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Isostructurality in one and two dimensions: isostructurality of polymorphs

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A set of polymorphic crystal structures was retrieved from the Cambridge Structural Database in order to estimate the frequency of isostructurality among polymorphs. Altogether, 50 structures, the polymorphs of 22 compounds, were investigated. It was found that one-, two- or three-dimensional isostructurality is exhibited by approximately half of the compounds analyzed. Among the isostructural polymorphs, the frequency of one-, two- and three-dimensional isostructurality is similar. From the examples, it appears that three-dimensional isostructurality is connected to the gradual ordering of crystal structures, while one- and two-dimensional isostructurality can often be related to specific packing interactions. The possibility of many similar interactions seems to decrease the probability of the occurrence of isostructural polymorphs. Conformational polymorphs do not exhibit isostructurality.

1. Introduction

Isostructurality refers to the similarity of the spatial arrangements of the molecules of different compounds in their crystals (Fábián & Kálmán, 1999). It is traditionally interpreted in three dimensions, *i.e.* isostructurality involves whole structures, which are infinite in three dimensions by means of three crystallographic translations. However, it is possible to extend the interpretation of the phenomenon to one- and two-dimensional isostructurality. If two crystal structures contain similar infinite two-dimensional molecular arrangements (layers) then they are termed two-dimensionally isostructural. Accordingly, structures with similar rows of molecules are one-dimensionally isostructural. The crystallographic relevance of such an extended interpretation is justified by a report on the successful co-crystallization of one-dimensionally isostructural materials (Anthony *et al.*, 2000). Note that this interpretation does not depend on unit-cell parameters and space-group symmetries, and is incompatible with the classical term isomorphism, which is often used synonymously with isostructurality.

While isostructurality implies similar crystal structures for different compounds, polymorphism is defined as the existence of two or more different crystal structures for the same compound. Thus, the two phenomena seem contradictory. Recently, we have reported on polymorph pairs that are composed of similar layers (Fábián *et al.*, 1999; Kálmán *et al.*, 2003). Since these dimorphs can be considered two-dimensionally isostructural, we decided to estimate the frequency of one- and two-dimensional isostructurality between polymorphs by using the Cambridge Structural Database (CSD; April 2003 issue; Allen, 2002). Additionally, some cases of

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Table 1
Polymorphic structures retrieved from the CSD.

References to the crystal structures are given in the text.

Structure	CSD refcode	Isostructurality	Fig.
6-Hydroxy-4,4,5,7,8-pentamethyl-3,4-dihydrocoumarin			2
Polymorph 1	MEZKEH02	Three-dimensional: 1, 2, 3	
Polymorph 2	MEZKEH04		
Polymorph 3	MEZKEH12		
7*b*-(2,4-Dinitrophenyl)fluoradene			3
Polymorph 1	RAKWIJ	Three-dimensional	
Polymorph 2	RAKWIJ03		
m-Tetrachlorodicyanobenzene hexamethylbenzene			4
Polymorph I	MOCCOW01	Three-dimensional	
Polymorph II	MOCCOW		
2,3,7,8-Tetrahydrobenzo[1,2-*b*:4,5-*b*′] bis[1,4]dithiin-5,10-dione			5
Polymorph I	GUKPEH01	Three-dimensional	
Polymorph II	GUKPEH		
4,6-Dimethoxy-3-methyl-2,3-dihydrotriazine-2-one			6
Low-temperature form	ZEXXOP01	Three-dimensional	
High-temperature form	ZEXXOP03		
5-Bromobenzfurazan-1-oxide			7
High-temperature polymorph	BBZFRO01	Three-dimensional	
Low-temperature polymorph	BBZFRO02		
p-Tetrachlorodicyanobenzene hexamethylbenzene			8
Polymorph I	ADULEQ01	One-dimensional: I, II	
Polymorph II	ADULEQ02	Two-dimensional: II, III, IV	
Polymorph III	ADULEQ03		
Polymorph IV	ADULEQ04		
Glycine			9
α form	GLYCIN19		
β form	GLYCIN	Two-dimensional, one-dimensional	
γ form	GLYCIN16		
5-Oxatricyclo[5.1.0.0^{1,3}]octane-4-one			10
Orthorhombic polymorph	FAFDAS01	Two-dimensional	
Monoclinic polymorph	FAFDAS02		
Acetonitrile			11
α form	QQQCIV05	One-dimensional	
β form	QQQCIV04		
4,6-Dimethoxy-3-methyl-1,3,5-triazine-2(3*H*)thione			12
Monoclinic polymorph	QOYNOH	One-dimensional	
Orthorhombic polymorph	QOYNOH01		
Maleic hydrazide			13
MH1 triclinic polymorph	MALEHY11	One-dimensional	
MH2 monoclinic polymorph	MALEHY01		
MH3 monoclinic polymorph	MALEHY12		
4,4′-Bipyridyl (*S*)-malic acid			14
Monoclinic polymorph	MOBZAE	None	
Triclinic polymorph	MOBZAE01		
Benzoylmethyl phenyl sulfone			15
Orthorhombic polymorph	KADTEO01	None	
Monoclinic polymorph	KADTEO02		
N,*N*′-dithiodiphthalimide			
Monoclinic polymorph 1	QOGNEF	None	
Orthorhombic polymorph	QOGNEF01		
Monoclinic polymorph 2	QOGNEF02		
Ethylenediammonium 3,5-dinitrobenzoate			
Triclinic polymorph	VUJXIH	None	
Monoclinic polymorph	VUJXIH02		
Aplysistatin			
Orthorhombic polymorph	APLYSU10	None	
Hexagonal polymorph	APLYSU11		
Ethyl *N*-(2-amino-6-benzyloxy-5-nitrosopyrimidin-4-yl)-β-alaninate			
Polymorph I	OFEXAY01	None	
Polymorph II	OFEXAY		
4-Nitro-4′-methylbenzylideneaniline			
Triclinic polymorph	NMBYAN	None	
Monoclinic polymorph	NMBYAN01		
(μ_2-Oxo)bis[bis(*N*,*N*-diethyldithiocarbamato-*S*,*S*′)oxomolybdenum]			
Triclinic polymorph	XETCMO	None	
Monoclinic polymorph	XETCMO03		
Phenol			
Low-pressure polymorph	PHENOL03	None	16
High-pressure polymorph	PHENOL11		
Hexatriaconta(phenylseleno)pentacontaselenadotriaconta mercury			
Cubic polymorph	TUJFUZ01	None	
Trigonal polymorph	TUJFUZ02		

three-dimensional isostructurality were also found during our analysis.

2. Method

To obtain reasonable estimates, a random set of polymorphic systems is necessary. Since there is no automated tool to check for one- or two-dimensional isostructurality, this set has to be kept small. [Gelbrich (2003) is developing a program for the automatic recognition of similar packing arrangements.] To obtain such a set, the CSD was searched for structures (*a*) that were published in the 2001 or 2002 issues of *Acta Crystallographica* Section B and (*b*) for which the CSD entry contained a reference to polymorphism. If an entry contained three-dimensional coordinates then other forms of the respective compound were retrieved by a full search of the CSD. Coordinates of more than one form were found for 22 polymorphic systems. Only the best model was retained from redeterminations of a given structure. Each system was checked for one-, two- or three-dimensional isostructurality among the modifications by visual comparison of the structures.

3. Results

Altogether, 50 crystal structures (Table 1), the polymorphs of 22 compounds, were examined. Ten of the compounds crystallized without isostructurality between their polymorphs. These structures included conformational polymorphs, polymorphs that differ in the geometry of a common hydrogen-bond pattern and modifications with identical molecular

geometry but with completely different intermolecular interactions.

Six examples of three-dimensional isostructurality were found. They are mainly pairs of disordered symmetric structures and an ordered pseudosymmetric structure. Similar reduction of symmetry was also observed for a fully ordered structure pair. Polymorphism is the existence of two or more different arrangements of the molecules of the same compound in the solid state. While possible interpretations of 'the same compound' were discussed in recent reviews (Dunitz & Bernstein, 1995; Dunitz, 1995; Threlfall, 1995), the meaning of 'different arrangements' attracted less attention. All three-dimensionally isostructural forms are at the borderline of polymorphism, and their classification as polymorphs depends on an individual interpretation of the term 'different arrangements'. Nevertheless, these cases were retained in our data set, since the original authors always demonstrated an experimental proof of the thermodynamic and/or structural difference between the crystal forms.

