Short Communications

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Molecular structure of bis(cyclopentadienyl)beryllium in the crystal at –120° and in the gas phase

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The molecular structure of bis(cyclopentadienyl)beryllium in the crystal at −120 °C is different from that in the gas phase. The origin of the difference is discussed.

We have previously found that the electron scattering pattern from gaseous $(C_5H_5)_2Be$ at about 70° is consistent with a molecular model of C_{5v} symmetry in which the two cyclopentadienyl (Cp) rings lie parallel and staggered, and the beryllium atom alternates between two positions on the fivefold axis h_1 = 1·472 (6) Å from one ring and h_2 = 1·903 (8) Å from the other (Almenningen, Bastiansen & Haaland, 1964; Haaland, 1968). It has subsequently been estimated that the average lifetime of the Be atom in one of these positions is of the order of 10^{-13} to 10^{-12} sec (Ionov & Ionova, 1970).

Recently, Wong and co-workers published the result of an X-ray diffraction investigation of crystalline Cp_2Be at −120° (Wong, Lee, Chao & Lee, 1972). The crystal structure is disordered, but the molecular structure may be described as follows: The Be atom lies h_1 = 1·53 (3) Å above one ring on the (approximate?) fivefold symmetry axis. The second ring is parallel, or very nearly parallel, to the first and is lying at a perpendicular distance h_2 = 1·81 (5) Å from the Be atom, but has slipped about 1·20 Å sideways, with the result that the shortest beryllium carbon bond, Be–C(5′), is perpendicular to the plane of the Cp ring.

We have now compared this structure with our old electron diffraction data, and we can confirm the statement of Wong and co-workers that the crystal molecular structure is incompatible with the gas phase electron-diffraction data. It was assumed that the Cp rings are exactly parallel, that they have the same size and D_{5h} symmetry, and that the Be atom is lying on the symmetry axis of one ring. The molecular structure is then determined by five independent parameters: the C–C and C–H bond distances, h_1 and h_2 and the magnitude of the slip. Attempts to refine these parameters simultaneously were not successful. Least-squares refinement of the first four as well as the ten most important vibrational amplitudes was therefore carried out with a diagonal weight matrix with the slip varied from 0·0 to 1·4 Å in 0·2 Å increments. The generalized *R*-index ratio, $\mathscr{R}$, (Hamilton, 1965) increased monotonically as the slip was increased, reaching a value of 1·06 at slip = 0·6 Å and levelling off at about $\mathscr{R}$ = 1·10 above slip = 0·8 Å. Comparison of experimental and theoretical radial distribution curves showed that disagreement was introduced in the region between 1·8 and 2·7 Å, *i.e.* in the region of the Be–C distances. This agreement, therefore, cannot be substantially improved by relaxing the assumptions listed above. It would appear then that models with slip = 0·6 Å or greater can be rejected at the 0·005 significance level.

The infrared spectra of gaseous and solid Cp_2Be have been recorded by McVicker & Morgan (1970). The gas phase spectrum is very simple, consisting mainly of the very few bands expected for Cp rings of D_{5h} symmetry, while the crystal spectra are considerably more complex. The difference was interpreted as evidence for change in the nature of the metal to ring bonding on going from the gas phase into the crystal. It now appears that the phase transition is accompanied by some geometrical rearrangement as well.

Since the dipole moment of Cp_2Be (in cyclohexane) is 2·24 ± 0·09 D (Fischer & Schreiner, 1959) the rapid oscillation between alternate positions of the Be atoms in neighbouring molecules in the crystal would become coupled and slowed down as the temperature is lowered. Since the bonding between the Be atom and the far ring is very weak and not strongly directed, intermolecular forces may be sufficient to explain the slip of 1·2 Å sideways. The heat of vaporization of liquid Cp_2Be is about 12·2 k.cal. mole^{-1} (Scheren, 1961).

Wong and co-workers suggest that the molecular structure in the crystal can be described as containing one π-bonded and one σ-bonded ring. This is a matter of taste, but we would prefer to describe the structure as containing two π-bonded rings one of which has slipped (or as containing one *penta-hapto* and one *poly-hapto* ring) and for the following reasons: The Be–C(5′) bond is perpendicular to the plane at the ring and appears to be longer, 1·81 (5) Å, than the single Be–C(Me) bond distance in $(C_5H_5)BeCH_3$, 1·706 (7) Å (Drew & Haaland, 1971); the Be–C(1′) and Be–C(4′) bond distances, 2·38 (5) Å and 2·30 (5) Å respectively, are similar to the bond distance between Be and the five C atoms in the far ring of gaseous Cp_2Be, 2·256 (7) Å.

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