Three pairs of polymorphs of solvated crystals, which are of the same solvent and stoichiometries, were obtained for indantrione 1,2-dioxime (1) and alcohols. The crystal structures of these polymorphs, formulated as \( \alpha^- \) and \( \beta^- \cdot \text{MeOH} \), \( \alpha^- \) and \( \beta^- \cdot \frac{1}{2}\text{MeOH} \), and \( \alpha^- \) and \( \beta^- \cdot \text{EtOH} \), were investigated using X-ray crystallographic analyses.
Polymorphism in Solvate Crystals of Indantrione 1,2-Dioxime

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ABSTRACT: Indantrione 1,2-dioxime (1) afforded crystals solvated by different species of alcohols and in different stoichiometries. Among those, three pairs of polymorphic forms, which are of the same solvent and stoichiometry, were obtained. The crystal structures of those polymorphs, formulated as α- and β-1·MeOH, α- and β-1·½MeOH, and α- and β-1·EtOH, were elucidated along with that of 1·i-PrOH. The common building block in the crystal structures is a centrosymmetric planar dimer linked by bifurcated hydrogen bonding. The dimer is further assembled through alcohol molecules to form tapelike linear chains. The difference in crystal structure between all pairs of the polymorphs is principally attributed to a distinct hydrogen bonding motif between the dimer and solvated alcohol molecules. Carbonyl-carbonyl interaction is also recognized to play a role in molecular alignment in most cases; the carbonyl groups of neighboring molecules are in close contact and have an all-planar antiparallel arrangement.

Introduction

Predictions of polymorphism,1 the ability of a molecule to crystallize in different structures, are still in their infancy,2,3 although it is important in pigments,4 pharmaceuticals,5 and organic conductors.6 The observed differences in the properties of polymorphs have been interpreted on the basis of structural findings. Conformationally flexible molecules may possess a greater
propensity to exhibit polymorphism as energies required for rotation about single bonds are often comparable to lattice energy differences between polymorphs. The term "conformational polymorphism" has been used to describe such systems. For rigid molecules, on the other hand, the occurrence of conformational polymorphism may be rare because of a lack of conformational freedom, and their plausible polymorphism would instead principally be attributed to differences in packing motifs and/or topologically distinct molecular interactions. Such polymorphism is considered to be more favorable for multi-functionalized rigid molecules because of a variety of intermolecular interactions possible for distinct crystalline networks.

For multi-component crystals such as co-crystals and crystalline host-guest inclusion complexes (clathrate crystals or crystal solvates), the existence of two or more crystalline forms that differ in the type or stoichiometry of the component molecules has been known. It seems likely that multi-component crystalline materials are less prone to polymorphism. Thus, the polymorphs of solvate crystals, in which both the component species and the stoichiometries are identical but the crystal packings are different, are much less frequently encountered than the existence of solvate crystals, which consist of identical guest components but are of different stoichiometries. In this paper, we report unique examples of the former in solvate crystals; one compound gives rise to three pairs of polymorphic solvates. The molecule in question is indantrione 1,2-dioxime (1). Compound 1 bears substantial donor and acceptor sites for hydrogen bonding in a rigid planar framework. Such an amphoteric nature leads to a variety of molecular interactions and hence provides high probability for the existence of polymorphism. Although the oxime group remains relatively unexplored as a supramolecular synthon, existence of polymorphism in oxime compounds has been known. As expected, compound 1 has been found to form supramolecular polymorphic crystals with alcohols. For methanol and ethanol we have found the existence of polymorphs. In Scheme
1, the relationship of a single molecule to polymorphic solvates found in this study is shown. To our knowledge, gossypol, a naturally occurring polyphenolic terpene, has also a tendency to form polymorphic structures with same guest molecules, e. g., solvates formed with dichloromethane\textsuperscript{15} and acetone.\textsuperscript{16,17}

![Scheme 1. From a single molecule to solvates and further to polymorphs of solvates.](image)

To gain insight into the differences in molecular interactions between the polymorphs, we have undertaken X-ray crystallographic studies of these polymorphs. Here, we present characteristic crystal structures of the solvates of 1, focusing on hydrogen bonding motifs and supramolecular arrays.