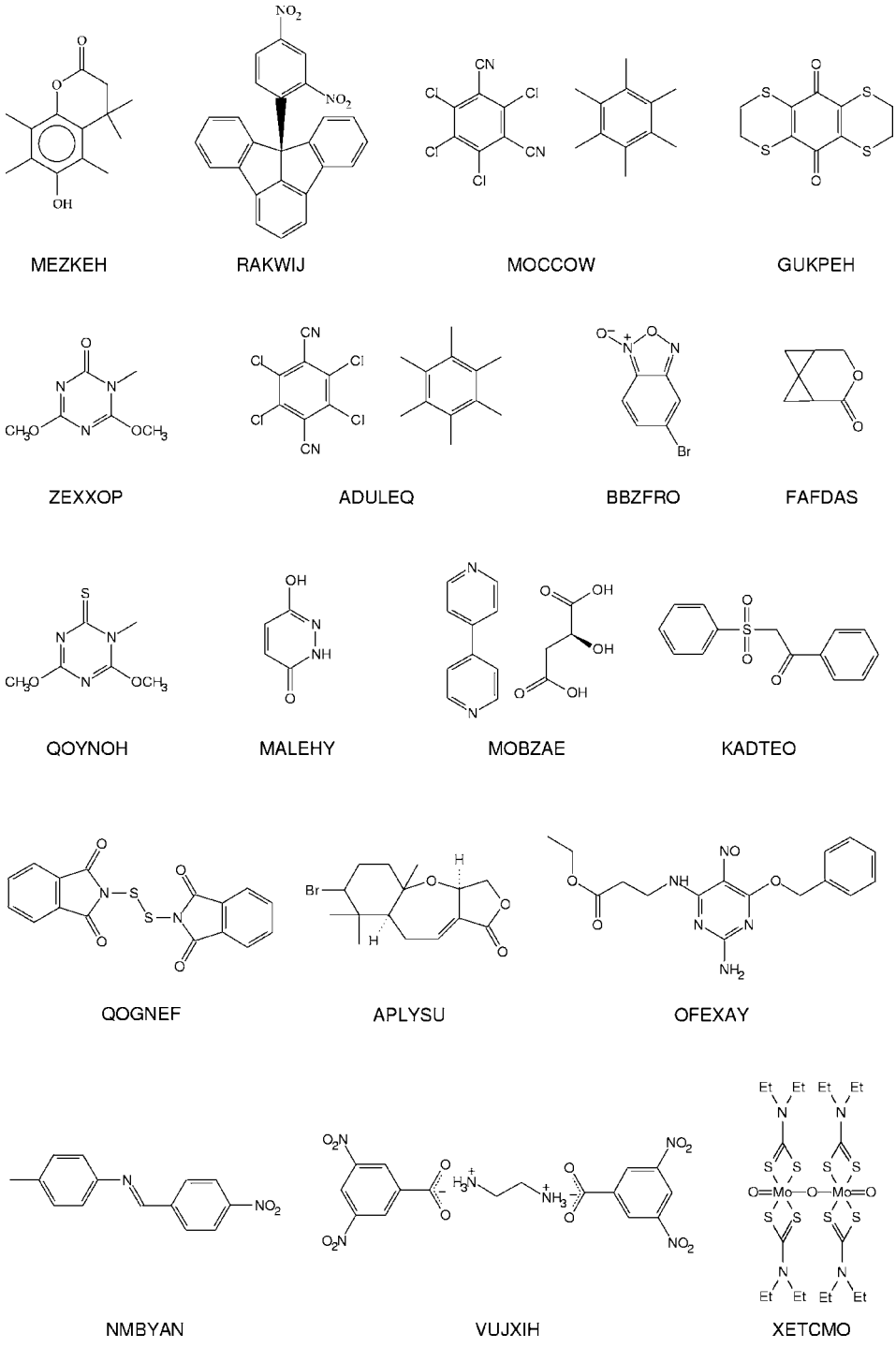

Figure 1
Chemical line drawings.

The crystal forms of three compounds exhibited two-dimensional isostructurality. They exemplified polytypism (Schneer, 1955) and the different stacking modes of similar layers. One-dimensional isostructurality was observed for the polymorphs of five compounds. In two cases, both one- and two-dimensional isostructurality were exhibited by the polymorphs of the same compound.

3.1. Compounds with isostructurality among their polymorphs

3.1.1. 6-Hydroxy-4,4,5,7,8-pentamethyl-3,4-dihydrocoumarin (MEZKEH). The lactone ring (Fig. 1) is disordered in the high-temperature crystal form (1 in Fig. 2) of 6-hydroxy-4,4,5,7,8-pentamethyl-3,4-dihydrocoumarin (Budzianowski & Katrusiak, 2002). Below 300 K, the ring inversion becomes gradually ordered (form 2), and the space group of the crystals changes to $P2_1/c$ from $P2_1/m$ (Table 2). At 225 K, abrupt inversion of the lactone ring (form 3) changes the translational symmetry (space group $P2_1/n$).

Despite the changes in symmetry, the arrangements of the molecules remain similar in all three phases. Therefore, they can all be regarded as three-dimensionally isostructural. This example indicates that polymorphs related by an order–disorder

Table 2
Space-group symmetries, unit-cell parameters and calculated densities of the structures retrieved from the CSD.

Unit-cell axes and volumes are given in Å, angles in ° and densities in g cm^{-3}. References to the crystal structures are given in the text.

Refcode	Space group	Z	a	b	c	α	β	γ	V	D_x
MEZKEH02	$P2_1/m$	2	9.753	6.933	9.572	90	94.39	90	645	1.206
MEZKEH04	$P2_1/c$	4	9.768	6.933	19.130	90	94.39	90	1292	1.205
MEZKEH12	$P2_1/n$	4	13.429	6.784	13.792	90	91.54	90	1256	1.239
RAKWIJ	$P2_1/c$	4	7.758	15.550	17.179	90	110.72	90	1938	1.393
RAKWIJ03	$P2_1/c$	8	15.372	15.414	17.004	90	109.24	90	3804	1.419
MOCCOW01	$P\bar{1}$	1	7.5290	8.9503	9.0513	118.425	109.414	95.139	483	1.473
MOCCOW	$P\bar{1}$	4	14.064	8.9554	18.117	118.407	90.832	76.460	1939	1.467
GUKPEH01	*Ibam*	4	9.441	16.583	7.184	90	90	90	1125	1.703
GUKPEH	*Pccn*	4	9.401	16.515	7.053	90	90	90	1095	1.749
ZEXXOP01	$P2_1/n$	8	13.480	14.172	8.433	90	92.07	90	1610	1.412
ZEXXOP03	*Pnma*	4	8.481	6.780	14.284	90	90	90	821	1.384
BBZFRO01	$P2_1/n$	4	7.954	7.297	12.574	90	90.124	90	730	1.957
BBZFRO02	$P2_1/c$	8	14.5294	7.4121	14.5587	90	115.676	90	1413	2.021
ADULEQ01	$P\bar{1}$	1	7.513	8.615	9.029	114.24	113.30	91.92	476	1.494
ADULEQ02	$P\bar{1}$	1	7.5567	8.8956	8.9921	116.697	112.099	92.101	485	1.467
ADULEQ03	$C2/m$	2	9.754	15.410	7.5550	90	116.88	90	1013	1.404
ADULEQ04	$P\bar{1}$	2	7.4982	9.0371	15.4538	85.080	81.795	71.168	980	1.451
GLYCIN19	$P2_1/n$	4	5.0993	11.9416	5.4608	90	111.784	90	309	1.615
GLYCIN	$P2_1$	2	5.077	6.268	5.38	90	113.2	90	157	1.584
GLYCIN16	$P3_2$	3	6.975	6.975	5.473	90	90	120	231	1.621
FAFDAS01	$P2_12_12_1$	4	9.9644	8.1854	7.4422	90	90	90	607	1.358
FAFDAS02	$P2_1/c$	4	9.9533	8.1831	7.8129	90	108.61	90	603	1.367
QQQCIV05	$P2_1/c$	4	4.102	8.244	7.970	90	100.1	90	265	1.028
QQQCIV04	$Cmc2_1$	4	6.187	5.282	7.887	90	90	90	258	1.058
QOYNOH	$P2_1/c$	4	7.657	14.361	8.433	90	110.99	90	866	1.436
QOYNOH01	*Pnma*	4	15.231	6.778	8.626	90	90	90	891	1.396
MALEHY11	$P\bar{1}$	2	5.8181	5.800	7.309	78.80	99.36	107.13	230	1.620
MALEHY01	$P2_1/c$	4	6.891	9.674	6.946	90	100.07	90	456	1.631
MALEHY12	$P2_1/n$	4	6.6070	6.9070	10.539	90	104.00	90	467	1.595
MOBZAE	$C2$	4	20.500	4.6656	14.201	90	99.68	90	1339	1.440
MOBZAE01	$P1$	1	5.1647	6.2749	10.2126	83.235	89.808	79.601	323	1.491
KADTEO01	$P2_12_12_1$	4	4.8177	9.4100	26.719	90	90	90	1211	1.427
KADTEO02	$P2_1/c$	4	9.2145	5.3594	25.665	90	98.448	90	1253	1.379
QOGNEF	$P2_1/c$	8	7.6037	33.9046	11.9404	90	93.058	90	3074	1.540
QOGNEF01	$Pna2_1$	4	7.1298	30.7247	6.8691	90	90	90	1505	1.573
QOGNEF02	$P2_1/c$	8	13.5052	7.8740	29.2050	90	98.9640	90	3068	1.543
VUJXIH	$P\bar{1}$	1	6.737	7.803	10.444	94.747	108.30	97.43	512	1.569
VUJXIH02	$P2_1/c$	2	5.4549	10.6869	17.4420	90	95.704	90	1012	1.589
APLYSU10	$P2_12_12_1$	4	9.982	7.182	20.586	90	90	90	1476	1.482
APLYSU11	$P3_121$	6	7.59	7.59	43.99	90	90	120	2195	1.494
OFEXAY01	$P2_1/c$	4	5.2399	31.1630	9.792	90	100.200	90	1574	1.458
OFEXAY	$P2_1$	4	7.4830	16.6110	13.5378	90	91.5420	90	1682	1.364
NMBYAN	$P\bar{1}$	4	12.561	14.372	7.108	96.02	93.72	72.65	1217	1.311
NMBYAN01	Pc	2	7.305	11.495	7.240	90	109.71	90	572	1.393
XETCMO	$P\bar{1}$	1	8.493	12.232	9.775	107.52	114.40	95.82	852	1.624
XETCMO03	$C2/c$	4	10.886	17.769	18.06	90	104.01	90	3389	1.632
PHENOL03	$P112_1$	6	6.050	8.925	14.594	90	90	90.36	788	1.190
PHENOL11	$P2_1$	6	11.610	5.4416	12.217	90	101.47	90	756	1.239
TUJFUZ01	$P23$	1	22.245	22.245	22.245	90	90	90	11 008	1.982
TUJFUZ02	$P3_221$	3	22.753	22.753	22.753	90	90	120	23 771	2.753

