assigned to be artefacts of dynamic disorder in the crystals (Ogawa, Suzuki, Sakurai, Kobayashi, Kira & Toriumi, 1988; Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992).

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Classification of the Isostructurality of Organic Molecules in the Crystalline State*

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Abstract

Since its discovery by Mitscherlich in 1819, the isomorphism of crystals has been interpreted in various, sometimes controversial ways. This can be attributed to the fact that the word isomorphous refers only to the external similarities between crystalline substances. Identical or quasi-identical packing motifs of related organic substances should therefore be distinguished by a more appropriate terminology. For organic substances, in contrast with inorganic crystals, where the recommended term is isotypic, the term isostructural is unambiguous. The present work attempts to classify the main forms as isostructural and homeostructural. Within the former class, there are two subclasses distinguished by the degree of isostructurality. Special attention is also paid to the isostructurality of molecular associates (*e.g.* cloth-

* Dedicated to Dr Kálmán Sasvári on the occasion of his 80th birthday.

rates). To estimate the degree of isostructurality two descriptors are recommended: (*a*) the unit-cell similarity index, and (*b*) the isostructurality index.

1. Introduction

Studies on the packing similarities observed for the crystal structures of numerous bufadienolides and cardenolides resulted in the description of a phenomenon termed 'main-part' isostructuralism (Kálmán, Argay, Scharfenberg-Pfeiffer, Höhne & Ribár, 1991; Kálmán, Argay, Zivanov-Stakić, Vladimirov & Ribár, 1992). The isostructural pairs among the polymorphs of *para*-disubstituted benzylideneaniline derivatives (Bar & Bernstein, 1987, and references therein) helped to elucidate the conditions and limits of forming similar packing motifs. Finally, the identical packing of $Ph_3Si—SiMe_3$ with that of its germanium analogues ($Ph_3X—X'Me_3$, X = Ge, Si, Ge; X' = Si, Ge, Ge) (Párkányi, Kálmán, Pannell, Sharma & Nolen, 1993, and references therein) prompted us to rationalize the isostructurality of organic crystals in general.

Prior to this work, the stuctural similarities exhibited by inorganic substances were classified in *The Nomenclature of Inorganic Structure Types* (Lima-de-Faria, Hellner, Liebau, Makovicky & Parthé, 1990). As far as organic crystals are concerned, only an early suggestion by Kitaigorodskii (1961) is to be found. Nevertheless, Kitaigorodskii made it clear that 'isomorphism in organic crystals has some important features which force us to consider this vital topic from a viewpoint different from that for inorganic compounds.'

2. The forms of packing similarity between organic crystals

The above works demonstrated that the similarities in the packing motifs of organic molecules cannot be classified properly in the terms recommended by Lima-de-Faria *et al.* (1990). That is, the hierarchy of terms (isopointal, configurationally isotypic, crystal-chemically isotypic and homeotypic structures) is built up along the identical Wyckoff positions (both in letters and their multiplicity), which, for most organic substances, are limited only to general positions.

Kitaigorodskii (1961) states that the 'approximate isomorphism'* of molecules is a prerequisite for their similar packing. Consequently, the word isostructural is unambiguous. Within this term, the classification given below is recommended.

(*A*) Isostructural crystals. The formation of identical packing motifs can be expected if the related molecules are isometric, *i.e.* exhibit only small differences on their surface. This phenomenon was previously termed the 'main-part' isostructuralism of related molecules (Kálmán *et al.*, 1991).

They may differ only (*a*) in the substituent (*Q*) or chirality (*R* or *S*) of one atom on their surface, or (*b*) in one or more multivalent shielded core atoms if the atomic radii of the interchangeable atoms do not differ substantially (*e.g.* Si and Ge in the $Ph_3X—X'Me_3$ analogues).

(*A*1) Isometric molecules differing in one substituent are in general characterized by high isostructurality indices (> 80%).

(*A*2) Crystal pairs formed by molecules differing only in the chirality of one atom are termed configurationally isostructural. Since a configurational difference is accompanied by internal rotations (conformational differences), such crystal pairs have isostructurality indices in the range 40–80%.

(*B*) Homeostructural crystals. Substitution concerns more than one atomic site on the related molecules. If isostructurality is still observed, then the isostructurality indices are low (< 40%) and only 'relaxed' packing similarities can be recognized. This gives room for a great variety of 'isostructural forms', including packing motifs which are related only by non-crystallographic symmetries and/or disorder.