**Results and Discussion**

**Formation of alcohol solvates of indantrione 1,2-dioxime.** The recrystallization of 1 from methanol, ethanol, and isopropyl alcohol gave rise to seven solvate crystals (experimental section). Their crystal data are listed in Table 1. Among these, $\alpha$- and $\beta$-1-MeOH crystals are polymorphs solvated by methanol in a 1:1 composition, and $\alpha$- and $\beta$-1·½MeOH are those in a 2:1 composition. The crystals of $\alpha$- and $\beta$-1-EtOH are also polymorphs, which include ethanol in a 1:1 composition. In all the crystals obtained, solvent molecules were released.
within a day as crystallinity collapsed. Solvent-free crystals of 1 suited for an X-ray crystallographic study could not be isolated in spite of all our attempts at recrystallization from a variety of solvents.

### Table 1. Crystallographic data of solvated compounds of 1.

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<tr>
<th></th>
<th>α-1 · MeOH</th>
<th>β-1 · MeOH</th>
<th>α-1 · %MeOH</th>
<th>β-1 · %MeOH</th>
<th>α-1 · EtOH</th>
<th>β-1 · EtOH</th>
<th>1 · i-PrOH</th>
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<td>223</td>
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<td>C_{19}H_{16}O_{7}N_{4}</td>
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<td>monoclinc</td>
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<td>P2_1/c</td>
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Molecular structure and dimeric units. The characteristic feature of the solvate crystals of 1 is the dimeric assembly of molecule 1 by bifurcated hydrogen bonding of the hydroxyl group with the O and N atoms. This dimeric unit was found in all the solvates examined in this research, and its structure is basically always the same. Figure 1 shows a typical example of a dimeric arrangement for α-1·MeOH. The molecule is planar including the two hydroxyl groups. The N-O bond of the oxime group on C1 is directed toward the benzene ring of the indan framework and that on C2 is directed toward the C1=N1 site, that is, both being in s-trans conformations. These configurations bring about a close intramolecular contact of 2.739 Å between the N1 and O2 atoms.

Figure 1. ORTEP drawing of a dimeric unit of 1 in the α-1·MeOH polymorph. 50% thermal ellipsoids are shown.

The O1-H group of the C=N-OH function on C1 forms bifurcated hydrogen bonds with the O2 and N1 atoms of the other molecule of 1 to bring about a centrosymmetric cyclic hydrogen bonding motif. For example in α-1·MeOH, the O1(H)···N1 distance is 2.799 Å, and the O1(H)···O2 distance is 2.930 Å. This observation is to be anticipated, because the oxime group tends to form head-to-tail cyclic dimers, which held together by complementary OH···N hydrogen bonds.14,18 On the other hand, the hydroxyl group O2-H plays no role as a H-donating function within the dimeric assembly, and hence is available to form hydrogen bonds with the solvent molecules or between dimers. This is also the case for the carbonyl
oxygen O₃ and the oxime nitrogen N₂, which are open as hydrogen bonding acceptors for solvent molecules. Thus, the dimer of 1 is regarded as a fundamental building block in these supramolecular structures. Scheme 2 shows a summary of the supramolecular networks formed by the hydrogen bonding of the dimeric units in a diagrammatic representation.

Scheme 2. Diagrammatic representation of hydrogen-bond networks observed in pseudo-polymorphs of 1 and their polymorphs. (a) α-1·MeOH, α-1·EtOH, 1·i-PrOH. (b) β-1
Supramolecular arrays of polymorphs $\alpha$-I·MeOH and $\beta$-I·MeOH. In polymorph $\alpha$-I·MeOH, the guest molecules bridge the dimeric units of I by hydrogen bonding with the oxime group N2=O2-H2 at the 2-position, resulting in the formation of a centrosymmetric cyclic assembly consisting of two dimers and two methanol molecules. Thus, the oxime group acts as both a H-donating site and a H-accepting site to methanol. The MeO···N= distance is 2.990Å, and the NO···OMe distance is 2.590 Å. The carbonyl group of I is not involved in intermolecular interactions: the distance between the oxygen atoms of MeOH and the carbonyl group is 3.235 Å. The MeOH molecules are positioned in approximately the plane formed by the dimers; therefore, a tapelike linear array is formed by alternant arrangements of methanol molecules and the dimeric unit (Figure 2). There are two tapes running along the $b$-axes that result in packing in a $P2_1/c$ space group.