transition can exhibit a high degree of isostructurality.

3.1.2. 7*b*-(2,4-Dinitrophenyl)fluoradene (RAKWIJ). Both crystalline modifications of 7*b*-(2,4-dinitrophenyl)fluoradene crystallize with space group $P2_1/c$ (Xia *et al.*, 2001). Only one of their unit-cell parameters is different; the *a* axis is twice as long in form 2 as in form 1 (Table 2). The two structures are isostructural in three dimensions. A pseudo-translation in form 2 becomes a crystallographic translation in form 1 (Fig. 3).

Although both forms appear ordered, some diffuse scattering was recorded near half-integral *h* indices for form 1. The background scattering was much reduced and Bragg peaks appeared at the originally half-integral *h* values for form 2. This behavior suggests an order (form 2)–disorder (form 1) transition.

3.1.3. *m*-Tetrachlorodicyanobenzene hexamethylbenzene (MOCCOW). Crystals of the complex of *m*-tetrachlorodicyanobenzene (*m*-TCB) and hexamethylbenzene (HMB) were obtained in two distinct forms (Britton, 2002). The two forms both crystallize with space group $P\bar{1}$, but have $Z = 1$ (form I) and $Z = 4$ (form II), respectively (Table 2). In both forms, the two kinds of molecules form alternating planar layers (Fig. 4). In form I, *m*-TCB molecules are located on inversion centers and are disordered with two orientations of the cyano groups. In form II, these molecules are partially ordered; the asymmetric unit contains one disordered molecule located around a center of symmetry (degree of disorder 0.5/0.5) and another, partially ordered, molecule in a general position (0.85/0.15 occupancies). The packing arrangements of the molecules in the two forms are identical; they differ only in the degree of disorder. The similarity is so high that the coordinates of form I can be refined with the data measured for form II after an appropriate index transformation and the omission of the transformed reflections with non-integral indices (three-fourths of the data).

3.1.4. 2,3,7,8-Tetrahydrobenzo[1,2-*b*:4,5-*b*′]bis[1,4]dithiin-5,10-dione (GUKPEH). A high- (I) and a low-temperature (II) form of 2,3,7,8-tetrahydrobenzo[1,2-*b*:4,5-*b*′]bis[1,4]dithiin-5,10-dione (Fig. 1) were described by Matsumoto & Mizuguchi (2001). The two forms have almost identical unit-cell parameters but form (I) crystallizes in *Ibam* and form (II) in *Pccn* (Table 2). The reversible transition between the two forms was monitored by differential scanning calorimetry (DSC) measurements and by the appearance and disappearance of the reflections that are systematically absent for the body-centered lattice.

In form I, the molecules occupy special positions with $2/m$ symmetry, and the non-planar ethylene fragments between the S atoms are disordered. In form II, the site symmetry is reduced to 2, and the molecules are ordered (Fig. 5). Since no other structural change occurs on phase transition, the two forms are three-dimensionally isostructural.

3.1.5. 4,6-Dimethoxy-3-methyldihydrotriazine-2-one (ZEXXOP). A reversible single-crystal-to-single-crystal transformation of 4,6-dimethoxy-3-methyldihydrotriazine-2-one was identified in DSC measurements (Kaftory *et al.*, 2001). The asymmetric unit of the low-temperature form (space group $P2_1/c$) contains two molecules, which are related by a pseudo-

inversion center (Fig. 6). The high-temperature form crystallizes with space group *Pnma*. In this form, the molecules are located on a crystallographic mirror plane, and the pseudo-inversion is replaced by a crystallographic center of symmetry. Since the phase transition is accompanied by only a small molecular rearrangement, the two modifications remain isostructural in three dimensions.

3.1.6. 5-Bromobenzfurazan-1-oxide (BBZFRO). The high- and low-temperature forms of 5-bromobenzfurazan-1-oxide can be interconverted without any breaking of the single crystal (Pink & Britton, 2002). The two forms are composed of identical layers and differ by a *ca* 0.7 Å relative shift between adjacent layers and by the degree of disorder. Namely, both forms contain 6-bromobenzfurazan-1-oxide as a minor component, but on lowering the temperature, the isomerization equilibrium is shifted toward 5-bromobenzfurazan-1-oxide (see Pink & Britton, 2002). The small difference in the relative position is hardly noticeable visually (Fig. 7), so the two forms are considered three-dimensionally isostructural.

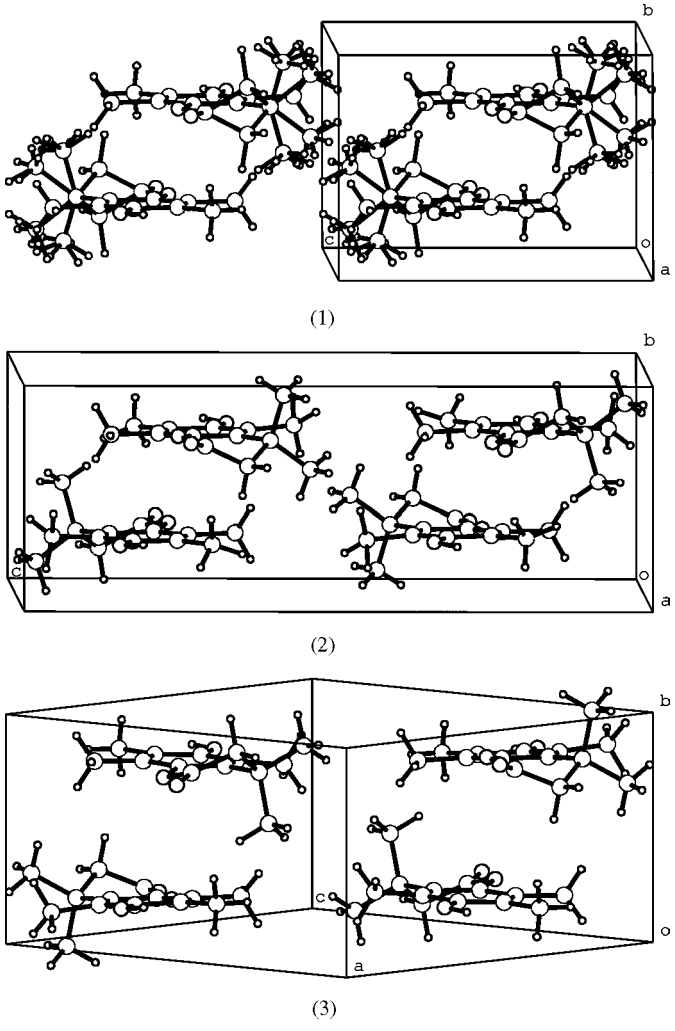

Figure 2
Crystal structures of the three polymorphs of 6-hydroxy-4,4,5,7,8-pentamethyl-3,4-dihydrocoumarin (Budzianowski & Katrusiak, 2002): (1) MEZKEH02, (2) MEZKEH04 and (3) MEZKEH12.