(*A*/*B*) The crystals of molecular associates (clathrates, *etc.*) are occasionally 'isostructural', possessing similar host skeletons with different guest molecules (*e.g.* dioxane *versus* chloroform) in their voids. Depending on the chemical and/or topological relationship between the guest molecules, such crystal pairs may vary between the high and low forms of isostructurality; the latter are included among the homeostructural cases.

3. Descriptors of isostructurality

The degree of similarity was earlier defined by three descriptors (Kálmán *et al.*, 1991). However, since the increment of the packing coefficient [Δ(pc)] is closely related to the unit-cell similarity index, the former is regarded as superfluous.

3.1. *Unit-cell similarity index*

In addition to the similar axial ratios and interaxial angles, the internal motion of the lattice parameters can be estimated *via* equation (1), where *a*, *b*, *c* and *a'*, *b'*, *c'* are the orthogonalized lattice param-

* Molecular isomorphism is a morphological property which exists independently of the crystalline state. Nevertheless, to avoid confusion, whenever possible the word isomorphous is replaced by its synonym isometric. Similarly, the present work does not aim to discuss crystallographic isomorphism, *i.e.* the ability of related crystals to form solid solutions.

eters of the related crystals:

$$\Pi = (a + b + c)/(a' + b' + c') - 1 \simeq 0 \qquad (1)$$

In the event of great similarity of two unit cells, Π is practically zero.

3.2. *Isostructurality index*

This was earlier termed degree of isostructurality I_D^n (Kálmán *et al.*, 1991),

$$I_i(n) = \left| \left[\frac{\sum(\Delta R_i)^2}{n} \right]^{1/2} - 1 \right| \times 100, \qquad (2)$$

where n is the number of distance differences (ΔR_i) between the crystal coordinates of identical non-H atoms within the same section of the asymmetric units of the related (A and B) structures. It is worth noting that $I_i(n)$ takes into account both the differences in the geometry of the molecules and the positional differences caused by rotational and translational operations. In contrast, a full or partial least-squares fit of the positions occupied by the identical (i_A and i_B) atoms results in different 'possible superpositions' of the molecules. When these refined ΔR_i* values are used in equation (2), the new index $I_i(n^*)$, termed the molecular isometricity index, is a direct measure of the degree of approximate isomorphism (Kitaigorodskii, 1961) of molecules A and B. Since the H-atom positions are generally less precisely determined than those of the heavy atoms (at least by X-ray diffraction), they are advisably excluded from both kinds of $I_i(n)$ calculations.

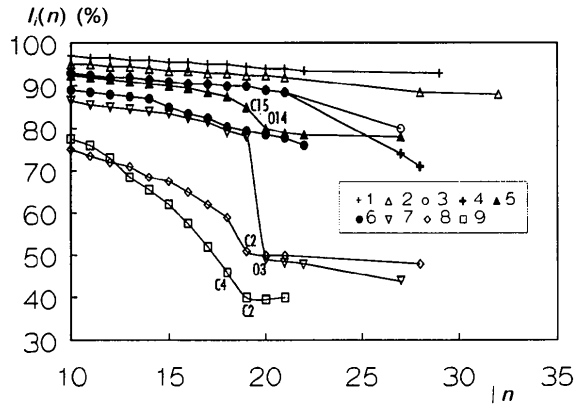


Fig. 1. $I_i(n)$ (%) *versus* n curves for nine isostructural steroid pairs. Each starts from n = 10 and runs until the last common atom of the isostructural pairs. After n = 21 or 22, the atoms of the γ- and δ-lactone rings are treated as compact units. In curve 2, there is an additional 16β-acetoxy group with four non-H atoms: (1) arenobufagin–gamabufotalin; (2) cinobufotalin–cinobufagin; (3) (21S)-methyldigitoxigenin–digitoxigenin; (4) (21R)- and (21S)-methyldigitoxigenins; (5) digitoxigenin–digirezigenin; (6) 5α-androstane-3β,17β-diol monohydrate–5-androstene-3β,17β-diol monohydrate; (7) 3-epidigitoxigenin–digitoxigenin showing the dramatic change in the function when O(3) is taken into account in equation (2); (8) scillarenin–bufalin; and (9) 5α- and 5β-epimers of androstane-3α,17β-diol.

