A Supramolecular Approach to Organic Alloys: Three and Four-Component Solid Solutions Formed by DABCO and 4-X-Phenols (X = Cl, CH₃, Br)

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1. General Conditions. Solvents purchased from Pharmco, and DABCO and phenols purchased from Alfa Aesar were used as received in the crystallization experiments. Dueterated chloroform and acetone were purchased from Norell. Crystals were grown by slow evaporation of benzene solutions containing DABCO and phenols in the required quantities. Before the crystals were used for spectral, thermal or diffraction analysis, they were subjected to microscopic investigation for morphological consistency.

2. Single Crystal X-Ray Diffraction. Crystals suitable for diffraction were selected under a microscope and mounted on a glass fiber using a small amount of paratone oil. X-ray data were collected using a Bruker SMART diffractometer equipped with a CCD detector and an Oxford Cryostream low-temperature device operating at 193 K. Data were measured using ω scans of 0.3° per frame; each frame was exposed to X-rays for 30 seconds. A total of 1271 frames, covering a hemisphere, were collected with a maximum resolution of 0.76 Å. The first 50 frames were recalculated at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software and refined using the program SAINT on all observed reflections. Data reduction was performed using the program SAINT and absorption corrections were applied using the SADA BS multiscan technique. The structures were solved by the direct methods and refined by the least squares methods on $F^2$ using the program SHELXL-97 incorporated in SHELXTL-PC (version 6.10). The rotational disorder of DABCO in ClCl is ClBr is modeled such that each of the six methylene C-atoms occupied two positions. In ternary solid solutions, two different phenols are statistically disordered over two positions on both sides of DABCO. The result is that groups in the para position of the phenols (viz. Cl/CH₃, Cl/Br, CH₃/Br) are superimposed on each other on both sides. In ClMe and ClBr, each of the superimposed groups (Cl, Me, or Br) is assigned 50% occupancy on both phenols. In these two solid solutions, refining the occupancies of Cl/CH₃ or Cl/Br groups led only to minor changes. In MeBr, however, fixing the occupancies of CH₃/Br groups resulted in larger thermal parameters and higher $R$-values. In this case, refining the occupancies on both sides (with total occupancy per each group is fixed at 100%) led to a more stable refinement with lower thermal parameters and $R$-values etc. The aromatic and methylene H-atom positions were calculated by geometrical methods and refined using a riding model. Phenolic H-atoms (except in the case of ClBr and MeBr) were taken from Fourier maps. Structural analysis was performed by a combination of programs that include XP (SHELXTL-PC, version 6.10), Platon (version 200905), and Mercury (version 1.4.1).

The formation of a given ternary complex (ClMe, ClBr or MeBr) is confirmed by NMR spectroscopy and powder X-ray diffraction. In addition, the change in the volume of the unit cell (Table 1) clearly indicated the formation of ternary solid solution. Because it is difficult to obtain the exact ratio of the components (NMR gives a reasonable approximation), we assigned 50% occupancy to the superimposed pairs of groups on both the phenols.
3. Additional Structural Diagrams.

*Figure S1.* Hydrogen bonded trimolecular assemblies in binary cocrystals and ternary solid solutions.

*Figure S2.* Crystal structure of MeMe. Compare this to Figure 1 to note that MeMe is isostructural to ClCl.
Figure S3. Crystal structures of ternary solid solutions. Note that ClMe and ClBr adopt the structure of ClCl/MeMe whereas MeBr adopts the structure of BrBr.
4. IR Spectroscopy. The IR spectra were recorded in ATR mode on a Perkin Elmer Spectrum One spectrometer. For each measurement only one crystal was taken, which was washed with benzene and dried in air with filter papers immediately prior to the experiment. The broad double hump seen in the region 1600-2800 cm\(^{-1}\) is characteristic of O–H···N hydrogen bonding between DABCO and phenols. An important feature of these spectra is that the broad peak at 3000-3600 cm\(^{-1}\) (corresponding to O–H···O hydrogen bonding in pure phenols) is absent in all of them. These spectra conclusively show that binary cocrystals as well as ternary solid solutions contain only heteromolecular assemblies.