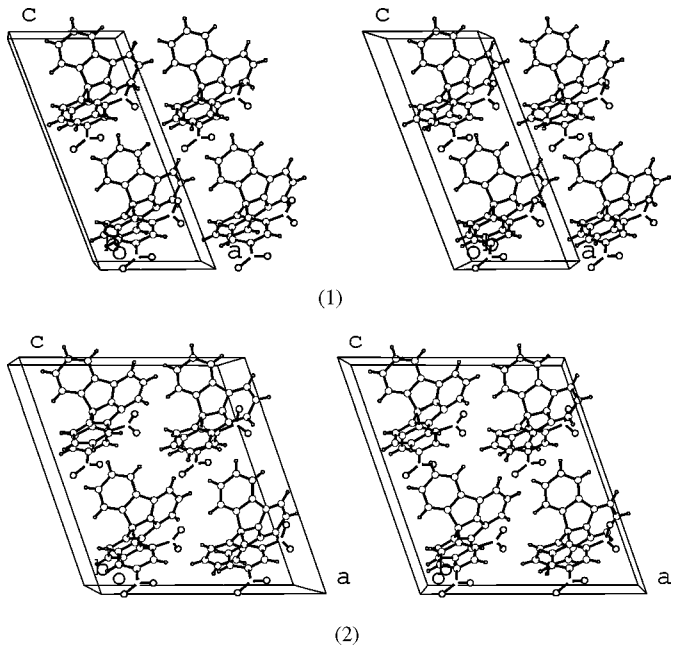

Figure 3
Parts of the crystal structures of the 7*b*-(2,4-dinitrophenyl)fluoradene dimorphs (Xia *et al.*, 2001): (1) RAKWIJ and (2) RAKWIJ03. Only half of the molecules in the unit cells are shown for clarity.

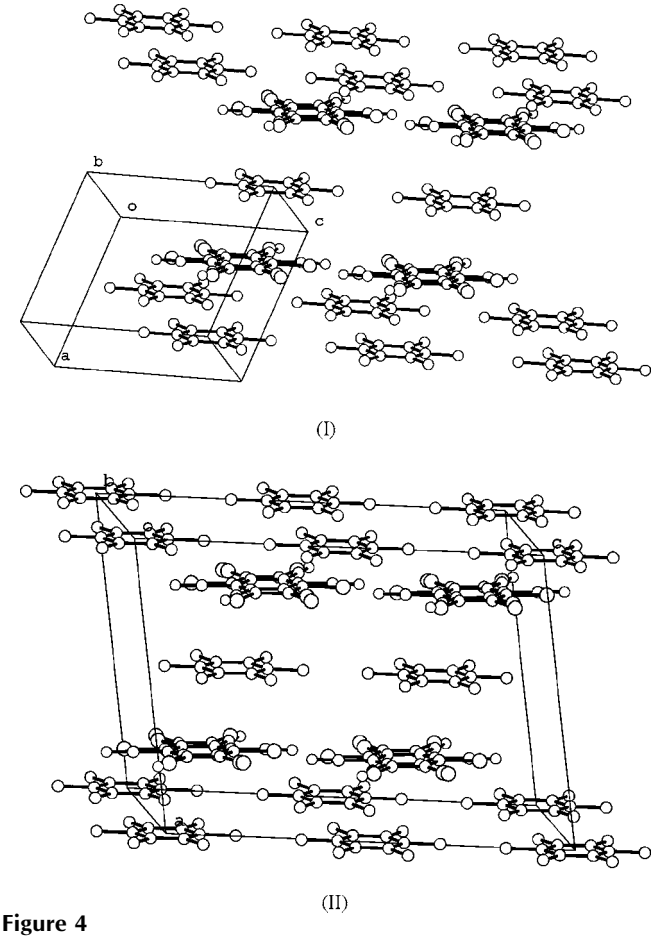

Figure 4
Packing arrangements of the crystals of the complex of *m*-tetrachlorodicyanobenzene and hexamethylbenzene (Britton, 2002): (I) MOCCOW01 and (II) MOCCOW. H atoms have been omitted for clarity.

3.1.7. *p*-Tetrachlorodicyanobenzene hexamethylbenzene (ADULEQ). Four crystal forms of the 1:1 complex crystal of *p*-tetrachlorodicyanobenzene (*p*-TCB) and hexamethylbenzene (HMB) were reported by Britton (2002). Polymorph III ($C2/m$, $Z = 2$) is assembled from alternating layers of *p*-TCB and HMB molecules (Fig. 8). Polymorph II ($P\bar{1}$, $Z = 1$) is assembled from slightly distorted variants of the same layers, so it is two-dimensionally isostructural with form III. These two modifications differ in the stacking of the layers. In form III, the molecules of subsequent layers exactly overlap, while in form II, an offset parallel to the C—N bonds is present between the layers.

In polymorph IV ($P\bar{1}$, $Z = 2$), the *p*-TCB layers have different topology from those in polymorphs II and III. (See the orientations of the cyano groups in Fig. 8.) Because of the $D6_h$ symmetry of the HMB molecules, the topology of HMB layers remains the same. Despite some geometrical distortion, HMB layers of II, III and IV are two-dimensionally isostructural.

Each layer of form I ($P\bar{1}$, $Z = 1$) is built from both kinds of molecules, in contrast to the separate HMB and *p*-TCB layers of the other forms. Nevertheless, the same offset molecular stacks are present in polymorphs I and II (Fig. 8, perpendicular to the plane of the paper). The relative offset between adjacent stacks along the stacking direction is different in the two forms, and thus they are isostructural in one dimension.

3.1.8. Glycine (GLYCIN). The coordinates for three forms of glycine are archived in the CSD (α: Langan *et al.*, 2002; β: Iitaka, 1960; γ: Kvick *et al.*, 1980). The α and β forms are built from similar layers (Fig. 9, bottom layers of α and β). The layers are distinguished only by a minor conformational difference between the molecules and so are two-dimensionally isostructural. Subsequent layers are related by inversion centers in the α form (space group $P2_1/n$) and by screw axes in the β form (space group $P2_1$). In the γ form (space group $P3_2$), no such layers are present, but hydrogen-bonded chains of glycine molecules are formed with a geometry similar to that

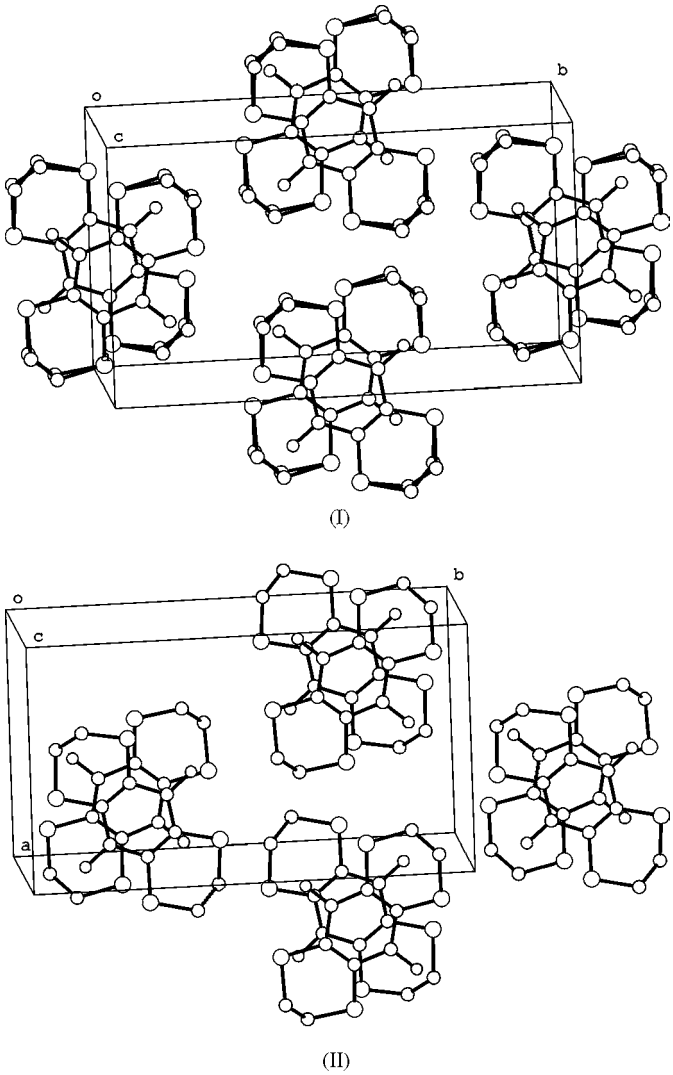

Figure 5
Crystal structures of the low- and high-temperature forms of 2,3,7,8-tetrahydrobenzo[1,2-*b*:4,5-*b*′]bis[1,4]dithiin-5,10-dione (Matsumoto & Mizuguchi, 2001): (I) GUKPEH01 and (II) GUKPEH. H atoms have been omitted for clarity.