Table 1. *Descriptors [Π, $I_i(n)$ and $I_i(n^*)$] for two isostructural series of halogen derivatives: X = Cl, Br and* I

	Π	$I_i(4)$ (%)	$I_i(21)$ (%)	$I_i(22)$ (%)	$I_i(23)$ (%)	$I_i(22^*)$ (%)
(*a*) $C_{16}H_{17}XO_6$ (Ianelli *et al.*, 1992)						
Cl/Br	0.006	99	—	96	95	96
Br/I	0.012	98	—	94	93	95
I/Cl	0.018	97	—	90	88	92
(*b*) $C_{19}H_{24}XNO$ (Stanković *et al.*, 1992)						
Cl/Br	0.003	99	95	95	—	95
Br/I	0.009	97	92	91	—	93
I/Cl	0.018	95	87	86	—	89

$I_i(n)$ can be calculated not only for the total set of common non-H atoms (Kálmán *et al.*, 1991), but as a function of n also. In this form, n starts from a well chosen 'isostructural core' and goes to the last of the common pair of atoms, each relevant group being taken into account in stepwise mode (Fig. 1). The minimum of an isostructural core for two molecules, which simultaneously fixes their chirality, is defined by the four shortest ΔR_i values. For the relatively large steroid molecules (*cf.* Table 6 in the paper by Kálmán *et al.*, 1991), the isostructural core was defined deliberately by the ten shortest ΔR_i values pertaining to the steroid skeleton. From these ten up to the total of 19 skeletal atoms, the atomic sequence is determined by the monotonically increasing ΔR_i values. In the next step, the adjoining functions (*e.g.* γ- or δ-lactone rings) are taken into account. Of course, in general, $I_i(n)$ calculations may involve different groupings of atoms. In this case, however, the $I_i(n)$ function depends on an arbitrary sequence of ΔR_i values, especially if there are substantially different ΔR_i values. Nevertheless, it is just this ambivalency of the $I_i(n^*)$ and $I_i(n)$ calculations that enables us to explore marked differences in molecular isometricity and isostructurality in the crystalline state.

4. Conditions and limits of isostructurality

4.1. *Substituent pairs tolerated by isostructural crystals*

There are only a few substituent pairs whose members (*e.g.* CH_3 *versus* H atom) can replace each other without altering the existing packing of the crystals. This is one reason why isostructurality is so rare.

As substantiated by the literature, the most cooperative substituents are halogen atoms. For example, the three 2′-halo-1′,2′,3′,4′-tetrahydrospiro[1,3-dioxolane-2,1′-naphthalene]-4,5-dicarboxylates (halo = Cl, Br and I, *cf.* Table 1*a*) exhibit almost perfect isostructurality (Ianelli, Nardelli, Giordano, Coppi & Restelli, 1992).

The closeness of the van der Waals radii of Cl and the methyl group permit the isostructurality of 6′-(4-methylbenzyl)guanine and its 4-chlorobenzyl analogue (Zacharias, Glusker, Moschel & Dipple, 1992). Despite full or at least partial freedom of rotation about four single bonds, the $C_{18}H_{21}N_5O_5$ and $C_{17}H_{18}ClN_5O_5$ molecules exhibit highly similar packing motifs.

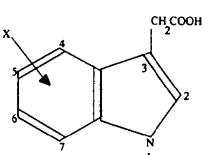
Even a methyl → ethyl replacement is tolerated by hydrophobic molecules such as phenothiazines [1-ethylphenothiazine ($C_{14}H_{13}NS$) and 1-methylphenothiazine ($C_{13}H_{11}NS$), space group $P2_1/c$, $Z = 4$] if the voids formed between them are large enough to accommodate the new substituent without alteration of the existing van der Waals close contacts (Chu, Napoleone, Ternay & Chang, 1982). Indeed, as shown by the high indices $I_i(4) = 89$ and $I_i(15) = 79\%$, they are isostructural.

In contrast, hydrophilic moieties such as —OH and =O are cooperative only in special circumstances. Cinobufagin and cinobufotalin (Kálmán, Fülöp, Argay, Ribár, Lazar, Zivanov-Stakić & Vladimirov, 1988) are isostructural since the —OH group is embedded in the *A*/*B* ring junction. It forms only an intramolecular hydrogen bond. The =O atom in arenobufagin that replaces two H atoms in the isometric gamabufotalin (Argay, Kálmán, Ribár, Vladimirov & Zivanov-Stakić, 1987) is prevented from participating in hydrogen bonding.