![IR Spectra](ClCl, ClMe, MeMe, ClBr, BrBr)

*Figure S4.* IR spectra of binary cocrystals and ternary solid solutions. Note that **ClMe** and **ClBr** adopt the structure of **ClCl/MeMe** whereas **MeBr** adopts the structure of **BrBr**. In all the spectra, % transmittance is plotted on the y-axes.

5. NMR Spectroscopy. \(^1\)H NMR spectra were recorded on a Bruker 400 MHz spectrometer using deuterated chloroform or acetone as solvents. As with IR spectroscopy, only one crystal (washed and dried) was used in each experiment to avoid contamination from any physisorbed materials. The peaks corresponding to different phenols and DABCO are assigned using colored circles and polygons in Figure S5; same scheme of assignment is followed for the NMR spectra of series of ternary solid solutions (Figure S6-S8). In binary cocrystals there are eight phenolic protons (two distinct sets; each consisting of four protons) and twelve DABCO protons. In order to aid in the analysis of ternary solid solutions, the total proton content (eight) of the phenols is integrated to be ~200 units. The twelve protons on DABCO then integrate to ~300 units. These NMR spectra reveal the relative content of different phenols and DABCO in the multicomponent solids described in this work.
Figure S5. $^1$H NMR spectra of binary cocrystals. Notice the integrations given below the peaks. In this figure and Figures S6-S8 the x-axis refers to chemical shift (δ) in ppm units. The peaks at 2.05 and 7.36 ppm correspond to acetone (solvent used in collecting the spectra) and benzene (solvent used in growing and washing the crystals).
Figure S6. $^1$H NMR spectra of ClMe series of ternary solid solutions. Peaks marked with green circles and pentagons belong to 4-chlorophenol; peaks marked with grey circles and pentagons belong to p-cresol. Only the regions corresponding to the phenolic protons are shown. The discrepancies between peak integrations that were expected and found arise from the manual errors in weighing the samples for crystallization. The peak at 7.36 ppm corresponds to benzene.
Figure S6. continued…
Figure S6. continued…
Figure S7. $^1$H NMR spectra of ClBr series of ternary solid solutions. Peaks marked with green circles and pentagons belong to 4-chlorophenol; peaks marked with magenta circles and pentagons belong to 4-bromophenol. Only the regions corresponding to the phenolic protons are shown. The discrepancies between peak integrations that were expected and found arise from the manual errors in weighing the samples for crystallization. The peak at 7.36 ppm corresponds to benzene.
Figure S7. continued…
Figure S7. continued…
Figure S8. $^1$H NMR spectra of MeBr series of ternary solid solutions. Peaks marked with grey circles and pentagons belong to p-cresol; peaks marked with magenta circles and pentagons belong to 4-bromophenol. Only the regions corresponding to the phenolic protons are shown. The discrepancies between peak integrations that were expected and found arise from the manual errors in weighing the samples for crystallization. The peak at 7.36 ppm corresponds to benzene.
Figure S8. continued…
Figure S8. continued…
6. **Differential Scanning Calorimetry** measurements of cocrystals and solid solutions were made on a TA Instruments differential scanning calorimeter (model DSC-2920). In each case a well-washed and dried crystal was loaded into an aluminium pan. The pans were crimped nonhermetically and the samples were heated from 30-350 °C at a rate of 10 °C/min under a purge of nitrogen gas. All the multicomponent solids showed a melting endotherm that is different from the individual components. One of the components, DABCO (m.p. 78 °C), undergoes decomposition at ~150-170 °C. We noted that the onset of decomposition varied from sample to sample. This onset of DABCO decomposition can be seen (after the melting endotherm) in some of the thermograms of ClMe ternary solid solutions shown in Figure S9.

![DSC traces of ClMe and MeBr series of solid solutions](image-url)

*Figure S9.* DSC traces of ClMe and MeBr series of solid solutions. Compare this figure with Figure 4.
7. **Powder X-Ray Diffraction.** The powder X-ray data were collected on a Rigaku Geigerflex D-MAX/A diffractometer using Cu-Kα radiation. The instrument was equipped with a vertical goniometer and a scintillation counter as a detector and applied Bragg-Brentano geometry for data collection. Samples were finely ground using a mortar and pestle and transferred to a glass sample holder that had loading dimensions 1.6 cm × 2 cm. The data were collected in the 2θ range 5-50° (step size = 0.05°) and at a scan rate of 2° per minute. Figure S10 shows the diffraction patterns of binary cocrystals and ternary solid solutions; it is similar to Figure 3 except that the data were shown from 5-35° in 2θ.

