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A CNDO/2 Study of the Polymerization of Beryllium Chloride

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The LCGO-CNDO/2 method has been applied in a study of polymer molecules of the type $(BeCl_2)_n$ for values of n between 2 and 6. The calculations predict chain stretching and increasing covalent character of the Be–Cl ring bonds as polymerization proceeds.

Key words: Polymerization of $BeCl_2$ – Beryllium Chloride

Apart from ground-state equilibrium bond angle calculations of the monomeric species BeX_2 ($X = F$, Cl) [1, 2], no molecular orbital studies of the polymerization process of beryllium halides appear to have been reported. In the present paper, we have applied the LCGO-CNDO/2 method [3] in a study of the polymerization mechanism and the nature of the bonds in $BeCl_2$ chains comprising 2 to 6 units. Particular attention was devoted to the formation of the beryllium chloride dimer, since this species is of primary importance in determining the subsequent polymerization steps.

The atomic orbitals employed in this work are represented by linear combinations of gaussian functions using numerical values for $2s$(Be), $3s$(Cl) and $3p$(Cl) published by Roos and Siegbahn [4]. The orbital exponent α for the three $2p$ orbitals of beryllium was estimated by optimization of the Be-Cl distance in the linear $BeCl_2$ monomer molecule, taking the experimentally determined Be–Cl bond length of 1.77 Å as a guide [5, 6]. A satisfactory fit was found when $\alpha(2p) = 0.45$, and this value was used for the computation of each polymeric species up to and including $(BeCl_2)_6$.

In the calculation of different static geometries of condensed $BeCl_2$ molecules in the polymerization sequence, we considered two polymerization schemes based on the experimentally established structure of solid beryllium chloride ($d_{Be-Be} = 2.63$ Å; $d_{Be-Cl(ring)} = 2.02$ Å) [7] (Fig. 1).

Scheme 1 represents the progressive condensation of $BeCl_2$ molecules resulting from bond formation of two Cl-atoms of the same molecule with the Be-atom of another $BeCl_2$ unit. In Scheme 2, the interaction of two linear $BeCl_2$ molecules

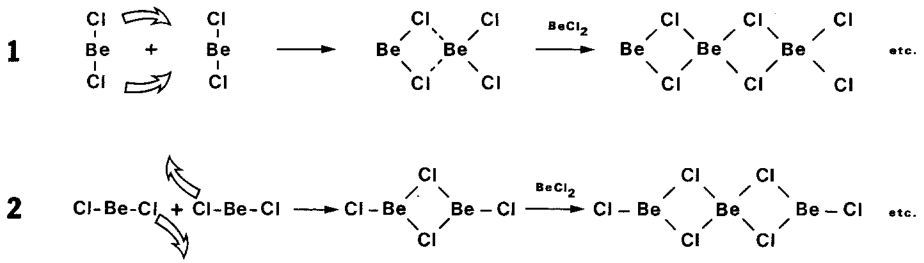

Fig. 1. Polymerization schemes for $(BeCl_2)_n$. Distances and ring angles as in polymeric $BeCl_2$ [7]

Table 1. Total energies and electronic charge distribution for terminal atoms in $(BeCl_2)_n$

Value of n in $(BeCl_2)_n$	Total energy (a.u.)		Charge on first Be-atom		Charge on terminal Cl-atoms	
	Scheme 1	Scheme 2	Scheme 1	Scheme 2	Scheme 1	Scheme 2
2	− 73.1670	− 73.3446	0.63	0.30	−0.31	−0.24
3	−109.8649	−110.0963	0.68	0.30	−0.36	−0.25
4	−146.5831	−146.8447	0.71	0.30	−0.38	−0.25
5	−183.3092	−183.5892	0.72	0.30	−0.39	−0.25
6	−220.0370	−220.3291	0.74	0.30	−0.39	−0.25

approaching end to end along the bond axis leads to a symmetrical cyclic system comprised by one Cl-atom from each molecule. Calculated values for these models are given in Table 1.

It is evident that the total energy calculated for corresponding polymers is markedly lower for Scheme 2. This is consistent with the fact that in this model less deformation is required for the Cl–Be–Cl bond angle of the reacting monomer molecule. Moreover, the initial Be atom in Scheme 2 has more favorable (i.e., sp^2) hybridization.

Although the observed charge distribution would in itself account for the addition of further $BeCl_2$ units in the polymerization process, a more representative interpretation is given by the polymerization energy associated with the reaction

$$(BeCl_2)_{n-1} + BeCl_2 \longrightarrow (BeCl_2)_n + \Delta E$$

Taking the calculated total energy of −36.6317 a.u. for the linear $BeCl_2$ monomer, it is found for the energetically favored second scheme that ΔE corresponds to negative energy increments and hence favorable energies of polymerization for each step of the sequence up to and including the formation of the hexamer (Table 2).