Figure 2. Crystal structure of the $\alpha$-I·MeOH polymorph, showing the tapes made by dimeric units and methanol molecules running along the $b$-axis. Hydrogen bonds are shown by dashed lines.
Polymorph β-1·MeOH is packed in the $P2_1/c$ space group similarly to α-1·MeOH, but the supramolecular array is considerably different from that of the α-1·MeOH polymorph. First, the dimer unit is linked only by one methanol molecule, which shows hydrogen bonding with the carbonyl group C3=O3 as a H-donor. Thus, the MeO⋯O=C distance is significantly
shortened from 3.235 Å in α-1·MeOH to 2.840 Å in β-1·MeOH. On the other hand, the C=N···OMe distance is markedly longer, from 2.990 Å in α-1·MeOH to 3.351 Å in β-1·MeOH. This means that the hydrogen accepting site in the host molecule is exchanged in α-1·MeOH and β-1·MeOH polymorphs, between the oxime nitrogen (N2) in the former and the carbonyl oxygen (O3) in the latter. Thus, the oxime group acts only as a H-donating site for a guest methanol molecule with a NO···OMe distance of 2.605 Å. Second, the neighboring dimer units are linked at a tilt in contrast with the planar linkage in the α-1·MeOH form (Figure 3). This may result from cross linking of the dimers due to a hydrogen bonding motif as described previously. Third, noncovalent carbonyl-carbonyl interactions due to the >C(δ+)−O(δ−) dipole are observed in β-1·MeOH (Figure 4). The carbonyl groups of the neighboring molecules are in close contact with the antiparallel arrangement and a zero torsional angle, indicating an all-planar antiparallel arrangement of the two C=O groups. The C···O distance is 3.024 Å (Table 2), which is markedly shorter than 3.6 Å, which is the accepted value for carbonyl···carbonyl interactions.19 This observation is reasonable, taking into consideration that the carbonyl group, being at the same time hydrogen-bonded and consequently highly polarized, is advantageous for both hydrogen bonding and the carbonyl interaction.

**Supramolecular arrays of polymorphs α-1·½MeOH and β-1·½MeOH.** Polymorphs α-1·½MeOH and β-1·½MeOH are in a 2:1 composition with methanol as solvated species. In α-1·½MeOH, a methanol molecule connects two dimeric units as a H-donor for the >C=O and as a H-acceptor for the =NOH group (Figure 5). Beside the inter-heteromolecular hydrogen bonding (MeO···O=C): 2.798 Å, NO···OMe: 2.568 Å), inter-homomolecular hydrogen bonding between the dimeric units is observed: the oxime OH shows bifurcated hydrogen bonding as a H-donor to both the carbonyl oxygen and the nitrogen of the oxime group
(NO···O=C: 3.055 Å, NO···NO: 2.889 Å). These hydrogen bonding motives bring about linear tapes, which stack in layered arrangements. No specific interactions are observed between the layers. It is interesting to note that the crystal structures of α-I·½MeOH and α-I·MeOH seem to be related. Thus, α-I·½MeOH is formed by removing one MeOH molecule from α-I·MeOH, while α-I·MeOH is formed by inserting one MeOH molecule to α-I·½MeOH by breaking inter-homomolecular hydrogen bonds.

The polymorph β-I·½MeOH also shows a linear tape, the geometry of which is essentially the same as that observed in α-I·½MeOH (MeO···O=C: 2.960 Å, NO···OMe: 2.593 Å, NO···O=C: 3.022 Å, NO···NO: 2.907 Å) (Figure 6). The difference between the α-I·½MeOH and β-I·½MeOH polymorphs is in the alignment of the adjacent tapes. For β-I·½MeOH, the all-planar antiparallel C=O···C=O interaction is observed between the tapes (Table 2), which results in less overlap of the dimers between the adjacent tapes compared with that for α-I·½MeOH (Figure 7).