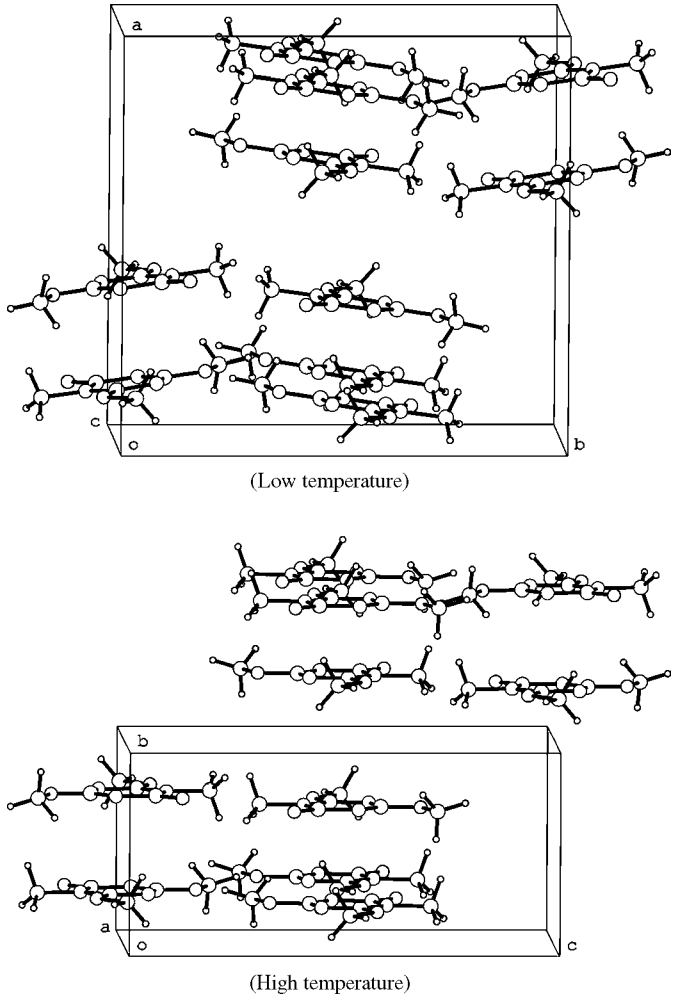

Figure 6
Crystal structures of the low- (ZEXXOP01) and high-temperature (ZEXXOP03) forms of 4,6-dimethoxy-3-methyldihydrotriazine-2-one (Kaftory *et al.*, 2001).

in the α and β polymorphs (Fig. 9). Hence the γ form is one-dimensionally isostructural with the α and β forms.

3.1.9. 5-Oxatricyclo[5.1.0.0^{1,3}]octane-4-one (FAFDAS). Two polytypes of 5-oxatricyclo[5.1.0.0^{1,3}]octane-4-one (Fig. 1) were found in the same composite crystal (Yufit *et al.*, 2002). They have similar unit-cell parameters (Table 2) but crystallize with different space groups: $P2_12_12_1$ and $P2_1/c$, respectively. The two forms are composed of identical layers (two-dimensional isostructurality). Neighboring layers are related to each other either by *c*-glide planes (monoclinic form) or by twofold screw axes (orthorhombic form; Fig. 10). While the monoclinic form contains both enantiomers, the orthorhombic structure comprises only one of them, *i.e.* it is the product of a spontaneous resolution. Consequently, the molecular constituents of the two forms are not strictly identical, and their classification as polymorphs is questionable.

3.1.10. Acetonitrile (QQQCIV). Two forms of acetonitrile were described by Enjalbert & Galy (2002). Both forms are assembled from layers (Fig. 11). In the low-temperature β form (space group $Cmc2_1$), the molecules in a layer are related to each other by screw axes and translation. The symmetry of the layers in the α form ($P2_1/c$) is governed by screw axes and inversion centers. The one-dimensional isostructurality of the two forms stems from the stacking of the layers (Fig. 11, perpendicular to the plane of the paper). The chains of screw-related molecules within a layer are similar in the two forms, but the geometry of the C—H···N interactions is different. The C—C(H)···N—C dihedral angle is 74° in the α form and 58° in the β form.

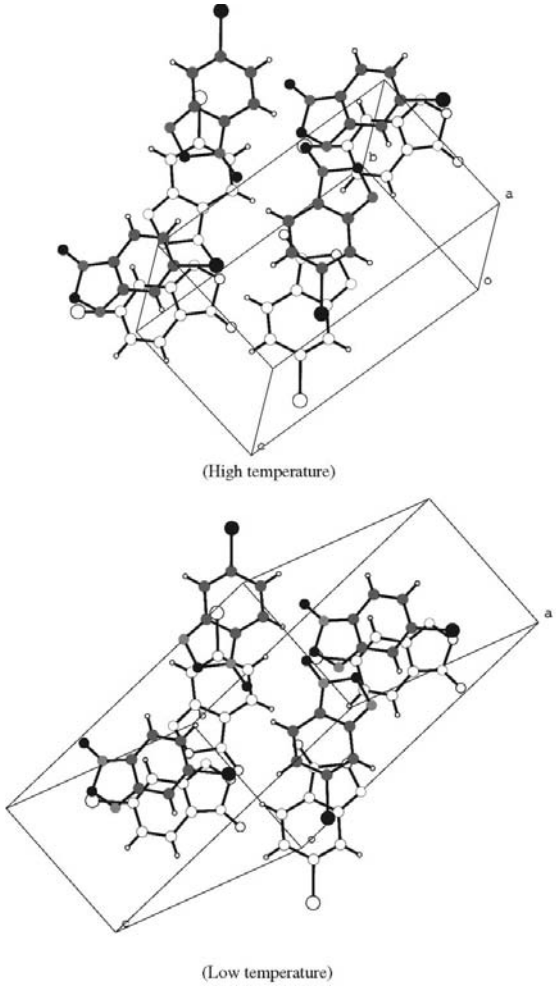

Figure 7
Crystal structures of the high- (BBZFRO01) and low-temperature (BBZFRO02) forms of 5-bromobenzfurazan-1-oxide (Pink & Britton, 2002).

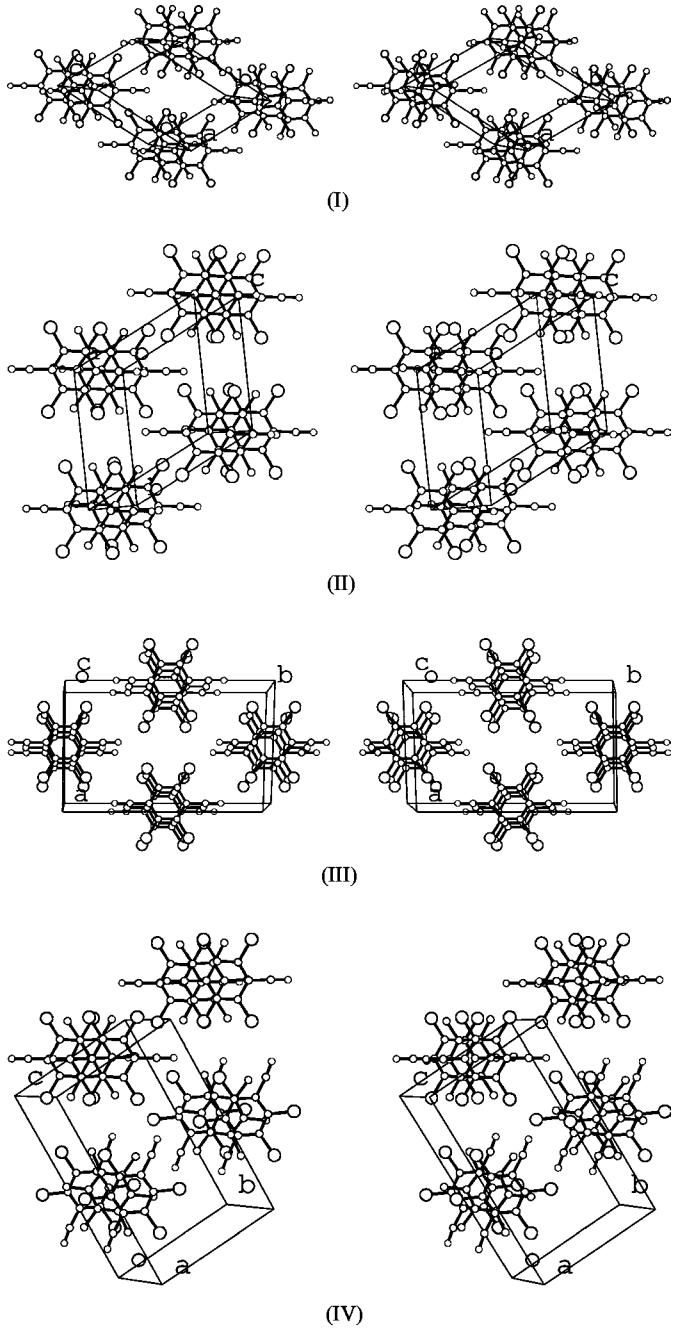

Figure 8
Stereoviews of the crystal structures of *p*-tetrachlorodicyanobenzene hexamethylbenzene polymorphs (Britton, 2002): (I) ADULEQ01, (II) ADULEQ02, (III) ADULEQ03 and (IV) ADULEQ04.

3.1.11. 4,6-Dimethoxy-3-methyl-1,3,5-triazine-2(3*H*)-thione (QOYNOH). 4,6-Dimethoxy-3-methyl-1,3,5-triazine-2(3*H*)-thione (Fig. 1) crystallizes with monoclinic ($P2_1/c$) and orthorhombic (*Pnma*) symmetry (Greenberg *et al.*, 2001). The two forms comprise similar chains of molecules (Fig. 12) with short O—CH_3···N contacts. These contacts are formed between translation-related molecules along the *c* axis in both structures. Consequently, these dimorphs exhibit one-dimensional isostructurality.

