

Beryllocene: A Microwave Dielectric Loss Study

Stephen J. Pratten, Mervyn K. Cooper, and Manuel J. Aroney*

Department of Inorganic Chemistry, University of Sydney, Sydney, New South Wales 2006, Australia

Stephen W. Filipczuk

Commonwealth Scientific and Industrial Research Organisation, Division of Applied Physics, Sydney, New South Wales 2070, Australia

Microwave dielectric loss measurements at 1.141, 3.031, and 8.543 GHz are reported for beryllocene [bis(cyclopentadienyl)beryllium] in cyclohexane, decalin, benzene, and 1,4-dioxane solutions. The dipolar nature of beryllocene is confirmed. Anomalously large atomic polarization is found. The dielectric absorption is interpreted to suggest rocking movements of the cyclopentadienyl groups synchronous with oscillation of the beryllium atom between two equivalent positions in an η^5, σ structure. Evidence is presented for interaction with solvating benzene and 1,4-dioxane molecules.

Controversy has surrounded the structure of beryllocene, $\text{Be}(\text{cp})_2$ ($\text{cp} = \text{C}_5\text{H}_5$), since its discovery in 1959.¹ Electron-diffraction data for the gas phase were interpreted in terms of a model having an asymmetric sandwich structure (I) in which the Be atom can occupy two alternate positions on the five-fold rotation axis.²⁻⁴ An X-ray crystal-structure analysis at -120°C indicated a slip-sandwich (II) where one of the two parallel rings has slipped sideways by *ca.* 1.2 Å and the Be is π bonded to one ring and σ bonded to the other.⁵ This has been confirmed by the recent X-ray structure determination of Nugent *et al.*,⁶ who rule out the possibility of a η^3 ring with allyl character. Theoretical molecular orbital studies⁷⁻¹¹ favour a model (III) similar to the X-ray structure but with non-parallel rings so that the carbon σ bonded to Be is no longer sp^2 but has significant tetrahedral character.

The structure of $\text{Be}(\text{cp})_2$ in solution is not precisely known. A recent i.r. spectroscopic study indicates η^5, σ bonding.¹² Values of the dipole moment of $\text{Be}(\text{cp})_2$ in cyclohexane, benzene, and 1,4-dioxane, determined previously by the refractivity method,^{13,14} should be considered with caution since they depend significantly on a quite arbitrary estimate of solute atomic polarization which is a necessary feature of this procedure. It is known that the refractivity method cannot be safely applied to metal complexes which are 'flexible',¹⁵⁻¹⁷ and its utilisation with $\text{Be}(\text{cp})_2$ may not be appropriate in view of the dynamic behaviour of the Be atom which oscillates between two equivalent positions relative to the cp rings, and of the rings themselves which interchange and are fluxional.

The purpose of this work was to explore further the dielectric properties of $\text{Be}(\text{cp})_2$ in relation to structure and solvent environment. Accordingly, microwave dielectric loss measurements have been made in the region 1–9 GHz for $\text{Be}(\text{cp})_2$ in

cyclohexane, decalin (decahydronaphthalene), benzene, and 1,4-dioxane (diox). From these are derived 'loss moments' and dielectric relaxation times.

Experimental

$\text{Be}(\text{cp})_2$ was prepared by the method of Fischer and Hofmann¹ and purified by vacuum sublimation (colourless crystals, m.p. 59°C ; lit.,¹ $59-60^\circ\text{C}$). Samples were vacuum sublimed into Schlenk flasks into which solvent was directly distilled under dry nitrogen to give clear colourless solutions. The solvents used were purified, dried with sodium and benzophenone, then fractionated. Dielectric loss measurements were made at 25°C using a Central Research Laboratories Inc. (Red Wing, Minnesota, U.S.A.) microwave dielectrometer, in accordance with the standing-wave method of Roberts and von Hippel¹⁸ for measurements with short-circuited waveguides. Solutions were introduced into the dielectrometer cell under dry nitrogen, and the top of the cell was sealed with thin Mylar film to exclude oxygen and water vapour. The frequencies (ν) employed were 1.141, 3.031, and 8.543 GHz. Dielectric loss tangents ($\tan\delta$) were calculated from primary data using the Dakin and Works equation (1),¹⁹ which applies accurately to situations where loss tangents are smaller than 0.1. The parameters Δx , x_0 , d , and λ_g constitute the primary data that are obtained directly from the dielectrometer; Δx is the distance between double-minimum power points¹⁸ located on either side of the voltage node nearest (distance x_0 from) the air-dielectric interface; d is the depth of the liquid dielectric at the short-circuit end of the waveguide; λ_g is the wavelength of the standing wave in the air above the dielectric. The term λ_c is the cut-off wavelength for hollow, circular waveguides: for a given mode of propagation it