**Figure 5.** Arrangement of the dimer units and methanol molecules in the α-I·½MeOH polymorph.
**Figure 6.** Arrangement of the dimer units and methanol molecules in the β-1·½MeOH polymorph.

**Figure 7.** Overlapping pattern of molecule 1 in (a) α-1·½MeOH and (b) β-1·½MeOH polymorphs.

**Supramolecular arrays of polymorphs α-1·EtOH and β-1·EtOH.** The supramolecular hydrogen bonding network of α-1·EtOH is the same as that observed in α-1·MeOH. The molecules are arranged in tapes (NO···OEt: 2.580 Å, 2.940 Å). The carbonyl group (C3=O3) is again free from hydrogen bonding. The difference between this structure and α-1·MeOH is that in α-1·EtOH all tapes align in the same direction without cross orientation (Figure 8). The carbonyl-carbonyl interaction is also observed between the tapes in a parallelogram arrangement of the two C=O groups (Table 2).
Figure 8. Crystal structure of the $\alpha$-1·EtOH polymorph.

The crystal structure of polymorph $\beta$-1·EtOH is characterized by centrosymmetric dimeric unit without crystallographic inversion center, which was not found in other solvates of 1. This is observed from the molecular structure of 1 in the dimeric unit: the bond length of the carbonyl groups is different between the two molecules of 1, one being 1.204 Å, while the other is 1.227 Å. The longer C=O bond participates in a hydrogen bond with the ethanol molecule. Thus, the $\beta$-1·EtOH polymorph includes two crystallographically independent molecules of 1 and of ethanol in a unit cell, and it crystallizes in the space group $P2_1/c$. One of the ethanol molecules participates in a cyclic hydrogen bonding motif consisting of four molecules (NO···OEt: 2.555 Å, 2.913 Å), while the other connects the dimers by a single molecule to split the tapes (EtO···O=C: 2.807 Å, NO···OEt: 2.603 Å) (Figure 9). In the latter, the oxime group plays a role only as a H-donor and its nitrogen atom accepts no hydrogen bonding (C=N: 1.285 Å).
Å and 1.277 Å). The carbonyl-carbonyl interaction is observed, which is slightly deformed from a parallelogram with a torsion angle of 0.7° (Table 2). This is attributed to a large difference in C=O bond length, as noted in Table 2.

![Crystal structure of the β-1·EtOH polymorph.](image)

**Figure 9.** Crystal structure of the β-1·EtOH polymorph.

**Supramolecular array of 1·i-PrOH.** The packing arrangement of 1·i-PrOH crystal is the same as that of α-1·EtOH. Thus, two guest molecules link the dimeric units by the cyclic hydrogen bond motif to form infinite tapes running along the diagonal direction of the \(ab\)-plane (Figure 10). Carbonyl-carbonyl interactions are observed between the tapes (Table 2). The two carbonyl groups are arranged in close proximity (C=O···C=O: 3.023Å) compared with other cases observed in this study. It may be interesting to explore a correlation between the C=O bond length and the intensity of dipolar carbonyl interactions. We could not find such a relation in this study, although we did observe that the C=O bond that is not involved in the dipolar carbonyl interaction in α-1·MeOH is 1.220 Å, which is relatively long.
Figure 10. Crystal structure of 1·i-PrOH, showing two molecules of 1 arranged for carbonyl-carbonyl interaction.