4.2. *Size of molecules as a prerequisite to isostructurality*

Small molecules such as urea (CH_4N_2O) and thiourea (CH_4N_2S) cannot develop isostructural lattices since the difference in volume of S and O is significant with respect to the volumes of these small molecules (Kitaigorodskii, 1961). Of course, tolerance toward substitution is increased as the molecular volume increases, and the possibility of an isostructural relationship becomes higher. To demonstrate this, three examples are presented.

The 5-halo-substituted indol-3-ylacetic acid (IAA) molecules (1), containing 14 non-H and eight H atoms ($C_{10}H_8NO_2X$), display quite a high isostructurality index of $I_i(14) = 87\%$ for the F→Cl replacement.



4-, 5-F-IAA $X = F$
4-, 5-, 7-Cl-IAA $X = Cl$
5-Br-IAA $X = Br$

(1)

However, the Br atom is too large to be accommodated in the voids occupied by F or Cl in the small 5-F-IAA and 5-Cl-IAA molecules (Kojić-Prodić, Nigović, Tomić & Duax, 1992).

In contrast, with 22 non-H atoms and 24 H atoms, the Cl, Br and I analogues of 17-halo-3-methoxy-16,17-secoestra-1,3,5-triene-16-nitrile (Stanković, Petrović, Miljković, Pejanović, Kovacević, Stefanović & Bruvo, 1992) are large enough to remain isostructural (Table 1*b*).

Possessing 52 non-H atoms with 62 H atoms, the biosides (a 'twinned' sugar side chain bearing three OH groups) of digitoxigenin and gitoxigenin (16-OH-digitoxigenin) are isostructural (Go & Bhandary, 1989), but in the lattice of gitoxigenin glycoside there are two additional hydrogen bonds. These are strong enough to reduce the unit-cell volume significantly (by 48 Å^3) without changing the packing array.

4.3. *Influence of site of substitution*

The isostructurality of cinobufagin and cinobufotalin (Kálmán *et al.*, 1988) can be attributed to the special site of the H→OH replacement. The types of isostructural pairs that occur among *para*-disubstituted benzylideneaniline derivatives (Bar & Bernstein, 1987)

$$R—C_6H_4—CH=N—C_6H_4—R'$$

support this conclusion. Although conformational disorders hinder precise refinement of these structures, it is certain that the *R* and *R*′ positions are not equivalent. [The lattice parameters of the related homo- and heterosubstituted (*R*, *R*′ = CH_3, Cl and Br) derivatives are listed in Table 2 and their relationship is depicted in Fig. 2.

The replacement of either substituent of Cl—C_6H_4—CH=N—C_6H_4—Cl (ClCl) and Br—C_6H_4—CH=N—C_6H_4—Br (BrBr) by the opposite function is ambivalent. While ClBr remains isostructural with ClCl, its contrasubstitutional analogue BrCl is isostructural with BrBr. This asymmetrical packing relationship of ClBr and BrCl with the homodisubstituted pair indicates that the substituent on the benzylidene ring plays the most important role in determining the crystal structure (Bar & Bernstein, 1987). A similar phenomenon is exhibited by the analogous *meta*-dihalo-substituted benzylideneanilines (Zamir & Bernstein, 1993) (Table 2).

5. Isostructural crystal pairs (*A*)

5.1. *Isometric substitution on an identical atom* (*A*1, *a*)

Since the isostructurality of several related steroid crystals has been analysed earlier (Kálmán *et al.*,

Table 2. *Lattice parameters of isostructural and non-isostructural crystals of disubstituted benzylideneanilines* $R—C_6H_4—CH=N—C_6H_4—R'$