![Figure S10](image_url)

**Figure S10.** Powder X-ray diffraction patterns of series of ClMe, ClBr and MeBr solid solutions. In each series, patterns of corresponding binary cocrystals are given at the top and bottom.
8. Structural Comparison between ClMe, ClBr, and MeBr Series of Solid Solutions. The 50Cl-50Me ternary solid solution is isostructural to ClCl and MeMe; the volume of its unit cell lies between the volumes of unit cells of ClCl and MeMe (Table 1). Powder X-ray analysis of the ClMe series (from 90Cl-10Me to 10Cl-90Me; Figure S10) shows gradual change of the structure from ClCl to MeMe. The 50Cl-50Br solid solution adopts the crystal structure of ClCl, albeit with decreased symmetry (C2/c → P2_1/c; Table 1; Figure S3). Yet the volume of its unit cell is close to that of BrBr indicating the presence of bromine in the crystal. Powder X-ray analysis of the ClBr series (Figure S10) shows that these solid solutions adopt the ClCl structure up to 40Cl-60Br; from 30Cl-70Br to 10Cl-90Br they adopt the BrBr structure. In contrast to ClBr, the 50Me-50Br solid solution adopts the structure of BrBr (Table 1). Figure S10 shows that MeBr solid solutions adopt MeMe structure only upto 90Me-10Br. From 80Me-20Br to 10Me-90Br they adopt the structure of BrBr.

The Br-atom is larger than Cl-atom and CH3 group; it also participates in polarization induced attractive Br···Br interactions. Given these two facts, one would expect that ClBr and MeBr would adopt the structure of BrBr to accommodate the larger Br atoms and attractive Br···Br interactions. It is therefore surprising that ClBr adopts the structure of ClCl and not BrBr. The Cl-atom in ClCl forms 5 contacts to non H-atoms at vdw+0.2 Å separation, and 7 contacts at vdw+0.3 Å separation. If ClBr were to adopt the BrBr structure, the Cl-atom would form no contacts even at the separation of vdw+0.3 Å. In contrast, the vdW contacts made by the CH3 group do not change significantly between MeMe or BrBr structure. It is possible that ClBr adopts the ClCl structure because in this structure the Cl-atoms are involved in intermolecular contacts that are of stabilizing nature.

9. ClMeBr – Quaternary Solid Solution. The following figures show the characterization of ClMeBr by various methods (DSC, IR, NMR and PXRD). The unit cell parameters of ClMeBr reported in Table 1 are determined by single crystal X-ray diffraction. The IR spectrum (Figure S11) shows that a single crystal of ClMeBr has only heteromolecular assemblies and the 1H NMR spectrum (Figure S12) shows that DABCO and three phenols are in 1.5:1:1:1 ratio. The DSC thermogram shows that ClMeBr has a distinct melting point that is different from the corresponding binary cocrystals or ternary solid solutions (Figure S13). Single crystal and powder x-ray diffraction analysis (Figure S14) shows that ClMeBr adopts the structure of BrBr.

Figure S11. IR spectrum of ClMeBr showing the double hump (in the region 1600-2800 cm⁻¹) characteristic of hydrogen bonding between DABCO and phenols.
Figure S12. $^1$H NMR spectrum of ClMeBr. The peak at 5.63 belongs to CH$_2$Cl$_2$ that contaminated acetone-d$_6$.

Figure S13. DSC trace of ClMeBr (in open circles) showing the melting endotherm. DSC traces of binary cocrystals and ternary solid solutions are shown for comparison.
Figure S14. Powder X-ray diffraction pattern of ClMeBr (bottom trace). Powder X-ray diffraction patterns of BrBr and ClCl are shown for comparison. Note that ClMeBr adopts the structure of BrBr. In ClMeBr, diffraction peaks appear at slightly higher 2θ values indicating the reduced volume of its unit cell.