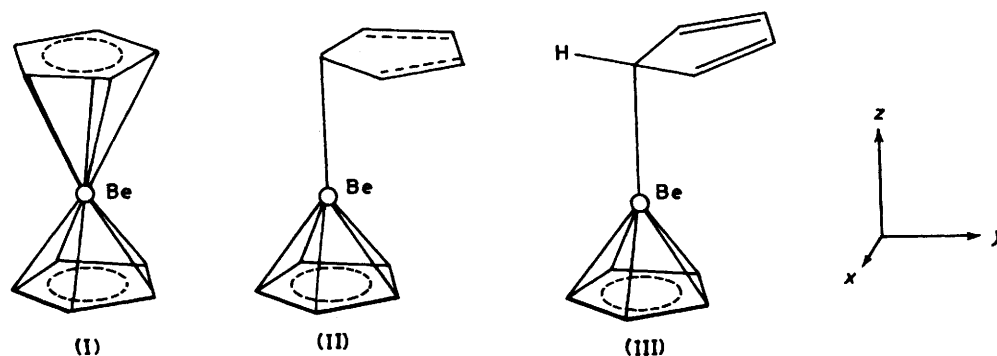


Table. Experimental and calculated values of the absorption factors, ψ , dipole moment, $\mu(\text{loss})$, and dielectric relaxation times, τ , of beryllocene in solution at 25 °C

Solvent	Frequency/ GHz	ψ (exp.) ^a	ψ (calc.)	$10^{30}\mu(\text{loss})/\text{C m}$	$10^{30}\mu(\text{static})/\text{C m}$	τ/ps
Cyclohexane	1.141	0.0638 ± 0.0066	0.0660	5.37 ± 0.43	7.47^b	11.8 ± 2.2
	3.031	0.169 ± 0.007	0.168			
	8.543	0.356 ± 0.019	0.355			
Decalin	1.141	0.0895 ± 0.0057	0.0866	5.64 ± 0.30		12.5 ± 1.6
	3.031	0.217 ± 0.009	0.220			
	8.543	0.455 ± 0.018	0.451			
Benzene	1.141	0.126 ± 0.005	0.128	6.77 ± 0.30	8.21^b	12.7 ± 1.5
	3.031	0.327 ± 0.013	0.324			
	8.543	0.657 ± 0.026	0.659			
diox	1.141	0.230 ± 0.009	0.235	7.58 ± 0.27	8.7^c	15.9 ± 1.9
	3.031	0.578 ± 0.023	0.578			
	8.543	1.029 ± 0.041	1.030			

^a Refer to text for determination of uncertainty in ψ . ^b From ref. 13. ^c From ref. 14.

$$\tan\delta = \frac{\Delta x}{d} \left[\tan^2\left(\frac{2\pi x_0}{\lambda_g}\right) + 1 \right] / \left\{ \left[1 + \left(\frac{\lambda_g}{\lambda_c}\right)^2 \frac{1}{D} \right] \left[D \tan^2\left(\frac{2\pi x_0}{\lambda_g}\right) + \frac{\lambda_g}{2\pi d} \tan\left(\frac{2\pi x_0}{\lambda_g}\right) + 1 \right] \right\} \quad (1)$$

is determined by the dimensions of the waveguide and becomes infinity for coaxial arrangements: $D = (\lambda_g \beta' d / 2\pi d)^2$, where β' is the phase factor for the standing wave in the dielectric; the appropriate value of $\beta' d$ is obtained from the relation (1a).¹⁹

$$\frac{-\lambda_g}{2\pi d} \tan\left(\frac{2\pi x_0}{\lambda_g}\right) = \frac{\tan(\beta' d)}{\beta' d} \quad (1a)$$

