Dynamics of Beryllocene [Bis(cyclopentadienyl)beryllium] Inversion by ^{13}C N.M.R. Spectroscopy

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The observation of partially relaxed coupling to ^{9}Be in the ^{13}C n.m.r. spectrum of beryllocene in solution leads to an estimate of 10^{10} s^{-1} for the rate of molecular inversion.

The polar nature of bis(cyclopentadienyl)beryllium [beryllocene, $(cp)_2Be$] has been known since the compound was first prepared in 1959.[1] From the *X*-ray crystal structure[2—4] the molecule can be described in the solid state as a 'slip-sandwich,' with the beryllium centrally bonded to one of the cp rings and peripherally bonded to the other. This may be described as a pentahapto–monohapto structure, using these terms in their original strict sense to denote connectivity, without specific bonding implications.[5] Even at 128 K, however, the beryllium is disordered and the two cp rings are crystallographically equivalent. There is reasonable experimental evidence, from vibrational spectroscopy[6,7] and recent dielectric loss measurements,[8] that this structure persists in solution. The molecule is fluxional in solution, for the low-temperature ^{1}H n.m.r. spectrum comprises a single resonance, indicating that the protons of both cp rings are magnetically equivalent, and implying that the movement of the beryllium atom between the two sites is rapid even at −135 °C.[9]

The ^{13}C n.m.r. spectrum, in both cyclohexane and diethyl ether solutions, also displays a single resonance at δ 106.3 (ether) and 107.5 (cyclohexane) downfield from $SiMe_4$. In the proton coupled ^{13}C n.m.r. spectrum this resonance is split into the expected doublet by the directly bonded C–H coupling of 168.5 Hz. Each component of the doublet is further split into a quintet by coupling (6.6 Hz) with the four remaining virtually equivalent protons in the cp ring, as has been observed in other cp spectra.[10] There is additional fine structure in the spectrum, however, with each line further split into an apparent doublet (Figure 1a). This additional splitting cannot be fitted satisfactorily by computer simulation of the full CH_{10} eleven-spin system.

This additional structure persists in the ^{1}H decoupled spectrum (Figure 1b), indicating that it arises from coupling between ^{13}C and the partially relaxed quadrupolar beryllium nucleus (100% ^{9}Be, $I = 3/2$). Coupling with a nucleus of $I = 3/2$ should give four lines of equal intensities, as observed in cyclopentadienylberyllium bromide.[10] Decoupling of the quadrupolar nucleus would, of course, give a single line. If the quadrupolar nucleus were incompletely decoupled, however, intermediate line shapes would result.[11,12] The observed spectrum is similar to that calculated from the theory in ref. 11 with the parameter $\eta^2 = 1.1$, and a coupling constant, J_{Be-C}, of about 2 Hz. The ^{9}Be relaxation time calculated from the ^{13}C spectrum of a cyclohexane solution at 305 K depends on the value used for this coupling constant. The best fit obtained gives T_1 (^{9}Be) of approximately 100 ms. This value compared well with one directly measured value of 130 ms at 298 K.[13] Because the ^{13}C linewidth in the absence of coupling is finite, the T_1 value estimated from the ^{13}C lineshape should be slightly below the directly measured value.

Quadrupolar relaxation occurs when the nuclear quadrupole interacts with a fluctuating electric field gradient. This may be due to molecular tumbling with a correlation time of the order of 10^{-11} s or to an intramolecular rearrangement with a suitable lifetime. The temperature and solvent dependence of the ^{13}C lineshape enable limits to be placed on possible mechanisms. As the temperature is decreased the ^{13}C linewidth decreases, *i.e.* the relaxation of the beryllium nucleus becomes more rapid, and the lineshape approaches a