The relatively large energy decrease observed in passing from the symmetric dimer to the trimer is compatible with the fact that the latter molecule is the first to contain a tetrahedrally bonded beryllium atom arising from the promotion from sp^2 to sp^3.

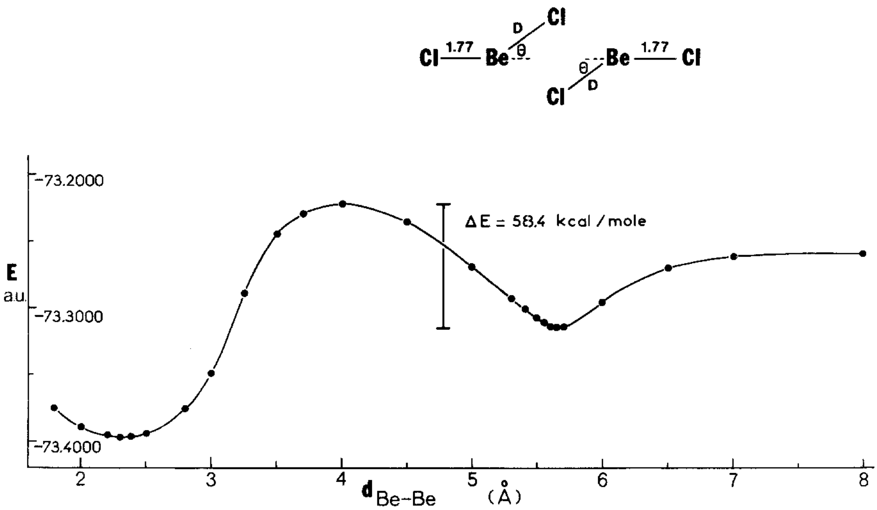

Fig. 2. Calculated total energy curve for the formation of $(BeCl_2)_2$

Table 2. Polymerization energy for $(BeCl_2)_n$

n	2	3	4	5	6
ΔE_n	−0.0812	−0.1200	−0.1167	−0.1128	−0.1083

Infrared spectroscopic studies by Büchler and Klemperer [8] suggest that the dimer has the cyclic chlorine-bridged structure considered above in Polymerization Scheme 2. Our molecular orbital calculations show that this model corresponds, in fact, to the most favorable configuration. In order to study the interaction energy relationships leading to this form, we considered the end-to-end approach of two linear $BeCl_2$ units (Fig. 2).

In this model, the "external" Be–Cl bond lengths were maintained at 1.77 Å [5] and the energy minimization was carried out for the optimal angle of deviation θ and the "internal" Be–Cl bond lengths D ($D \geqq 1.77$ Å) with respect to the Be–Be interatomic distance. The latter was chosen in the range 8.00 to 1.80 Å.

The resulting total energy curve (Fig. 2) indicates that at first a terminal Cl–Cl attraction interaction occurs between the linear molecules as the inter-beryllium distance decreases toward 5.65 Å. At this point, and in the range down to $d_{Be-Be} = 4.0$ Å, an energy increase sets in which can be rationalized by a repulsion interaction between the approaching chlorine atoms. The calculated activation energy ΔE of formation of the dimer is 58 kcal/mole of $(BeCl_2)_2$. This value would not appear excessive in the light of the experimentally observed temperature interval necessary for the conversion of pure monomeric $BeCl_2$ to detectable amounts of dimer ($\approx 400°$C [9]). The subsequent energy well is compatible with the formation of a cyclic dimeric molecule for which the calculated equi-

Table 3. Calculated interatomic distances at equilibrium (Å)

Polymer species	d_{Be-Be}	$d_{Be-Cl(ring)}$
Dimer	2.30	1.95
Trimer	2.44	1.96–1.97
Tetramer	2.46	1.97
Infinite polymer	2.63 (exp.)	2.02 (exp.)

exp.: experimental

librium geometry is $d_{Be-Be} = 2.30$ Å, $d_{Be-Cl(ring)} = 1.95$ Å and ∢ Cl–Be–Cl(ring) = 108°. This geometry corresponds to a symmetric dimer in which the Be–Cl ring bonds are equivalent.

The fact that the calculated ring dimensions in $(BeCl_2)_2$ are smaller than those found by X-ray structural determination for the infinite polymer chain is understandable in terms of the difference in bonding involved, viz. sp^2 bonding of beryllium in the dimer as opposed to sp^3 bonding in higher polymeric forms. The verification of this interpretation by optimization of the symmetrical trimer and tetramer of Scheme 2 was considered to be a useful check of the reliability of our computations, and in fact energy minimization of these species showed that the Be–Be distance increases noticeably with increasing degree of polymerization (Table 3).

A closer examination of the electronic structure of the beryllium-chlorine bonds in the dimer and tetramer shows that the ionic character of the terminal bonds is more pronounced than that of the ring linkages, in which the covalent character increases with the degree of polymerization. As would be expected, the most significant change in bond character occurs in the beryllium $sp \rightarrow sp^2$ promotion in the first reaction step.

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