Compounds *RR'*	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	Space group	*Z*	Reference
p-MeMe (I)	6.891 (1)	7.153 (1)	12.600 (1)	—	102.7 (1)	—	$P2_1$	2	(*a*)
p-MeMe (II)	6.089 (2)	7.751 (2)	26.766 (3)	—	103.16 (3)	—	$P2_1/c$	4	(*b*)
p-MeMe (III)	9.878 (5)	4.448 (1)	12.018 (3)	—	90.48 (2)	—	$P2_1/c$	2	(*c*)
p-MeCl	5.960 (1)	7.410 (1)	13.693 (3)	—	99.20 (2)	—	$P2_1/a$	2	(*d*)
p-ClMe	5.969 (1)	7.412 (2)	13.747 (4)	—	99.12 (2)	—	$P2_1/a$	2	(*d*)
p-ClCl (I)	5.986 (2)	3.933 (1)	12.342 (2)	87.38 (3)	78.40 (3)	89.53 (3)	$P1(\bar{P}1)$	1	(*e*)
(II)	24.503 (5)	6.334 (1)	7.326 (1)	—	—	—	*Pccn*	4	(*f*)
p-ClBr	24.880 (10)	6.379 (2)	7.436 (2)	—	—	—	*Pccn*	4	(*g*)
p-BrCl	24.692 (2)	5.912 (1)	4.022 (1)	—	92.10 (1)	—	$P2_1/a$	2	(*g*)
p-BrBr	24.912 (13)	5.877 (1)	4.046 (1)	—	92.42 (3)	—	$P2_1/a$	2	(*h*)
m-BrBr	9.646 (3)	31.522 (7)	4.007 (7)	—	—	—	$P2_12_12_1$	4	(*i*)
m-ClBr	9.615 (2)	31.336 (7)	3.967 (2)	—	—	—	$P2_12_12_1$	4	(*i*)
m-BrCl	7.842 (3)	13.644 (7)	11.096 (7)	—	—	—	$P2_12_12_1$	4	(*i*)
m-ClCl	25.231 (6)	3.943 (1)	12.002 (3)	—	102.64 (2)	—	$P2_1/n$	4	(*i*)

References: (*a*) Bar & Bernstein (1977); (*b*) Bar & Bernstein (1982); (*c*) Bernstein, Bar & Christensen (1976); (*d*) Bar & Bernstein (1983); (*e*) Bernstein & Schmidt (1972); (*f*) Bernstein & Izak (1976); (*g*) Bar & Bernstein (1987); (*h*) Bernstein & Izak (1975); (*i*) Zamir & Bernstein (1993).

1991, 1992) in detail [nine $I_i(n)$ functions are shown in Fig. 1] only the types of isometric replacement are summarized here. Similarly, other isostructural pairs mentioned above are listed here.

H→CH_3 substitution: digitoxigenin→(21*R*)- and (21*S*)-methyldigitoxigenins (Prasad & Gabe, 1983; Kálmán *et al.*, 1991) (the similar packing motif is shown by curve 3 in Fig. 1 and Figs. 3*a* and 3*b*); CH_3→C_2H_5 substitution: $C_{13}H_{11}NS$→$C_{14}H_{13}NS$ (Chu *et al.*, 1982); CH_3→Cl substitution: $C_{18}H_{21}N_5O_5$→$C_{17}H_{18}ClN_5O_5$ (Zacharias *et al.*, 1992); F→Cl substitution: $C_{10}H_8FNO_2$→$C_{10}H_8ClNO_2$ (Kojić-Prodić *et al.*, 1992); Cl→Br→I substitution: $C_{19}H_{24}ClNO$→$C_{19}H_{24}BrNO$→$C_{19}H_{24}INO$ (Stanković *et al.*, 1992), $C_{16}H_{17}ClO_6$→$C_{16}H_{17}BrO_6$→$C_{16}H_{17}IO_6$ (Ianelli *et al.*, 1992) [the indices *Π* and $I_i(n)$ for these two series are listed in Table 1].

Isometric substitutions (IS) among the disubstituted *p*-benzylideneanilides (Bar & Bernstein, 1987, and references therein) are depicted in Fig. 2. H→OH substitution: cinobufagin→cinobufotalin (Kálmán *et al.*, 1988) (see curve 2 in Fig. 1); digitoxigenin bisdigitoxoside→gitoxigenin bisdigitoxoside (Go & Bhandary, 1989); H_2→=O substitution: gamabufotalin→arenobufagin (Argay *et al.*, 1987) (see curve 1 in Fig. 1); H→—O—*Q* substitution: digitoxigenin→digirezigenin (Kálmán, Argay, Ribár, Vladimirov & Zivanov-Stakić, 1984) (see curve 5 in Fig. 1).