Results are given in the Table as infinite dilution absorption factors, ψ , obtained from the incremental loss tangents using equation (2) from Le Fèvre and Sullivan's modified form²⁰ of

$$\psi = \left[\frac{\Sigma \Delta \tan\delta}{\Sigma \omega_2} \right] = \frac{N_A \rho_1 (\epsilon_1 + 2)^2 \mu^2}{27kT\epsilon_1 M_2 \epsilon_0} \cdot \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (2)$$

the Debye theory of dielectric relaxation;^{15,21} μ is the dipole moment; τ is the dielectric relaxation time (or molecular relaxation time*); ρ_1 and ϵ_1 are respectively solvent density and permittivity; M_2 and w_2 are the solute molecular weight and weight fraction; N_A , k , T , and ω refer in turn to Avogadro's number, the Boltzmann constant, the absolute temperature, and the angular frequency at which ψ is measured. For $\text{Be}(\text{cp})_2$ in each solvent, it is observed that the mean experimental ψ values lie very close to a simple Debye curve (ψ versus frequency) (see Figure). In this Figure the error bars represent either $\pm 4\%$ of the corresponding value of ψ or \pm the standard error in the mean value of ψ at the 95% confidence level, whichever is the greater. Where error bars are not shown, these uncertainties lie within the open circles defining the points. Using best-fit Debye curves,† dipole moments, $\mu(\text{loss})$, and dielectric relaxation times, τ , were obtained from the experimental data. These values are tabulated together with their uncertainties in the Table. Dipole moments, $\mu(\text{static})$, determined previously^{13,14} from

relative permittivity measurements at kHz frequencies are also shown in the Table. Proton n.m.r. spectra were recorded on samples sealed under vacuum in 5-mm tubes on a JEOL FX-60 Q or Bruker WM-400 spectrometer. Coaxial tubes were utilised when non-deuteriated solvents were used to provide a deuterium lock. Tetramethylsilane was used as internal reference.

Discussion

The present results conclusively prove that beryllocene is dipolar in solution. The $\mu(\text{loss})$ values now reported are significantly lower than the molecular moments earlier obtained from measurements of the 'static-field' permittivities of $\text{Be}(\text{cp})_2$ solutions (Table). This difference may be due to inadequate estimates of the atomic polarisation of $\text{Be}(\text{cp})_2$ which in the earlier work^{13,14} were arbitrarily taken to be 15% of the measured sodium D-line molar refraction, regardless of solvent. It is possible, however that our $\mu(\text{loss})$ values may not refer to the total molecular moment since additional dielectric absorption may occur at frequencies higher than those of this study. This is further examined below. It should be noted that with each solvent used in this work, the observed absorption shows Debye behaviour over a range extending not less than one full decade of frequency (ca. 10–1 GHz) on the low-frequency side of the measured absorption. Given this, and the position of the observed absorption on the frequency scale, it is unlikely that any additional absorption related to dipole relaxation occurs below 1 GHz.

The first and most obvious conclusion to be drawn from the results is that $\text{Be}(\text{cp})_2$ in solution cannot have a non-dipolar ferrocene-like structure. From dipole moments it is not possible to differentiate between candidate structures (I)–(III). Complementary information may be obtained, however, by considering the relaxation time of the measured absorption in relation to possible mechanisms of dipole reorientation associated with these structures.

In the general case, embracing all three geometric models, the molecular dipole moment can be resolved into components μ_{\parallel} which is parallel to the (π -cp)–Be symmetry axis and μ_{\perp} which is perpendicular to that axis. For structure (I), μ_{\parallel} would equal the total molecular moment and μ_{\perp} would be zero. For structures (II) and (III), μ_{\parallel} and μ_{\perp} can be expressed in terms of

* Ref. 21, p. 298.

† For small, dipolar molecules in dilute solutions of low-viscosity, non-dipolar solvents, the dielectric absorption is usually described either in terms of a single Debye absorption or by a partial overlapping of two or more discrete Debye absorptions. A continuous distribution of Debye processes is often found for concentrated solutions and for pure dipolar liquids; in such cases the behaviour is best described using equations containing a dispersion parameter, see ch. 1 of ref. 21.