3.1.12. Maleic hydrazide (MALEHY). Maleic hydrazide is known to exist in three crystalline forms (MH1, $P\bar{1}$: Cradwick, 1975; MH2, $P2_1/c$: Katrusiak, 1993; MH3, $P2_1/n$: Katrusiak, 2001). The molecules form hydrogen-bonded ribbons in all three forms, with similar relative arrangements of the molecules, rendering the structures one-dimensional isostructural (Fig. 13). No hydrogen bonds exist between these ribbons in the three polymorphs, only weak van der Waals interactions.

3.2. Polymorphs without isostructurality

3.2.1. 4,4′-Bipyridyl (*S*)-malic acid (MOBZAE). From a solution in methanol, two forms of the 4,4′-bipyridyl (*S*)-malic acid complex crystallized concomitantly (Farrell, Ferguson *et al.*, 2002). Both the malic acid and the bipyridyl molecules assume similar conformations in the monoclinic (*C*2) and triclinic (*P*1) forms. The molecules form infinite chains, with COOH···N hydrogen bonds in both forms. These chains differ in the orientation of the malic acid molecules relative to the chains: either HOOC—CH(OH)—CH_2—COOH or HOOC—CH_2—CH(OH)—COOH (given the orientation of the chains in Fig. 14). This difference is clearly related to the presence of

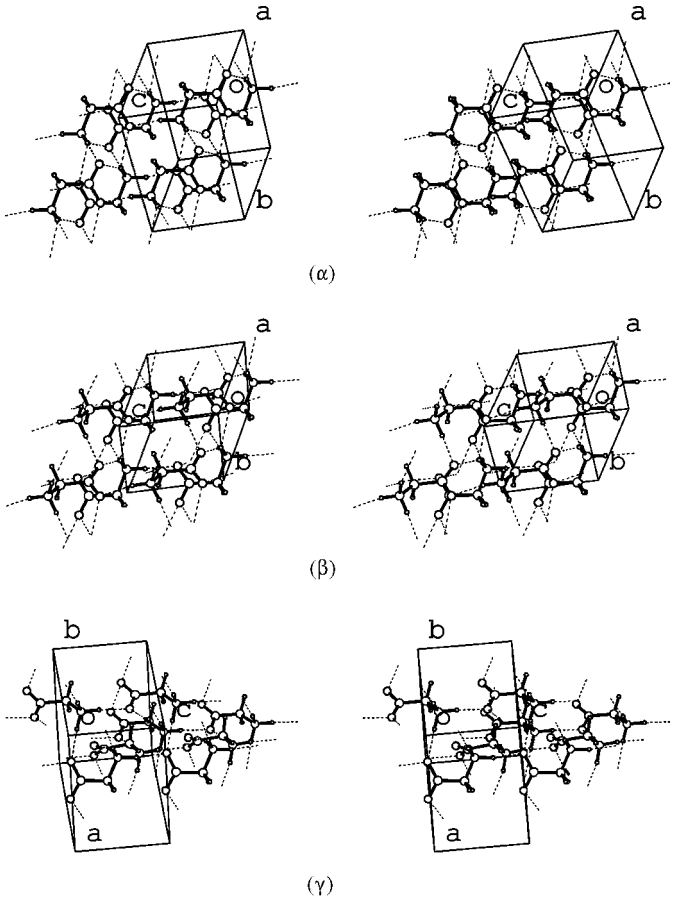

Figure 9
Stereoviews of the crystal structures of glycine polymorphs: (α) GLYCIN19 (Langan *et al.*, 2002), (β) GLYCIN (Iitaka, 1960) and (γ) GLYCIN16 (Kvick *et al.*, 1980).

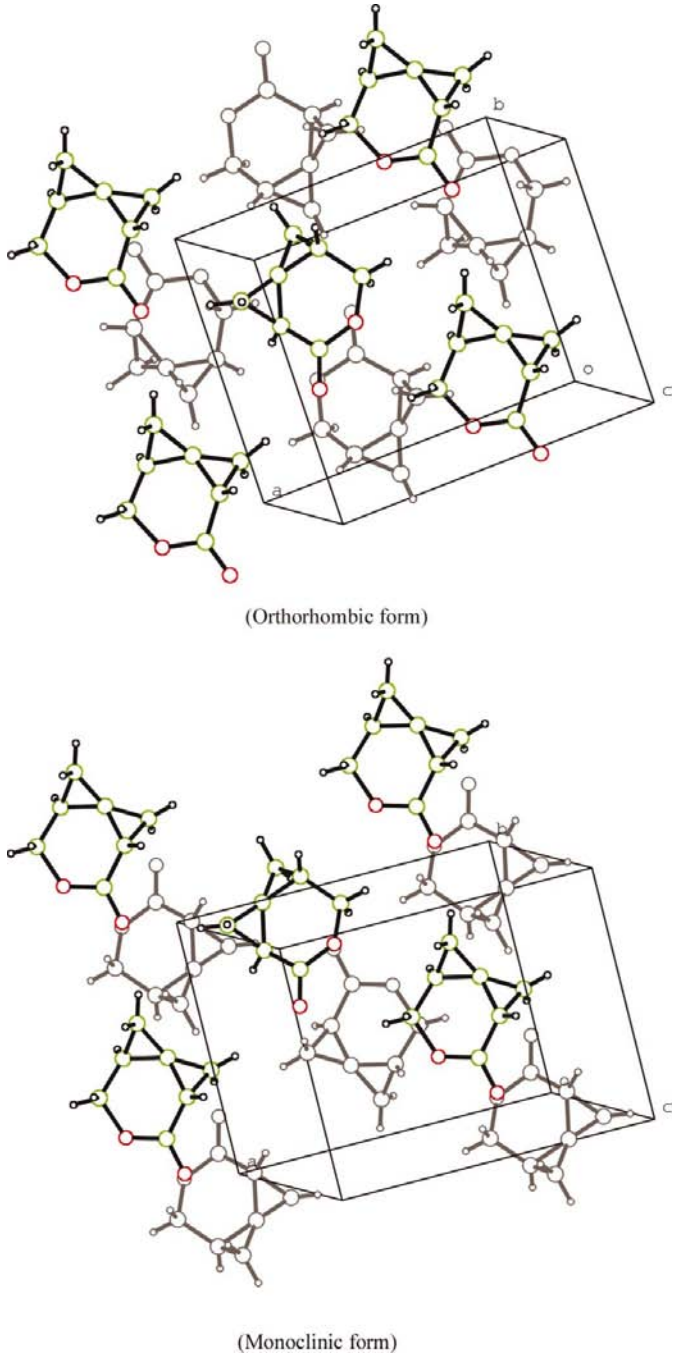

Figure 10
Crystal structures of 5-oxatricyclo[5.1.0.0^{1,3}]octane-4-one (Yufit *et al.*, 2002): orthorhombic (FAFDAS01) and monoclinic (FAFDAS02) forms. Molecules of an identically oriented layer are shown in color, while those in a symmetry-related layer are shown in gray.

another hydrogen bond: OH···O=C in the monoclinic form and OH···OH in the triclinic polymorph.

The 4,4′-bipyridyl moieties in the two chains are superposable, but the different orientations of the malic acid molecules prevent the whole chains from being superposable. Consequently, these polymorphs are not considered isostructural, but they represent a close approach to one-dimensional isostructurality.

3.2.2. Benzoylmethyl phenyl sulfone (KADTEO). The monoclinic ($P2_1/c$) and orthorhombic ($P2_12_12_1$) forms of benzoylmethyl phenyl sulfone are conformational polymorphs (Wolf, 2001). The synclinal $C_{Ph}-S-CH_2-C(=O)$ torsion angle [−43.2 (1)°] assumed in the monoclinic form rotates into the antiperiplanar range [−154.0 (2)°] in the orthorhombic form. This turn is accompanied by a rotation around the $CH_2-C(=O)$ bond [ψ = −90.2 (2) → 101.3 (2)°].

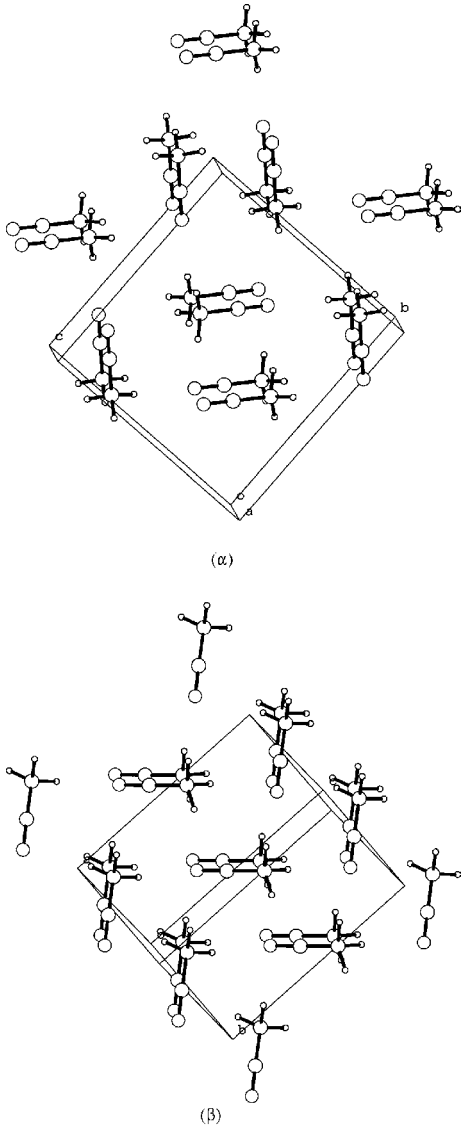

Figure 11
Crystal structures of acetonitrile polymorphs (Enjalbert & Galy, 2002): (α) QQQCIV05 and (β) QQQCIV04.

