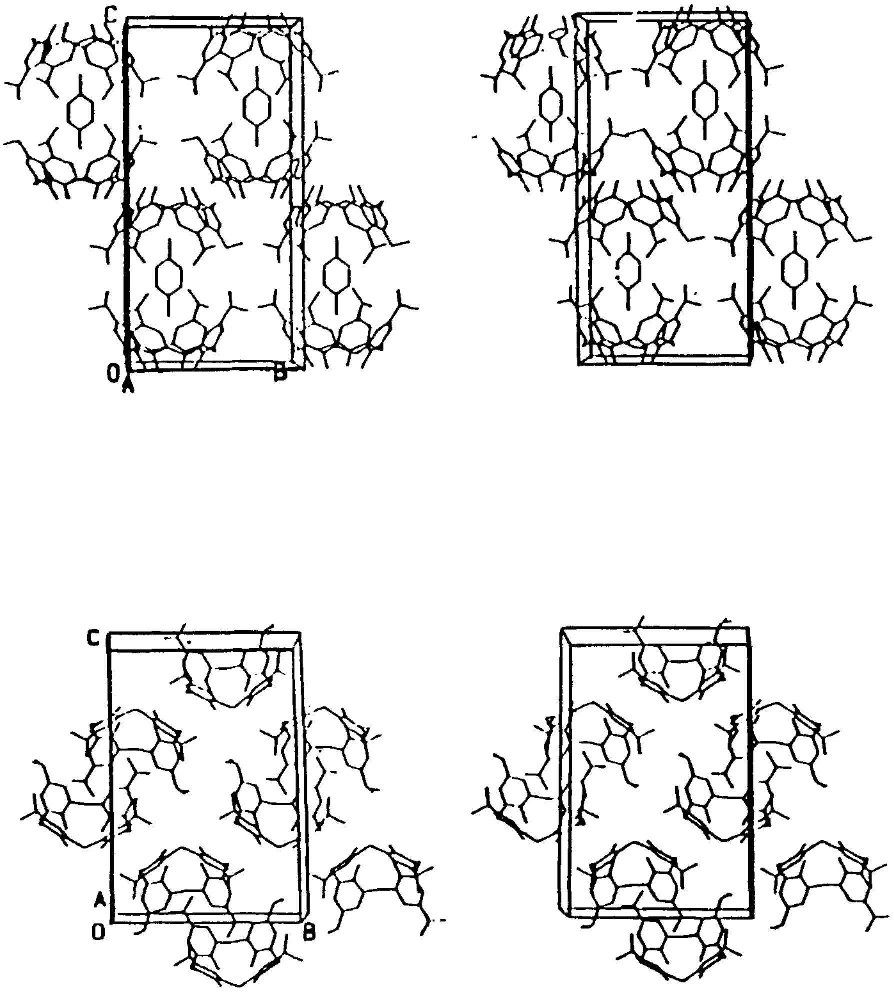

FIGURE 5 Stereoscopic view along [100] of the packing for the 2 : 1 complex and the empty form.

The crystal structures of the three compounds specify how the guest molecule is enclosed in the macrocycles ; the host macrocycle adapts its conformation with the shape and symmetry of the guest. On heating the rearrangement of the macrocycles is possible. From the 1 : 1 complex it seems rather easy to lose one half of the p-xylene molecule. In the 2 : 1 complex the guest molecule is well encapsulated in a closed cage and it will be more difficult to lose this p-xylene. However at higher temperature the guest is lost and the macrocycles rearranged to get as close as possible with new $CH_3\Pi$ interactions. The phenomena of thermal decapsulation with the rearrangement of the macrocyles can be schematized as follows (Figure.6) : the p-xylene molecule insides the macrocycle in the 1 : 1 complex ; by a translation two macrocycles set face to face and encapsulate the p-xylene molecule in the 2 : 1 complex ; the macrocycles rearrange as close as possible for better close packing in the empty form.

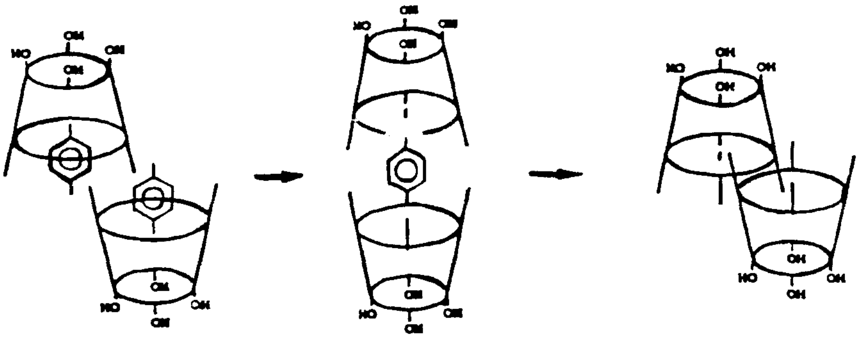

FIGURE 6 Scheme of decapsulation.

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