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# Specificity in Chemical Perturbation of Crystal Structures†

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The specificity in chemical perturbation of crystal structure is examined by investigating the effect of the position of a particular substituent group on the crystal structure. 1,2,3,5-tetrahalobenzenes are chosen for this study. A comparative study of Raman phonon spectra of 1,2,3,5-tetrachlorobenzene; 1,2,3-trichloro-5-bromobenzene; and 1,3,5-trichloro-2-bromobenzene crystals reveals that the former two have the same crystal structure, while the latter has a different crystal structure. It is inferred that a bromine group substitution in 2-position of 1,2,3,5-tetrachlorobenzene creates a lattice instability which gives rise to a different crystal structure for 1,3,5-trichloro-2-bromobenzene. The nature of this instability is discussed. Mixed crystals of 1,2,3,5-tetrachlorobenzene and 1,2,3-trichloro-5-bromobenzene are studied to establish phonon correlation and delocalization.

## INTRODUCTION

In a recent paper[1] we examined the nature of chemical perturbation on the crystal structure and showed the usefulness of Raman spectroscopy in such studies. In the *p*-dihalobenzene series the same crystal structure is observed[1] for the molecules $p$-$C_6H_4XY$ (X = Cl, Br; Y = Cl, Br, I) but the crystal structure changes when we go to $p$-$C_6H_4I_2$. It was found[1] that the lattice instability encountered in going from $p$-$C_6H_4XI$ (X = Cl, Br) to $p$-$C_6H_4I_2$ was a static instability arising mainly from the failure of the $p$-$C_6H_4XI$ close-packing[2] arrangement in yielding a true minimum of the potential energy surface for $p$-$C_6H_4I_2$. The present paper is an extension of the previous study, the objective being to determine any specificity in the nature of a chemical perturbation. Here we investigate the effect of the position of a particular substituent group on the crystal structure with the use of Raman techniques.

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Previous studies have revealed that in symmetric halobenzenes such as *p*-dihalobenzenes[1,3,4] and sym-tetrahalobenzenes,[5,6] the chloro and bromo compounds are isomorphous at room temperatures. This implies that in these systems substitution of a bromo group in place of a chloro group creates only a small perturbation on the crystal structure. This is confirmed by the observation that mixed halogen (chlorobromo)[7] compounds crystallize in the same space group as the parent pure halocompounds. On the other hand, in the series like 1,2,3,5-tetrahalobenzenes a preliminary study[8] of the crystal structure of 1,2,3,5-tetrachlorobenzene and 1,3,5-trichloro-2-bromobenzene reports them to be different. From the point of view of determining any specificity of the chemical perturbation it will be interesting to find if the 1,2,3-trichloro-5-bromobenzene has the same crystal structure as that of its isomer 1,3,5-trichloro-2-bromobenzene or it prefers to retain the structure of 1,2,3,5-tetrachlorobenzene. In this paper we investigate this problem by a comparative study of the phonon spectra of these three compounds. To further explore the nature of the lattice instability, their binary mixed crystals of various compositions are also examined by obtaining their phonon spectra.

## EXPERIMENTAL

1,2,3,5-tetrachlorobenzene (99% pure) was purchased from Aldrich Chemical Co. 1,2,3-trichloro-5-bromobenzene was synthesized from 2,6-dichloro-5-nitroaniline by substitution first of the amine group by chlorine using the Sandmeyer reaction. The resulting 3,4,5-trichloro-nitrobenzene was reduced with Sn/HCl to 3,4,5-trichloroaniline which was then converted to 1,2,3-trichloro-5-bromobenzene, again using the Sandmeyer reaction. 1,3,5-trichloroaniline was converted to 1,3,5-trichloro-2-bromobenzene also by using the Sandmeyer reaction. Both 1,3,5-trichloro-2-bromobenzene and 1,2,3-trichloro-5-bromobenzene were purified by recrystallization from ethanol followed by sublimation. Mass spectra and melting points indicate them to be the desired compounds.

Binary mixed crystals of these compounds were grown in glass tubing by the Bridgman method. The concentrations were 0, 0.15, 0.25, 0.5, 0.75, 0.85, and 1 mole fractions. The Raman spectra of the samples were obtained using a spex double monochromator (Model 14018) with 1800 grooves/mm holographic gratings. Excitation was provided by the 5145 Å line of an argon ion laser (Model CR-5) at 0.2 w. The sample was cooled by a stream of nitrogen vapor and the temperature was measured with a chromel-constantan thermocouple. The accuracy of the temperature measurement was ±5°K.

