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Evidence for a Plastic Crystalline Phase in *Closo*-N-Methylphosphorimide and *Closo*-N-Methylarsenimide

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One striking feature in phosphorus chemistry is its proclivity to form *closo*-type structures (or so-called "cage compounds"*), as for example in its oxides, sulphides, oxysulphides, imides, thioimides, and so on.[1] Several among these have T_d molecular symmetry and globular, nearly spherical shapes. Therefore the possibility exists that these molecules should easily recover their degrees of freedom in the solid and exhibit plastic phases[2] in which the molecules would undergo rapid restricted rotation in their unit cell, as well as self-diffusion in the crystalline solid. Such behaviour is well documented in the case of the structurally related adamantane and analogous compounds.[3]

We now wish to report the observation of plastic phases for $P_4(NMe)_6$ and $As_4(NMe)_6$.

A proton nmr signal becomes detectable for solid $P_4(NMe)_6$[1c,4] on a High Resolution 60MHz spectrometer (JEOL C-60 HL) from 40 °C upwards, which already supposes considerable rapid reorientational movement in the solid at that temperature. The peak width at half height abruptly changes from *ca.* 4,700 Hz (1.12 gauss) to *ca.* 400 Hz (0.1 gauss) within one degree at 56 °C when the sample is heated. This reflects a drastic change in molecular freedom, which we assign to a plastic phase transition T_P, above which the molecules suddenly begin to rotate, while maintaining their positional order in the solid.

This interpretation is further supported by the following facts: (i) there is a change in aspect of the crystalline material, which suddenly becomes translucent; (ii) differential scanning calorimetry (DSC) shows a sharp first order-transition at 330 ± 0.5 °K upon heating (ΔH = 7.57 KJ mol^{-1}, ΔS = 23.01 J mol^{-1} °K^{-1}). Upon cooling this transition is found at 323.5 °K, which denotes hysteresis, a common feature of plastic phase transitions; (iii) variable-temperature X-ray powder-diffraction shows a change in pattern at 323 ± 5 °K from monoclinic[5] to cubic upon heating. The diffraction lines, which are sharp and numerous for the "rigid" crystal, become few (5 reflexions) and less well-defined for the plastic crystal.[6] The original pattern is slowly recovered upon cooling, with lines corresponding to the cubic system still distinguishable down to 308 °K, again showing that, although it is reversible, there is an appreciable hysteresis in the process; (iv) the low entropy of melting (ΔH = 1.9 KJ mol^{-1}, ΔS = 4.8 J mol^{-1} °K^{-1} by DSC at T_m = 395 °K) is also characteristic of a plastic crystalline phase;[2] (v) the ^{31}P nmr signal, which becomes detectable at *ca.* 50 °C upwards, shows the same abrupt decrease in line width at 56° ± 1 °C.

The existence of a plastic phase transition for $P_4(NMe)_6$ should be considered collaterally with the relatively low symmetry of the space group (monoclinic, $P2_1/c$, two molecules per unit cell)[5] in which the highly symmetric molecule crystallises, and above all, with the disorder which has been found in the low temperature crystalline phase of related *closo*-compounds, which suggests that the globular shape of the molecule presents too few asperities to induce highly symmetric order, even in the rigid phase.

A second, less pronounced and smoother transition was also observed in the ^1H nmr line-width experiment: between *ca.* 338 and 348 °K, the signal is observed to narrow from 350 to 120 Hz, a change which we assign to self-diffusion,[8] which then becomes rapid enough to influence the nmr line shapes. On further heating the spectral resolution slowly improves until the fine structure (the two symmetric lines corresponding to $N = 2(J_{AX} + J_{AX'})$ = 32 Hz of the second-order spectrum[1c,4]) becomes apparent. There is no change in the nmr at the melting point.

A third transition, at lower temperature, is detected by DSC (309 °K, first-order upon cooling, ΔH = 3.01 KJ mol^{-1}, ΔS = 9.7 J mol^{-1} K^{-1}; higher order upon heating) which we tentatively assign to the rotation of the molecule about one of its C_3 axes. The fact that this process is higher order upon heating means that the onset of the rotation is concerted.[10]

Similar behaviour was found for solid $As_4(NMe)_6$, which exhibits a large plastic range (T_p = 346°, T_m = 393 °K) as shown by an abrupt narrowing of the ^1H nmr line width at 346 °K.

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*A rather misleading denomination, since there is no room whatever in the "cage".)

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