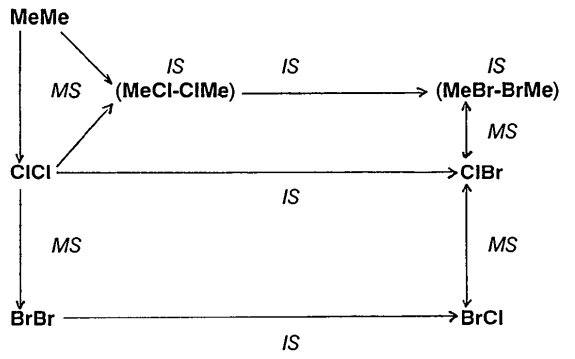


Fig. 2. Bernstein's cycles of morphotropic steps (MS) and isostructural substitutions (IS) of *para*-disubstituted benzylideneanilines ($R = R'$ = Me, Cl, Br).

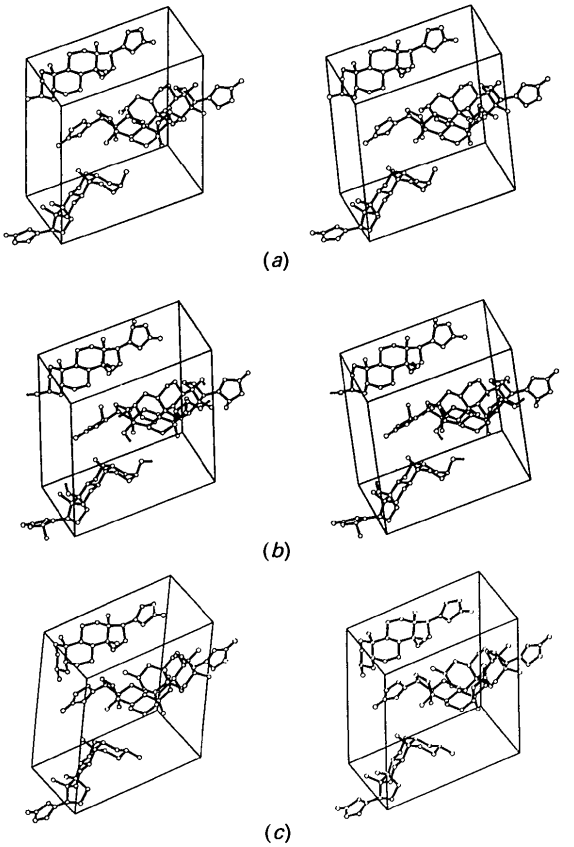


Fig. 3. Stereoviews of three cardiotonic steroids: (*a*) digitoxigenin; (*b*) (21*S*)-methyldigitoxigenin; and (*c*) 3-epidigitoxigenin, showing isostructural relationships with high [(*a*)–(*b*)] and medium [(*a*)–(*c*)], (*b*)–(*c*)] indices $I_i(n)$ in similar orthorhombic unit cells. Common space group $P2_12_12_1$.

5.2. *Isometric replacement of core atoms in organometallic compounds* (*A*1, *b*)

Ph_3X—$X'Me_3$ (X, X' = Si, Si; Ge, Si; Si, Ge; Ge, Ge). The high isostructurality index [$I_i(23)$ = 95%] of Ph_3Si—$SiMe_3$ (Fig. 4) (Párkányi & Hengge, 1982) with Ph_3Ge—$SiMe_3$ (Párkányi, Hernandez & Pannell, 1986) and Ph_3Si—$GeMe_3$ (Pannell, Kapoor, Raptis, Párkányi & Fülöp, 1990) indicates that the orientation of the Si—Ge dumbbell does not alter the molecular dimensions. They are, therefore, isostructural. Synthesis and structure determination of the missing Ph_3Ge—$GeMe_3$ (Párkányi *et al.*, 1993) showed that the simultaneous replacement of the shielded Si atoms by Ge atoms does not disturb their isostructurality either [index $I_i(23)$ with Ph_3Si—$SiMe_3$ = 94%].

Ph_3X—$SiMe_2[Fe(CO)_2(\eta^5\text{-}C_5H_5)]$ (X = Si or Ge). The isostructural relationship is also preserved when one of the methyl groups of Ph_3Si—$SiMe_3$ and Ph_3Ge—$SiMe_3$ is replaced by the bulky $Fe(CO)_2(\eta^5\text{-}C_5H_5)$ moiety (Párkányi & Hengge, 1982; Párkányi, Pannell & Hernandez, 1983). The spoiled threefold molecular symmetry (Fig. 5) gives rise to 32 symmetry-independent non-H atoms in the monoclinic space group $P2_1/c$ (Z = 4), with $I_i(32)$ = 95%.