Both conformers associate *via* C—H···O=S interactions (Fig. 15). The resulting molecular ribbons are packed along the shortest unit-cell axes by translation (Table 2). In the orthorhombic form, the methylene C atoms, which form the common chains, donate their other H atoms to the O=S groups of screw-related molecules. In addition, weak phenyl C—H···O interactions are also present. These additional interactions seem to account for the different packing symmetries. Although the overall layouts of the unit cells exhibit some degree of similarity, these polymorphs lack isostructurality. Their structures demonstrate that 'packing similarity' with conformational dissimilarity is insufficient for isostructurality.

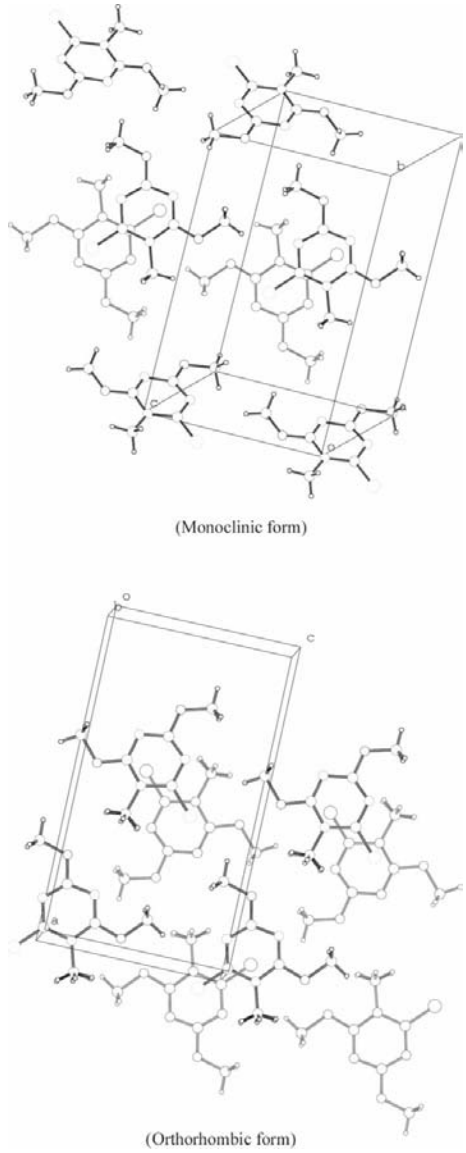

Figure 12
Crystal structures of the monoclinic (QOYNOH) and orthorhombic (QOYNOH01) forms of 4,6-dimethoxy-3-methyl-1,3,5-triazine-2(3*H*)-thione (Greenberg *et al.*, 2001). Molecules in a lower layer are drawn in gray. The central row in the figure of the monoclinic form and the bottom row in the figure of the orthorhombic form are identical.

Conformational polymorphism means that the molecules assume markedly different shapes in the polymorphs. The self-assembly of molecules of different shapes is highly unlikely to yield nearly identical spatial arrangements.

3.2.3. *N*,*N*′-dithiodiphthalimide (QOGNEF). Polymorphs and pseudo-polymorphs of *N*,*N*′-dithiodiphthalimide were studied by Farrell, Glidewell *et al.* (2002). In addition to an already known monoclinic polymorph (Skakle *et al.*, 2001), Farrell, Glidewell *et al.* (2002) described two solvent-free crystal forms. The two monoclinic forms crystallize with space group $P2_1/c$ and $Z' = 2$, while the orthorhombic form has space group $Pna2_1$ and $Z' = 1$. The molecules assume similar conformations in all three forms. The packing arrangements, however, are completely different. The packing differences emerge from different patterns of C—H···O hydrogen bonds and π–π stacking interactions.

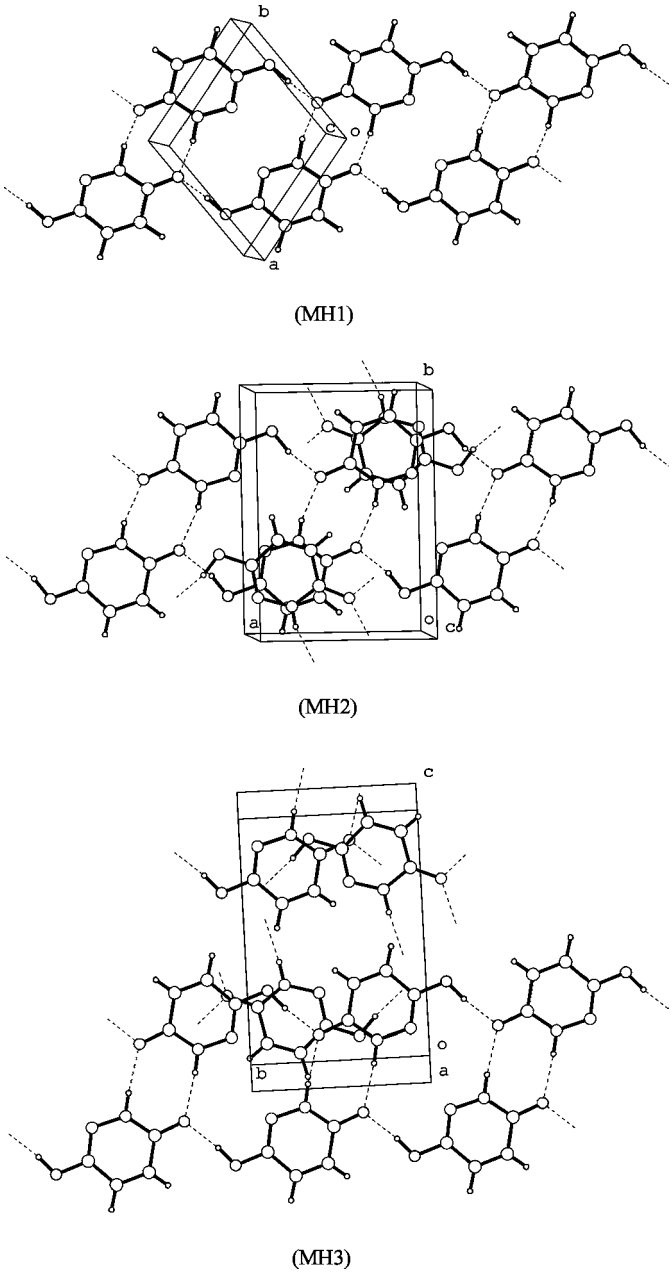

Figure 13
Crystal structures of the maleic hydrazide polymorphs (MALEHY11, 01, 12; Cradwick, 1975; Katrusiak, 1993, 2001).

3.2.4. Ethylenediammonium 3,5-dinitrobenzoate (VUJXIH). Crystals of the 2:1 salt of 3,5-dinitrobenzoic acid and 1,2-diaminoethane were obtained in monoclinic ($P2_1/c$; Burchell *et al.*, 2001) and triclinic ($P\bar{1}$; Nethaji *et al.*, 1992) forms. Even though both kinds of ions exhibit similar conformations in these forms, their hydrogen-bond interactions are completely different. This variety is facilitated by the high number of available donor and acceptor functions on the ions.

3.2.5. Aplysistatin (APLYSU). Aplysistatin is a sesquiterpene with a skeleton consisting of three fused rings (Fig. 1). The molecules assume the same conformation both in the orthorhombic ($P2_12_12_1$; von Dreele & Kao, 1980) and hexagonal ($P3_121$; Marsh, 2002) crystal forms. Nevertheless, no common motif could be identified in the two polymorphs.

3.2.6. Ethyl *N*-(2-amino-6-benzyloxy-5-nitrosopyrimidin-4-yl)-β-alaninate (OFEXAY). Crystal structures of ethyl *N*-(2-amino-6-benzyloxy-5-nitrosopyrimidin-4-yl)-β-alaninate were investigated by Quesada *et al.* (2002). They identified two polymorphs. Polymorph I crystallizes with space group $P2_1/c$ and $Z' = 1$, while polymorph II has space group $P2_1$ and $Z' = 2$. The two molecules in the asymmetric unit of form II and the single molecule in form I exhibit three different conformations. The symmetry-independent molecules in polymorph II form similar intra- and intermolecular hydrogen bonds. The hydrogen-bonding interactions in form I are different, and this leads to a different conformation and a different packing arrangement of the molecules.