## RESULTS AND DISCUSSIONS

The observed Raman phonon spectra of 1,2,3,5-tetrachlorobenzene (TCB); 1,2,3-trichloro 5-bromobenzene (TC5BB); 1,3,5-trichloro-2-bromobenzene (TC2BB) are displayed in Figure 1. The observed frequencies of the phonon bands in these three compounds are summarized in Table I. From the spectral correlation it appears that the TC5BB has the same crystal structure as that of TCB which is reported[8] to be $P2_1/C$ with eight molecules/unit cell. Thus, the substitution of chlorine by bromine in the 5 position causes no lattice instability. This is further confirmed by the observation that they form continuous solid solution as observed by the phonon amalgamation behavior[9,10] in the TCB-TC5BB mixed crystals of various compositions. This result is shown in Figure 2 where the observed phonon frequencies in this mixed crystal series are plotted vs the mole fraction of TC5BB. Mixed crystals of various compositions (mole fractions: 0.15, 0.25, 0.5, 0.75 and 0.85) were investigated. However, for simplicity only the result for the mixed crystals of 0.5 mole fraction is represented in Figure 2. The continuous monotonic shift of the phonon frequencies in the mixed crystal is typical of the amalgamation limit and is an excellent criterion to judge mutual solubility. In segregated phases, phonon amalgamation is not observed but rather the phonon spectra of the two segregated phases superimpose. The observed phonon amalgamation and spectral correlations throughout the concentration range confirm that both TCB and TC5BB have the same crystal structure. The magnitude of the crystal splittings of the phonon bands (factor group splittings at ~20 cm$^{-1}$ and ~45 cm$^{-1}$) do change in going from the TCB to TC5BB showing definite dynamical perturbations in the substitution

TABLE I

Observed phonon frequencies (in cm$^{-1}$)

| TCB | TC5BB | TC2BB |
|---|---|---|
| 17 | 14.5 | 13 |
| 18.5 | 15.5 | 17 |
| 23 | 19.5<br>21.5 † | |
| 30.5 | 28 | 29 |
| 35 | 31 | |
| 42 | 35.5 | |
| 44 | 39 | 44 |
| 49 | 45<br>48.5 † | 50.5 |
| 56 | 53 | |
| 62 | 57.5 | 61 |
| 84 | 80.5 | |

† Factor group splitting.