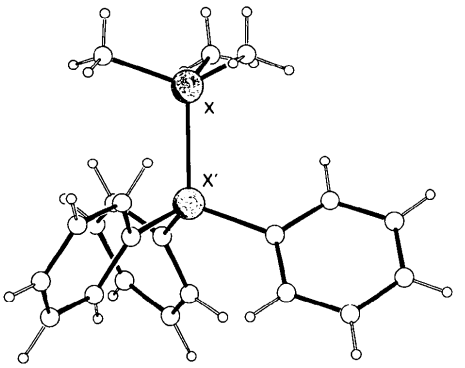


Fig. 4. Perspective view of the structure of Me_3X—$X'Ph_3$ (X, X' = Si, Si; Si, Ge; Ge, Si; Ge, Ge) molecules located on a threefold axis.

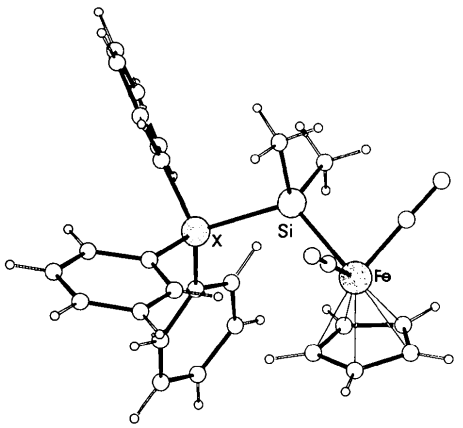


Fig. 5. Structure of the Ph_3X—$SiMe_2Fe(CO)_2(\eta^5\text{-}C_5H_5)$ pair (X = Si or Ge), showing the high degree of isostructurality in monoclinic unit cells with space group $P2_1/c$.

Table 3. *Lattice parameters* (Å) *of the germyl/silyl analogues* Ph_3X—$X'Me_3$ *and* Ph_3X—$X'Et_3$ (*space group* $P\bar{3}$ *and* $R\bar{3}$, *respectively*)

X	X'	$a_1 = a_2$	c	Reference
Ph_3X—$X'Me_3$				
Si	Si	11.313 (2)	8.817 (2)	(*a*)
Ge	Si	11.344 (1)	8.861 (1)	(*b*)
Si	Ge	11.307 (1)	8.910 (1)	(*c*)
Ge	Ge	11.335 (1)	8.939 (1)	(*d*)
Ph_3X—$X'Et_3$				
Si	Ge	15.522 (1)	16.022 (1)	(*e*)
Ge	Si	15.435 (2)	16.195 (2)	(*e*)

References: (*a*) Párkányi & Hengge (1982); (*b*) Pannell *et al.* (1990); (*c*) Párkányi *et al.* (1986); (*d*) Párkányi *et al.* (1993); (*e*) Pannell (1992).

Ph_3X—$X'Et_3$ (X, X' = Ge, Si or Si, Ge). The above-discussed pair Ph_3Ge—$SiMe_3$ and Ph_3Si—$GeMe_3$ (Párkányi *et al.*, 1986; Pannell *et al.*, 1990) are related by the interchange of the Si—Ge dumbbell on the threefold axes of the common space group $P\bar{3}$ with a high $I_i(23)$ of 81%. Similarly, Ph_3Ge—$SiEt_3$ and Ph_3Si—$GeEt_3$ (Pannell, 1992) crystallized in rhombohedral unit cells (common space group $R\bar{3}$) and are also isostructural (Table 3).

Ph_3X—$X'Me_3$ (X, X' = Ge, Sn or Sn, Ge). In contrast, when one of the Ge atoms of Ph_3Ge—$GeMe_3$ is replaced by the larger Sn atom, the new isomers are no longer isostructural with the parent compound. Such 'morphotropic' phase transitions were expected by Kitaigorodskii (1961) whenever the atomic replacement substantially diminishes the existing packing coefficient. Of course, Ph_3Ge—$SnMe_3$ and Ph_3Sn—$GeMe_3$ (Pannell, Párkányi, Sharma & Cervantes-Lee, 1992) remain isostructural, assuming new orthorhombic (pseudohexagonal) unit cells with space group $Pna2_1$. In these pseudohexagonal unit cells, the bumps of the molecules stacked with similar orientations along the polar c axis fit perfectly into the hollows of the adjacent columns generated by the glide planes, thereby forming new efficient close packing (Kálmán, Párkányi & Argay, 1993).