Table 2. Geometry of carbonyl-carbonyl interaction in solvated crystals of 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Torsion / °</th>
<th>O···O / Å</th>
<th>R / Å</th>
<th>α / °</th>
<th>β / °</th>
<th>C=O / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-1·MeOH</td>
<td>0.0</td>
<td>3.403(2)</td>
<td>3.024(2)</td>
<td>97.51(8)</td>
<td>82.49(8)</td>
<td>1.213(1)</td>
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<tr>
<td>β-1·½MeOH</td>
<td>0.0</td>
<td>3.607(4)</td>
<td>3.214(5)</td>
<td>98.8(2)</td>
<td>81.2(2)</td>
<td>1.218(4)</td>
</tr>
<tr>
<td>α-1·EtOH</td>
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<td>3.102(3)</td>
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<td>1.211(2)</td>
</tr>
<tr>
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<td>3.103(4)</td>
<td>95.9(2)</td>
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<tr>
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<td>3.023(3)</td>
<td>92.1(1)</td>
<td>87.9(1)</td>
<td>1.209(2)</td>
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</table>
**General remarks.** The O-N bond of the oxime group is held in *s-trans* conformation in all the crystals. If the OH at C2 has the *s-cis* conformation, the OH···N intramolecular hydrogen bond may form intramolecular six-membered rings via hydrogen bonding, which is highly predominant in the hydrogen bonding hierarchy. Nevertheless, compound 1 actually prefers the *s-trans* conformation, which may require more intermolecular hydrogen bonds for stabilization and hence resulting in the formation of dimers. Thus, differences in the crystal structures of the polymorphs are primarily attributed to distinct hydrogen bonding networks formed by the dimer of 1 and solvated alcohol molecules. These may be classified into three patterns; types [a], [b], and [c]. Type [a] is a four-molecule cyclic aggregation, in which two alcohol molecules connect the two dimers to place them in coplanar orientation, as seen in Scheme 2 (a). This pattern was observed in 1:1 crystals except for β-1·MeOH. The second pattern, type [b], is observed in 2:1 crystals of MeOH solvate, wherein neighboring dimers are linked by hydrogen bonding via one alcohol molecule and simultaneously with each other at the oxime groups, as shown in Scheme 2 (d). Thus, a three-molecule cyclic hydrogen bonding motif results, which also brings about the coplanarity of neighboring dimers. In type [c], one molecule of the alcohol plays the role of connector between two dimers, as seen in Scheme 2 (b). The hydrogen bonding motif is not cyclic; hence, this connector plays no role in making a coplanar alignment of the neighboring dimers. Hydrogen bonding in types [a] and [b] brings about tapelike linear chains including the alcohol molecules. This holds for polymorphs α-1·MeOH, α-1·½MeOH, β-1·½MeOH, α-1·EtOH, and 1·i-PrOH. On the other hand, in crystals including type [c] hydrogen bonding, the alcohol molecules link the dimers in a tilted orientation. This is the case for polymorphs β-1·MeOH and β-1·EtOH, which crystallize in the *P2_1/c* space group.

Another characteristic feature in addition to the hydrogen bonding pattern is the
carbonyl-carbonyl dipole interaction, which is observed in all the crystals except \( \alpha\cdot 1 \cdot \text{MeOH} \) and \( \alpha\cdot 1 \cdot \frac{1}{2} \text{MeOH} \). In Table 2, geometries related to carbonyl-carbonyl interactions found in this work are listed. The C=O bond length is slightly affected by carbonyl-carbonyl interactions. This is typically deduced by comparing the C=O bond length in \( \alpha\cdot 1 \cdot \text{EtOH} \) (1.211 Å), which is involved only in carbonyl interactions, with that in \( \alpha\cdot 1 \cdot \text{MeOH} \) (1.220 Å), in which neither hydrogen bonding nor carbonyl interactions are operative.

**Conclusions**

We demonstrated the occurrence of polymorphs in solvate crystals, that is, crystals solvated by identical solvent species with identical stoichiometries. Indantrione 1,2-dioxime afforded three sets of such polymorphs. The 1,2-dioxime is characterized by its great preference to form dimers by complementary hydrogen bonding of the oxime group. The neighboring carbonyl and oxime groups in the molecular framework are capable of acting simultaneously as hydrogen acceptors for bifurcated hydrogen bonding. The difference in supramolecular arrays between the polymorphs is basically attributed to the hydrogen bonding motif bridging the dimers and the solvent molecules. When cyclic hydrogen bonding occurs because of the participation of alcohol molecules, planar tapes of molecule 1 are realized, and they stack in layers. In the case that one molecule of alcohol acting as hydrogen donor and acceptor bridges the dimers linearly, the plane of the connected dimers is crossed and the crystals are packed in a \( P2_1/c \) space group. Besides hydrogen bonding, carbonyl-carbonyl dipolar interactions are observed in all-planar antiparallel geometry. The molecular interactions supporting the supramolecular array exert a subtle energy balance and influence each other.
**Experimental**