3.2.7. 4-Nitro-4′-methylbenzylideneaniline (NMBYAN). 4-Nitro-4′-methylbenzylideneaniline (Fig. 1) crystallizes in a monoclinic (*Pc*; Cole *et al.*, 2001) or triclinic ($P\bar{1}$; Filipenko *et al.*, 1976) form. In the monoclinic form, the molecules are planar. In the two symmetry-independent molecules of the

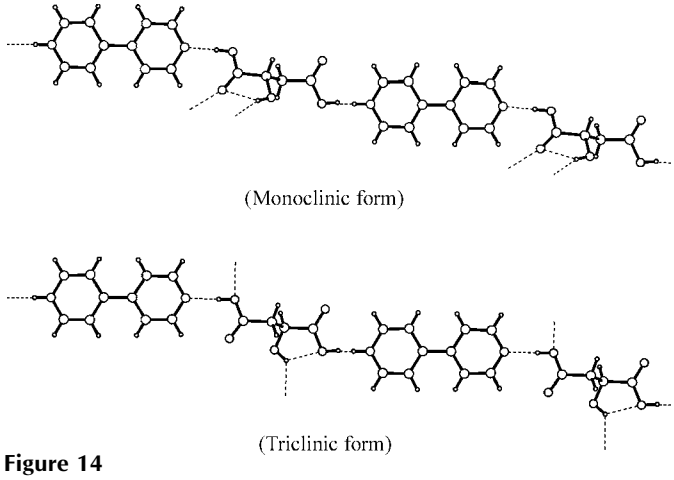

Figure 14
Chains of hydrogen-bonded molecules in the monoclinic (MOBZAE) and triclinic (MOBZAE01) forms of 4,4′-bipyridyl (*S*)-malic acid (Farrell, Ferguson *et al.*, 2002). One H atom is disordered between the two ions in each forms. Both disordered positions are shown.

triclinic form, the interplanar angles between the two phenyl rings of the molecules are 32 and 53°, respectively. Therefore, these forms are conformational polymorphs and do not exhibit isostructurality.

3.2.8. (μ_2-Oxo)bis[bis(*N*,*N*-diethyldithiocarbamato-*S*,*S*′)-oxomolybdenum] (XETCMO). Two polymorphs of the binuclear complex (μ_2-oxo)bis[bis(*N*,*N*-diethyldithiocarbamato-*S*,*S*′)oxomolybdenum] (Fig. 1) were found: a triclinic (Garner *et al.*, 1979) and a monoclinic (Marsh & Spek, 2001) form. These forms are conformational polymorphs, since their molecules differ in a rotation around the linear Mo—O—Mo bridge. Hence, these polymorphs do not exhibit isostructurality.

3.2.9. Phenol (PHENOL). Both the ambient-pressure and the high-pressure forms of phenol crystallize with space group $P2_1$ and $Z = 6$ (Zavodnik *et al.*, 1987; Allan *et al.*, 2002). The molecules form infinite chains of OH···OH hydrogen bonds in both forms (Fig. 16). These chains are pseudo-trigonal in the ambient-pressure form, while the hydrogen bonds are formed between twofold screw-axis-related molecules in the high-pressure form. Both crystals are built up from the same supramolecular entity: the infinite chain of hydrogen-bonded molecules. The geometries of these chains differ despite the similar conformation of the constituent molecules. The two modifications of phenol differ in the conformation of the same supermolecule, so they are supramolecular analogs of conformational polymorphs.

3.2.10. [$Hg_{32}Se_{14}(SePh)_{36}$] (TUJFUZ). Two crystal forms of the $[Hg_{32}Se_{14}(SePh)_{36}]$ nanocluster were prepared by Behrens *et al.* (1996). The two forms crystallize with cubic ($P23$) and trigonal ($P3_221$; Marsh, 2002) symmetry. The clusters possess T symmetry in both forms, and are consequently very similar. The trigonal structure contains channels of *ca* 7 Å diameter, which presumably contain disordered solvent molecules. Therefore, these structures can be regarded as pseudo-polymorphs rather than polymorphs, and the different composition may account for the lack of isostructurality.

4. Conclusion

This analysis has demonstrated that the occurrence of common packing patterns among polymorphs is frequent. Approximately half of the compounds investigated were shown to exhibit one-, two- or three-dimensional isostructurality between their crystal forms.

Three-dimensional isostructurality of polymorphs is always related to the gradual ordering of the structure. The relationship between three-dimensional isostructural polymorphs may be a symmetry–pseudosymmetry and/or an order–disorder transition. Some of the papers describing these structures report a single-crystal-to-single-crystal transition between three-dimensionally isostructural crystal forms.

Two-dimensional isostructurality is exhibited by polymorphs that differ either by the symmetry operation or by the relative offset between subsequent layers. In the former case, the relationship of the polymorphs is reflected by their space groups having common two-dimensional sublattices. Isostructurality in one dimension is connected to stacking interactions or the formation of hydrogen-bonded chains.

It is not clear from the present examples whether one- and two-dimensional isostructurality of polymorphs can be related

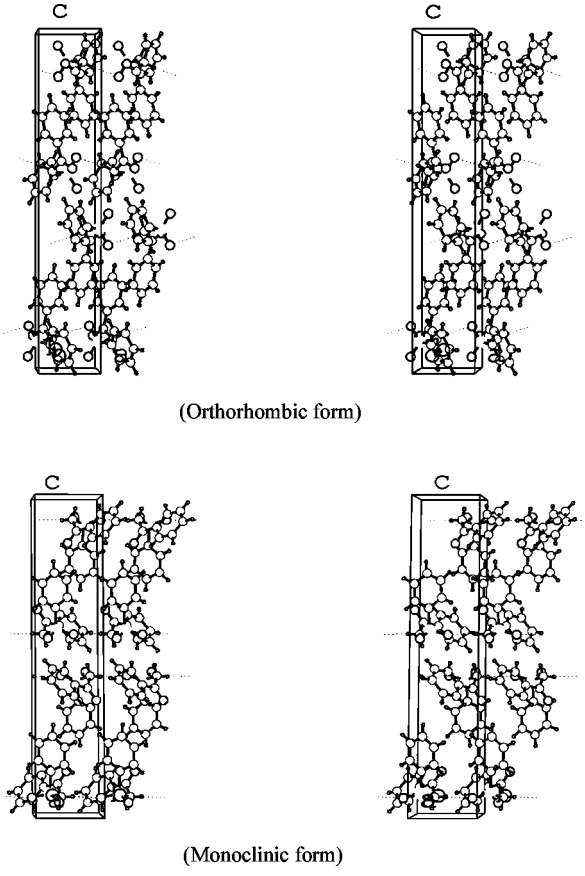

Figure 15
Chains of C—H···O═S-linked molecules in the orthorhombic (KADTEO01) and monoclinic (KADTEO02) dimorphs of benzoylmethyl phenyl sulfone (Wolf, 2001).

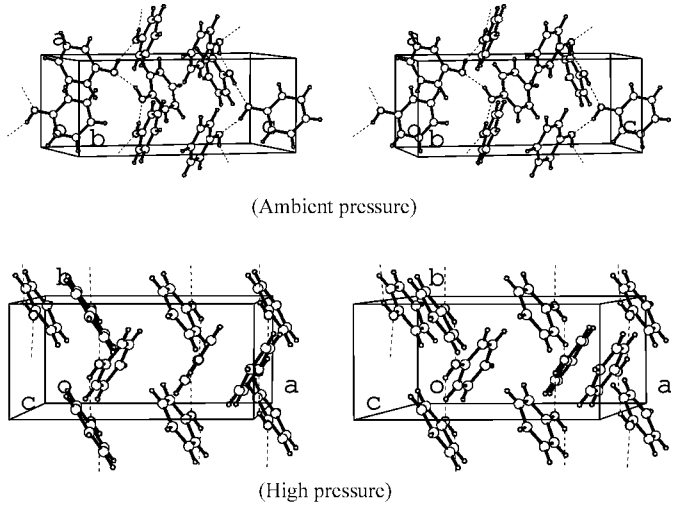

Figure 16
Crystal structures of the ambient- (PHENOL03; Zavodnik *et al.*, 1987) and high-pressure (PHENOL11; Allan *et al.*, 2002) forms of phenol.

to interaction energies or to crystal growth. While the hydrogen bonds that form tapes in all three forms of maleic hydrazide are clearly the strongest interactions in the structures, the ranking of interaction energies in glycine polymorphs is impossible without accurate calculations. Furthermore, even the identity of the interaction does not ensure isostructurality. The flexibility of a single hydrogen bond between phenol molecules, for example, allows a substantial difference between the shape of the OH···OH chains in the high-pressure and in the ambient-pressure forms. Because of this flexibility, it is sometimes hard to decide if isostructurality is present or not [see *e.g.* acetonitrile or 4,4′-bipyridyl (*S*)-malic acid].

Conformational polymorphism apparently excludes isostructurality. The similarity of association patterns, however, may approach it, as demonstrated by the dimorphs of benzoylmethyl phenyl sulfone. Beyond conformational dissimilarity, the abundance of available interactions (and interaction sites) with similar strengths seems to hinder the appearance of isostructural polymorphs.

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