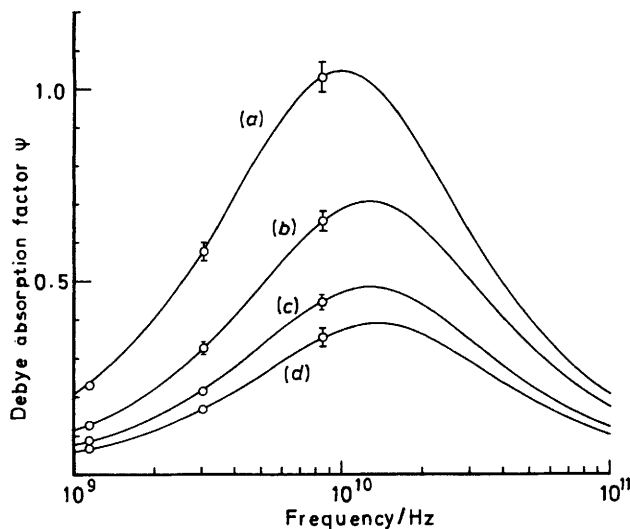


Figure. Dielectric absorption of beryllocene in (a) dioxane, (b) benzene, (c) decalin, and (d) cyclohexane

dipole moments associated with the σ -cp and $(\pi$ -cp)-Be-(σ -C) groupings, by equations (3) and (4), where θ is the angle between

$$\mu_{\parallel} = \mu[(\pi\text{-cp})\text{-Be-(}\sigma\text{-C)}] + \mu(\sigma\text{-cp}) \cos\theta \quad (3)$$

$$\mu_{\perp} = \mu(\sigma\text{-cp}) \sin\theta \quad (4)$$

the Be-(σ -C) bond axis and the σ -cp ring plane. Perrin²² and Budo²³ have generalised Debye's theory of rotational diffusion in a way which may be applied to structures (I)–(III) of beryllocene. They have shown that the mean molecular dipole moment, $\langle\mu\rangle$, in an alternating electric field, E^* , of angular frequency, ω , can be given by equation (5), where k is the

$$\langle\mu\rangle = \frac{E^*}{3kT} \left(\frac{\mu_{\parallel}^2}{1 + i\omega\tau_{\parallel}} + \frac{\mu_{\perp}^2}{1 + i\omega\tau_{\perp}} \right) \quad (5)$$

Boltzmann constant, T is the absolute temperature, and $i = \sqrt{-1}$. The terms τ_{\parallel} and τ_{\perp} are relaxation times characterising the relaxation of component orientation polarisations due to rotational diffusion of μ_{\parallel} and μ_{\perp} , respectively. It has been shown that $1/\tau_{\parallel}$ and $1/\tau_{\perp}$ can be regarded as the sum of two terms involving rotations of the respective moment components μ_{\parallel} and μ_{\perp} about the orthogonal axes perpendicular to these moments.^{22,23} From correlation function treatments, Cole²⁴ and Williams²⁵ regard dipole inversion as an additional polarisation relaxation mode. Inversion of both μ_{\parallel} and μ_{\perp} occurs with oscillation of the Be atom within the $(\text{cp})_2$ framework. Thus terms $1/\tau(\text{inv.})$ must be included in the overall expressions (6) and (7) for $1/\tau_{\parallel}$ and $1/\tau_{\perp}$. The equations are

$$\frac{1}{\tau_{\parallel}} = \frac{1}{\tau_{\parallel}^x} + \frac{1}{\tau_{\parallel}^y} + \frac{1}{\tau_{\parallel}(\text{inv.})} \quad (6)$$

$$\frac{1}{\tau_{\perp}} = \frac{1}{\tau_{\perp}^x} + \frac{1}{\tau_{\perp}^z} + \frac{1}{\tau_{\perp}(\text{inv.})} \quad (7)$$

given with reference to the molecule-fixed Cartesian axes xyz such that z is collinear with the direction of μ_{\parallel} , y is parallel to μ_{\perp} , and x is perpendicular to the symmetry plane of the Be-(σ -cp) group.

The relaxation times for rotations of moment μ_{α} ($\alpha = \parallel$ or \perp) about axis β ($\beta = x, y, \text{ or } z$) are designated $\tau_{\alpha\beta}$. It is clear that

$\tau_{\parallel}^x = \tau_{\perp}^x$ since μ_{\parallel} and μ_{\perp} undergo simultaneous rotation about the x axis with which each is perpendicular. Also $\tau_{\parallel}(\text{inv.}) = \tau_{\perp}(\text{inv.})$ since μ_{\parallel} and μ_{\perp} invert at the same rate as that of Be oscillation. It is unlikely that rotational diffusion of μ_{\parallel} about the y axis and of μ_{\perp} about the z axis will occur at exactly the same rate so that $\tau_{\parallel}^y \neq \tau_{\perp}^z$, although they may be close. If τ_{\parallel} and τ_{\perp} are not identical, it follows from equation (5) that two absorption regions may in principle be observed. Using the schemes of Perrin²² and Budo,²³ the measured absorption (ψ) would be expressed by the corresponding generalisation (8) of equation (2), where K is a grouping of solvent, solute, and standard physical constants.