**Preparation of compounds.** Compound 1 was prepared by the reaction of ninhydrin with hydroxylamine hydrochloride in aqueous ethanol in the presence of sodium acetate. Ninhydrin (3.5 g, 20 mmol) and hydroxylamine (3.4 g, 40 mmol) were refluxed along with sodium acetate (3.2 g, 40 mmol) in methanol (200 mL) for 3 h. Work-up of the reaction mixture, including extraction with CH$_2$Cl$_2$, washing, drying (MgSO$_4$), and evaporation of the solvent under reduced pressure, yielded a crude product that was purified by column chromatography on silica gel (dichloromethane as eluent) to provide 1 in 13 % yield. mp 171~172 °C (lit. 13 172~173 °C). $^1$H-NMR (500 MHz, DMSO-d$_6$) δ 7.70 (1H, t, $J = 7.8$ Hz), 7.85 (1H, t, $J = 7.6$ Hz), 7.89 (1H, d, $J = 7.6$ Hz), 8.57 (1H, d, $J = 7.6$ Hz), 12.90 (1H, s), 13.50 (1H, s).

**Formation of solvated crystals.** The solvated crystals of compound 1 were obtained as follows: Compound 1 (0.02 g) was dissolved by heating in methanol (5 mL). After storage for one month at room temperature, crystals were collected to give α-1·MeOH. The same procedure for 1 (0.05 mL) in methanol (2 mL) afforded α-1·½MeOH. With the intention of obtaining co-crystals, 1 (0.05 g) was recrystallized with hydroquinone (0.05 g) in methanol (3 mL). After one month, crystals of β-1·MeOH were deposited simultaneously with hydroquinone crystals. When 1 was dissolved in a mixed solvent of trifluoroethanol and methanol, β-1·½MeOH was obtained after one month. Compound 1 (0.01 g) was dissolved by heating in ethanol (2 mL). After storage for one month at room temperature, crystals were collected to give β-1·EtOH. With the intention of obtaining co-crystals, compound 1 (0.02 g) was recrystallized with catechol (0.01 g) in ethanol (3 mL). After one month, crystals of α-(1)(EtOH) were deposited simultaneously with catechol crystals. Crystals of 1·i-PrOH were
obtained by the recrystallization of 1 from 2-propanol.

**X-ray crystallography.** X-ray analysis was performed for a single crystal coated with adhesive immediately after it was taken out of solution. X-ray crystallographic data were collected at 223 K for 1·i-PrOH, at 223 K for β-1·MeOH, α-1·½MeOH, and β-1·EtOH, at 295 K for α-1·EtOH, and at 296 K for α-1·MeOH and β-1·½MeOH on a Rigaku RAXIS-RAPID imaging plate diffractometer using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). The crystal structures were solved by the direct method using SIR92 and refined by the full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically. Coordinates of hydrogen atoms bonded to each oxygen atom were determined from a difference Fourier map and refined isotropically. Other hydrogens were placed at calculated positions with C-H = 0.95 Å and refined using the riding model. All calculations were performed using the CrystalStructure 3.8 crystallographic software package. Crystal data have been submitted to CCDC.

Crystal data for α-1·MeOH: CCDC-798079. β-1·MeOH: CCDC-798080. α-1·½MeOH: CCDC-798081. β-1·½MeOH: 798082. α-1·EtOH: CCDC-798077. β-1·EtOH: CCDC-798078. 1·i-PrOH: CCDC-798083. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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**Supporting Information Available:** X-ray crystallographic reports (CIF) are available free of charge via the Internet at http://pubs.acs.org.
References


(12) After the preparation of this manuscript, the crystallographic study of metal complexes of indantrione 1,2-dioxime has been reported; Chen, Z.; Jia, M.; Zhang, Z.; Liang, F. Crystal Growth & Design, 2010, 10, 4806.


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Three pairs of polymorphs of solvated crystals, which are of the same solvent and stoichiometries, were obtained for indantrione 1,2-dioxime (1) and alcohols. The crystal structures of these polymorphs, formulated as $\alpha$- and $\beta$-1·MeOH, $\alpha$- and $\beta$-1·½MeOH, and $\alpha$- and $\beta$-1·EtOH, were investigated using X-ray crystallographic analyses.