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Isomorphism and disorder in o-chlorohalobenzenes studied by NQR

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ABSTRACT

In this work we present experimental results that allow to characterize different solid modifications found in o-chlorohalobenzenes. Three disordered phases have been found in o-chlorobromobenzene. The stable phase at high temperature (phase I) is also obtained by quenching the sample at 77 K. Slow cooling allow to obtain the low temperature phase III which, on heating, transforms to phase II at 183 K and this, in turns, transforms to phase I at $T \sim 210$ K. The disorder evidenced through the Nuclear Quadrupole Resonance spectra, is attributed to a random occupation of chlorine and bromine sites. In all phases there is evidence of molecular reorientations out of the benzene ring plane around the pseudo-symmetry axis between the atoms of Cl and Br. In o-chlorofluorobenzene two phases have been found depending on the cooling rate. One phase is disordered due to the random exchange of the occupation of Cl and F sites. In this case, there is also evidence of molecular reorientations out of the benzene ring plane, but in this case the reorientation is around the pseudo-symmetry axis that pass through the C–Cl bonds. Comparisons with the behavior of o-dichlorobenzene are also made.

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1. Introduction

The majority of organic compounds have the ability to exist in more than one crystal structure or phase that have different arrangements or conformations of the molecules in the crystal lattice, an ability which is known as polymorphism. Monotropic modifications of the same substance are most frequently encountered. For a monotropic system, the free energy curves do not cross, and therefore no reversible transition can be observed below the melting point. Controlling the formation of different polymorphs is still a challenge in crystal engineering and thus, different polymorphs are found randomly. Among the polymorphs, there are those with a certain disorder in the molecular arrangement including rigid disorder. Typical examples of this kind of disorder are p-chlorobromobenzene and p-chloriodobenzene, which are isomorphous with p-dichlorobenzene and the average molecule is obtained by centrosymmetric superposition of two molecules with half-weight atoms [1–3].

With the aim of finding if the disorder and isomorphism present in p-chlorohalobenzenes is also present in o-chlorohalobenzenes, three compounds of the chlorobenzene derivatives o-C₆H₄CIX (X=Br, Cl, F) have been studied using ³⁵Cl Nuclear Quadrupole Resonance (NQR) complemented with Differential Thermal Analysis (DTA) measurements. The first technique is very

useful because the electric field gradient is very sensitive to the crystal structure and dynamic properties can be inferred from the temperature behavior of spin-lattice relaxation time (T_1).

Little information can be found in literature about these compounds. The crystal structures of o-dichlorobenzene (ODCB) [4] and o-difluorobenzene [5] at 223 K and 123 K respectively, have been reported. Also infrared and Raman spectroscopy studies have been reported [6] in o-dichloro, o-chlorobromo and o-dibromobenzene. NQR frequencies of ODCB as a function of temperature, as well as the NQR frequency at two temperatures of o-chlorofluorobenzene (OCFB) and o-chlorobromobenzene (OCBB) have been reported [7–9].

In the present work different solid phases were obtained in OCBB and OCFB depending on the cooling rate. As in p-chlorohalobenzenes, phases with rigid disorder have been found and the static and dynamic characterization of the different phases has been made.

2. Experimental

The o-chlorohalobenzene samples (o-C₆H₄Cl₂, o-C₆H₄ClBr, and o-C₆H₄ClF) used in the experiments were obtained from Sigma-Aldrich (catalog # 240664, B60401, 162302 respectively) and used without further purification. ³⁵Cl NQR measurements were done using a Fourier transform pulse spectrometer with a Tecmag NMRkit II unit and a Macintosh-based real time NMR station. The sample container was a glass cylinder of length 3 cm and diameter 1 cm, closed under vacuum. The NQR spectra were obtained using the nuclear spin-echo Fourier transform mapping

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