$$\psi = K\omega \left(\frac{\tau_{\parallel} \mu_{\parallel}^2}{1 + \omega^2 \tau_{\parallel}^2} + \frac{\tau_{\perp} \mu_{\perp}^2}{1 + \omega^2 \tau_{\perp}^2} \right) \quad (8)$$

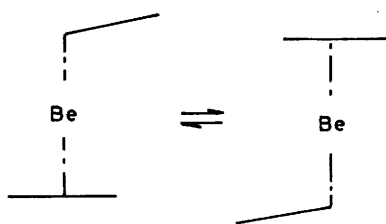
For structure (I) the second term of equation (8) vanishes and only one region of microwave absorption is predicted. The measured dipole moment, $\mu(\text{loss})$, would be the total molecular moment. Expressions (6) and (7) become simply equation (9),

$$\frac{1}{\tau(\text{exp.})} = \frac{1}{\tau(\text{mol.})} + \frac{1}{\tau(\text{inv.})} \quad (9)$$

where $\tau(\text{mol.})$ refers to the relaxation time associated with molecular rotational diffusion about axes x and y . The relaxation time, $\tau(\text{exp.})$, of the measured absorption in cyclohexane is 12 ps, hence, from equation (9) $\tau(\text{mol.})$ and $\tau(\text{inv.})$ must each be greater than this value. If, reasonably, $\tau(\text{mol.})$ were in the range 10–30 ps²¹ (cf. 36 ps for 1,2,3,4,5-pentachloroferrocene in cyclohexane²⁶) then $\tau(\text{inv.})$ would exceed 19 ps. Intuitively, however, a large $\tau(\text{inv.})$ value, *i.e.* of the order of molecular relaxation times, is improbable for oscillation of the very small, light Be atom between the two equivalent locations within the $(\text{cp})_2$ framework. Direct comparisons are not available, but an indication is given by $\tau(\text{inv.}) \leq 2$ ps for triphenylamine, aniline, and *N,N*-dimethylaniline.²⁵ Treating the Be atom in $\text{Be}(\text{cp})_2$ as a one-dimensional oscillator and assuming structure (I), Ionov and Ionova²⁷ have calculated the lifetime of Be in one of its two potential holes to be in the range 0.1–1.0 ps. For purposes of comparison it is pointed out that the measured dielectric relaxation time at infinite dilution may be equated with the microscopic (molecular) relaxation time (ref. 21, p. 298). The latter is a measure of the time required for the molecular dipole to change its orientation by an average of one radian of angle. The average time required to invert the dipole moment of beryllocene by Be oscillation is π times $\tau(\text{inv.})$, *i.e.* $\geq ca. 60$ ps. This value corresponds to the half-period of Be oscillation. Clearly structure (I) does not accord with our measurements.

For structures (II) and (III), both μ_{\parallel} and μ_{\perp} exist and according to equation (8) two regions of dielectric absorption are possible. If the two absorptions are well separated, the ratio of the absorption maxima would be $\mu_{\perp}^2/\mu_{\parallel}^2$. If on the frequency scale, the two absorptions are coincident or are very close, then the absorption maximum will be proportional to the square of the total molecular moment, or very nearly so. In the absence of absorption data at frequencies higher than 8.543 GHz, it is not possible to decide whether the $\mu(\text{loss})$ values of the Table refer to the total $\text{Be}(\text{cp})_2$ dipole moment or to μ_{\parallel} . For both structures (II) and (III), μ_{\perp} is the vector sum of C–C and C–H bond moments of the σ -cp group, so that even allowing for inductive effects, it would be small. The μ_{\parallel} component would predominate as it is collinear with the dipoles of the $(\pi$ -cp)-Be group and of the Be-(σ -C) bond. Given that the dipole moment of cyclopentadiene²⁸ is 1.4×10^{-30} C m, it is estimated that μ_{\parallel} would differ by no more than 0.3×10^{-30} C m from the overall molecular moment of $\text{Be}(\text{cp})_2$. It may reasonably be accepted