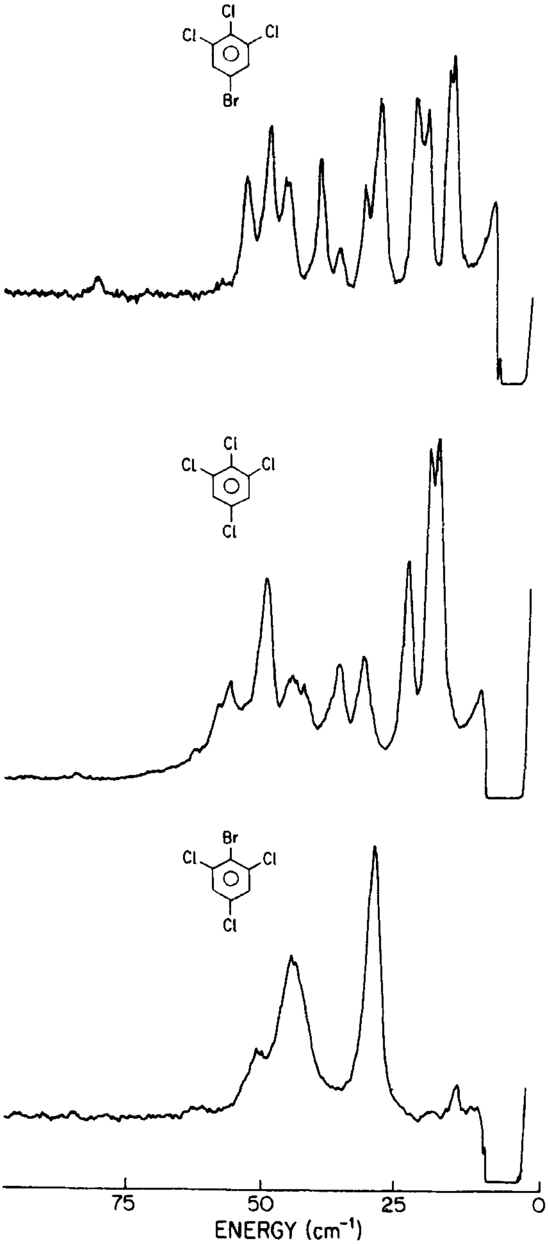

FIGURE 1 Raman Spectra of 1,2,3-trichloro-5-bromobenzene; 1,2,3,5-tetrachlorobenzene; and 1,3,5-trichloro-2-bromobenzene crystals at 120°K. The spectral resolution is ~1 cm$^{-1}$.

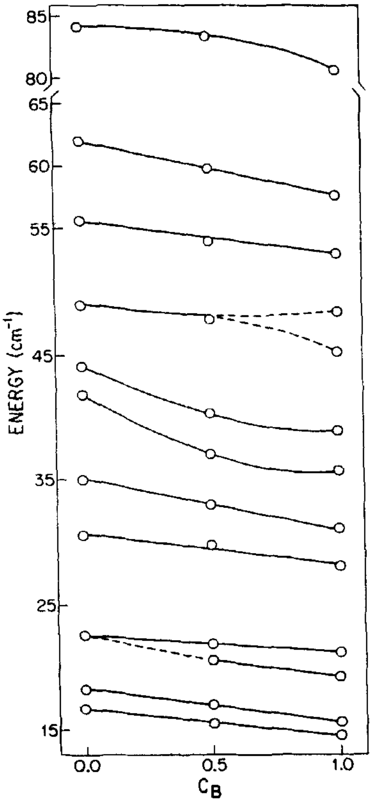

FIGURE 2 A graphical representation of the phonon frequencies observed at 125°K in pure and mixed crystals of 1,2,3,5-tetrachlorobenzene and 1,2,5-trichloro-5-benzene. $C_B$ is the mole fraction of 1,2,3-trichloro-5-bromobenzene.

of the chloro group by the bromo group in the 5 position. The amalgamation behavior also shows that these phonons are delocalized. A lower limit for their *k*-dispersion (bandwidth), which is estimated by the difference in frequencies of the pure components,[9,10] varies from 3 $cm^{-1}$ to 6 $cm^{-1}$.

TC2BB, on the other hand, has a phonon spectrum quite different from both that of TCB and TC5BB, asserting that its crystal structure is different from the latter two. TC2BB has been reported[8] to have tetragonal structure $P\bar{4}2_1m$ with four molecules per unit cell and site symmetry $C_s$. The difference in the crystal structure is further emphasized by the observation that TC2BB does not show appreciable solubility in the solid phase either with TCB or with TC5BB.

Thus a bromine substitution in position 2 of TCB does cause a lattice instability revealing a specificity in the effect of chemical perturbation on the lattice structure. Both TC2BB and TC5BB have the same molecular symmetry and mass coefficients. Furthermore, they are not expected to have widely varying force constants. Thus the dynamical perturbation in going from TC5BB to TC2BB is not significant. From this discussion the lattice instability caused by the bromine substitution in position 2 does not appear to be dynamic.[1] Also, if a dynamic instability[1] were involved it could be created by a thermal perturbation. This is because an increase in temperature shifts phonon frequencies to lower values and thus can soften a mode giving rise to a dynamic instability. On the other hand, our temperature dependence study (120°K to melting point) revealed no phase transition in these molecular crystals supporting the absence of a dynamic instability.[1] It is, thus, inferred that a bromine substitution in position 2 causes a static lattice instability[1] arising primarily from energetic considerations in close packing arrangement. Although the exact nature of the static instability can not be derived from the present experimental data, one possible cause might be the steric effect arising from the placement of a bigger bromine atom in the position 2. The position 2 is surrounded by chlorine groups on both sides and is a crowded region. The substitution in position 2 of a bromine atom with larger van der Waals radii distorts the structure in this region causing the lattice instability.

A likely mode of distortion would be an out of plane distortion of the bromine atom. The result is surprising that an intramolecular distortion of the bromine in position 2 which is surrounded by chlorine atoms and thus less exposed to the lattice for intermolecular interactions, shows such a large lattice instability. On the other hand, a bromine group in position 5, in spite of being fully exposed for lattice interactions, does not cause any instability.

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