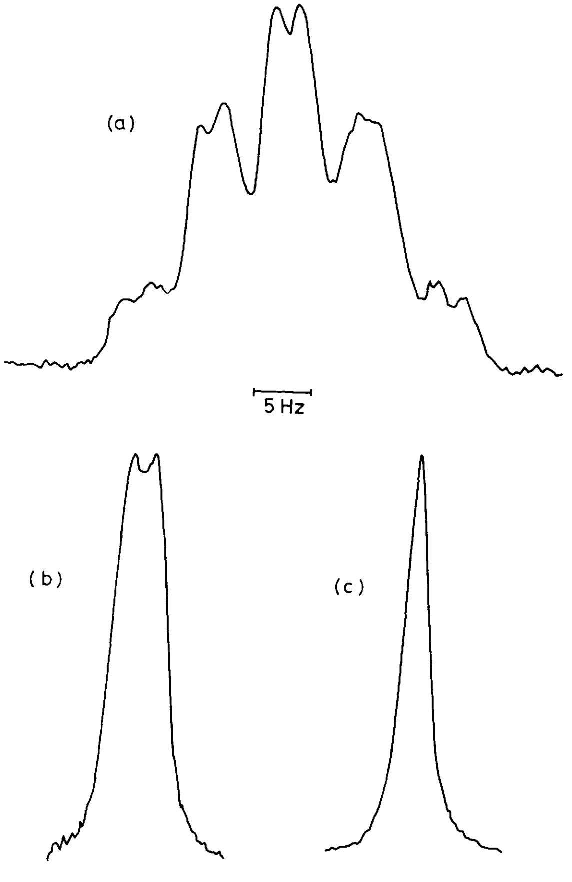

Figure 1. (a) One component of the proton coupled ^{13}C n.m.r. spectrum of beryllocene, showing the additional fine structure of the expected quintet. (b) Proton decoupled ^{13}C spectrum, 304 K. (c) Proton decoupled ^{13}C spectrum, 210 K.

sharp singlet at around 200 K in diethyl ether solution (Figure 1c). This implies that the relaxation process occurs with a correlation time shorter than the inverse of the ^9Be resonance frequency, ω_{Be}. By lowering the temperature the process causing ^9Be relaxation is slowed, and the decoupling increased. If the process had a correlation time longer than the inverse of ω_{Be}, the relaxation time of the beryllium nucleus would increase with a decrease in temperature. In addition, the linewidth would depend on the spectrometer frequency. The observed ^{13}C linewidth, however, is independent of spectrometer frequency between 2.1 and 9.4 T (90 and 400 MHz ^1H, 12.6 and 56.2 MHz ^9Be) indicating that the correlation time of the relaxation process for ^9Be is significantly less than 3×10^{-9} s ($1/\omega_{Be}$ at 9.4 T).

The lineshape is also virtually the same, at the same temperature, in both cyclohexane and diethyl ether solutions, despite the fact that these two solvents have significantly different viscosities. If the relaxation of the quadrupolar ^9Be were due to tumbling of the polar molecule in solution, the relaxation correlation time would depend on solvent viscosity and display the temperature dependence of the individual solvent viscosities. In this case the relaxation time of the ^9Be nucleus would be significantly shorter in the cyclohexane solution than in the ether solution. This is not observed (Figure 2). The temperature dependence of the linewidth is similar in the two solvents. In cyclohexane solution the observed temperature dependence is very much less than that expected for thermally activated tumbling of the molecule in solution.[14] These observations imply that the relaxation process is not due to molecular reorientation and the correlation time is consequently longer than the 10^{-11} s tumbling time.

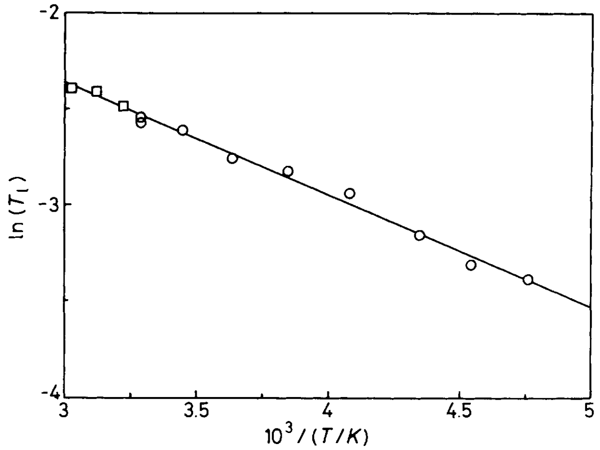

Figure 2. The temperature dependence of T_1 for the ^9Be nucleus (calculated from ^{13}C lineshapes): □ cyclohexane, ○ ether.

A consistent interpretation of these results is that the quadrupolar nucleus is relaxed by inversion of the molecular dipole caused by exchange of the beryllium between the two cp rings, *i.e.* the monohapto ring becomes pentahapto and the pentahapto ring becomes monohapto. This process occurs with a correlation time of the order of 10^{-10} s and an activation energy of ~5 kJ mol^{-1}. An accurate evaluation of the correlation time requires determination of the quadrupole coupling constant, which is difficult to measure for beryllium. Despite this limitation, the present results provide for the first time an order of magnitude determination of the beryllocene inversion frequency in solution.

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