that $\mu_{\parallel} \gg \mu_{\perp}$. The absorption associated with μ_{\perp} would comprise $< 10\%$ of that measured if the two absorptions are coincident and even less so if they are not. Thus the measured absorption is associated mainly with μ_{\parallel} and τ_{\parallel} would be very close to $\tau(\text{exp.})$. In addition, the peak of a composite absorption will fall between those of the contributing absorptions and it would be expected that τ_{\parallel} would be slightly greater than $\tau(\text{exp.})$. In any case, $\tau_{\parallel} \geq 12$ ps and it follows that each of the τ_{\parallel} terms in equation (6) will be greater than 12 ps. The terms τ_{\parallel}^x and τ_{\parallel}^y are associated with rotations of the whole molecule and it follows that the sum $1/\tau_{\parallel}^x + 1/\tau_{\parallel}^y$ would relate to the reciprocal of an overall molecular relaxation time. By argument similar to that given earlier, $\tau_{\parallel}(\text{inv.})$ would exceed *ca.* 19 ps, corresponding to a half-period for Be oscillation \geq *ca.* 60 ps.* This is considerably greater than the estimate of 2 ps for the period of Be oscillation in $\text{Be}(\text{cp})_2$ reported for structure (II) by Wong and Wang.²⁹ If the cyclopentadienyl rings in $\text{Be}(\text{cp})_2$ are not parallel, as is the case for structure (III), relocation of Be from one potential well to the other must be accompanied by a change in the relative dispositions of the cp groups as represented below. The coupling of the cp ring movements and Be oscillations would increase the period of the latter over that expected for structure (II). We believe that this model with non-parallel rings better accounts for the measured dielectric absorption of $\text{Be}(\text{cp})_2$ in solution.



An unusually large molar atomic polarisation is found for $\text{Be}(\text{cp})_2$ in solution. This is calculated as *ca.* 57 cm^3 from 'static' permittivity data of ref. 13 together with the $\text{Be}(\text{cp})_2$ loss moment in cyclohexane (the latter, as shown earlier, is equal to or alternatively, is very close to the overall molecular moment). Fischer and Schreiner¹³ had underestimated this as 7 cm^3 . The ratio, molar atomic polarisation/molar electronic polarisation, which for most molecular substances is 0.05–0.15,¹⁵ proves to be *ca.* 1.2 for $\text{Be}(\text{cp})_2$ in cyclohexane. Unusually large atomic polarisations in metal complexes have been attributed to field-induced bending deformations of dipolar metal–ligand groups.^{15–17,30} This is in intuitive accord with the flexible model we propose for $\text{Be}(\text{cp})_2$ in solution.

The measured dielectric relaxation time of $\text{Be}(\text{cp})_2$ is not much affected by increase of the macroscopic solvent viscosity in changing from cyclohexane to decalin. In diox the larger τ value reflects electrostatic interactions between the solute and the local C–O dipoles of the solvent. The $\mu(\text{loss})$ values are in the order cyclohexane \approx decalin $<$ benzene $<$ diox which agrees qualitatively with the order of the previously reported 'static' moments.^{13,14}

* A referee has suggested that 'the $\langle \mu \rangle$ arising from the oscillatory motion of the Be atom may well be the largest factor' in the dipole vector scheme for $\text{Be}(\text{cp})_2$ in solution, and this raises doubts about the relative magnitudes of μ_{\parallel} and μ_{\perp} . Relocation of Be from one potential well to the other during oscillation would reverse the direction of both μ_{\parallel} and μ_{\perp} for each of the η^5, σ configurations (II) and (III). Dipole vector arguments given earlier show reasonably that $\mu_{\parallel} \gg \mu_{\perp}$ for structures (II) and (III), and it could be argued that for the oscillating molecule it would be expected that $\langle \mu_{\parallel} \rangle \gg \langle \mu_{\perp} \rangle$. In any case, irrespective of the relative magnitudes of μ_{\parallel} and μ_{\perp} , equations (6) and (7) still apply, and from these it follows that $\tau(\text{inv.})$ must exceed *ca.* 19 ps and the half-period for Be oscillation would be greater than *ca.* 60 ps.

Morgan and McVicker³¹ have proposed the formation in benzene of a molecular complex of two moles of $\text{Be}(\text{cp})_2$ with one mole of benzene. They report, for slightly yellow solutions of $\text{Be}(\text{cp})_2$ in benzene, a proton n.m.r. signal which they attribute to the benzene protons of the $2\text{Be}(\text{cp})_2 \cdot \text{C}_6\text{H}_6$ complex. In the present work $\text{Be}(\text{cp})_2$ solutions in benzene up to *ca.* 20% concentration gave a single, sharp, proton resonance signal (other than that due to the solvent) which at low concentrations had δ 5.67 p.p.m. at 25 °C. Thus the existence of the $2\text{Be}(\text{cp})_2 \cdot \text{C}_6\text{H}_6$ complex is not confirmed. It would, moreover, be non-dipolar (see Figure 4 of ref. 31) and therefore not consistent with the dipole moment observed for $\text{Be}(\text{cp})_2$ in benzene. The i.r. spectrum of $\text{Be}(\text{cp})_2$ in benzene has been found to be very similar to the spectra in cyclohexane, carbon tetrachloride, carbon disulphide, and deuteriochloroform.^{12,32} This too suggests that no major structural changes occur in $\text{Be}(\text{cp})_2$ in benzene. The dipole moments of the Table show that $\text{Be}(\text{cp})_2$ does not form strong co-ordination complexes with diox as is the case with diethylberyllium for which the dipole moment changes from $3.3 \times 10^{-30} \text{ C m}$ in heptane to $14.3 \times 10^{-30} \text{ C m}$ in diox.³³ This further attests to the co-ordinative saturation of Be in $\text{Be}(\text{cp})_2$.¹²

Other $\text{Be}(\text{cp})_2$ -solvent interactions are now considered in which solvating benzene or diox molecules may be partly 'organised' within the solvent cluster about $\text{Be}(\text{cp})_2$ through statistically favoured stereospecific solute-solvent orientations.³⁴ Within $\text{Be}(\text{cp})_2$ the π -cp group is positively charged relative to the σ -cp group.^{5,7} The π -cp group preferentially attracts the π -electron region of benzene or the oxygen lone-pair electrons of diox. Such interactions result in effective electron displacement within $\text{Be}(\text{cp})_2$ in a direction which augments the dipole moment (see Table). The stereospecific solvation by benzene is well illustrated with the π -cyclopentadienylberyllium halides in which the cp protons experience a large benzene-induced upfield n.m.r. shift: for $\text{BeCl}(\text{cp})$, $\delta = 6.27$ p.p.m. in C_6D_{12} and 5.66 p.p.m. in C_6D_6 ; for $\text{BeBr}(\text{cp})$, $\delta = 6.29$ p.p.m. in C_6D_{12} and 5.66 p.p.m. in C_6D_6 . The proton shifts for $\text{Be}(\text{cp})_2$ are found to be $\delta = 5.73$ p.p.m. in C_6D_{12} and 5.67 p.p.m. in C_6D_6 . A lower benzene-induced upfield shift would be expected for the π -cp protons of $\text{Be}(\text{cp})_2$ since the dipole moment is much smaller [μ for $\text{BeCl}(\text{cp})$ in the gas state³⁵ has been reported as $14.2 \times 10^{-30} \text{ C m}$]. The near equivalence of the $\text{Be}(\text{cp})_2$ proton shifts in C_6D_{12} and C_6D_6 is interpreted as the net effect of benzene-induced shielding of the π -cp protons and benzene-induced deshielding of the σ -cp protons which, because of fluxional and cp ring interchanges, average out on the n.m.r. time-scale. The σ -cp protons are relatively electron rich^{5,7} so that incoming benzene molecules tend to approach them edge-on thereby deshielding them. This model can be extended to hexafluorobenzene solvation for which $\delta = 5.69$ p.p.m. [$\text{Be}(\text{cp})_2$] and 6.37 p.p.m. [$\text{BeCl}(\text{cp})$]. The negative periphery of C_6F_6 tends to approach the $\text{H}^{\delta+}$ atoms of the π -cp group in $\text{BeCl}(\text{cp})$ deshielding them and giving the small downfield shift observed. The magnitude of C_6F_6 induced shifts is usually smaller than those due to C_6H_6 because of inductive depletion of the aromatic π system.³⁶ The fluxional behaviour of $\text{Be}(\text{cp})_2$ results in a proton signal which is the average of those of the π -cp protons (deshielded) and the σ -cp protons (shielded).

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