5.3. *Isostructurality of molecules differing in the chirality of one atom* (*A*2)

The isostructural pairs (*ca* 20) presented in subclass *A*1 are formed by approximately isometric molecules and are related by substitution either on the surface or in the core of the molecules. Showing similarity, with high $I_i(n)$ and $I_i(n^*)$ values (>80%), they are the commonly known forms of isostructurality. Our previous studies (Kálmán *et al.*, 1991, 1992) additionally revealed that molecules differing only in atomic chirality may also form closely related pack-

Table 4. *Lattice parameters* (Å) *of N-carbomethoxy-carbonyl-prolyl-phenylalanyl-benzyl esters containing* L- *or* D-*phenylalanine* (*common space group* $P2_12_12_1$)

Values from Venkatramani & Helm (1992).

	a	*b*	*c*
LL	25.893 (5)	13.699 (2)	6.155 (1)
LD	26.588 (2)	11.656 (2)	7.281 (2)

ing motifs in similar unit cells. Since the superposition of such molecules is always limited, the differences between $I_i(n^*)$ values calculated for their conformationally identical parts and for the full molecules give an indication of how far they are from the 'approximately isometric' molecules. Furthermore, if the corresponding $I_i(n)$ values are considerably lower than the indices $I_i(n^*)$, then the translational and/or rotational differences between the positions occupied by these molecules in their similar asymmetric units are substantial.

Inversion of carbon chirality. (*a*) The smallest decrease in the $I_i(n)$ function (curve 4 in Fig. 1) is shown by the (21*R*)- and (21*S*)-methyldigitoxigenins (Prasad & Gabe, 1983; Kálmán *et al.*, 1991). The different orientation of the methyl group is minimized in the voids of the digitoxigenin lattice by sufficient rotation of the γ-lactone ring, resulting in $I_i(19) = 71\%$.

(*b*) In the presence of pure van der Waals forces between the relatively large $C_{17}H_{26}N_2O_2S$ molecules, the epimerization at C(12) of the cyclohexane ring, bringing the bulky isopropyl moiety from the equatorial to the axial position, can preserve the isostructurality of menthone- and isomenthonetosylhydrazones (Mullica, Garner, Prince, Mossman & Sappenfield, 1992).

(*c*) The structures of digitoxigenin (Karle & Karle, 1969) and 3-epidigitoxigenin (Messerschmidt, Höhne & Megges, 1981) differ only in the β- or α-position of the 3-OH moiety (Figs. 3*a* and 3*c*). Nevertheless, $I_i(26^*) = 88$ and $I_i(26) = 49\%$ differ substantially, indicating that the translational and rotational differences which protect the common packing motif against O(3) displacement (curve 7 in Fig. 1) follow the C(3) isomerization. The great similarity between their unit cells is indicated by $\Pi = 0.006$.

(*d*) The crystal structures of two dipeptides, *N*-carbomethoxy-carbonyl-prolyl-phenylalanyl-benzyl esters differing only in the L- or D- configuration of the phenylalanine, assume similar unit cells (Table 4), with a low Π value of 0.005. In spite of the conformational difference ($\varphi_2 = 177$ *versus* 122°), a good overlap was observed between the LL and LD isomers (Venkatramani & van der Helm, 1992). This suggests that a displacement of such a hydrogen-bond donor and acceptor as the NH— moiety can also be tolerated by isostructural crystals.

(*e*) The epimerization about C(5) of androstane-3α,17β-diol brings the *A*/*B* junction from *trans* (Précigoux, Busetta, Courseille & Hospital, 1972) to *cis* (Weeks, Cooper, Norton, Hauptman & Fisher, 1971), resulting in a somewhat altered but still similar packing motif (*cf.* curve 9 in Fig. 1). Rings *B*, *C* and *D* of the stereoisomers show excellent superposition [$I_i(16^*) = 90\%$]. Of course, when the four atoms forming ring *A* together with O(3) are also included, then the final $I_i(16^* + 5)$ is only 20%, *i.e.* the molecules are far from being isometric (Fig. 6). Alternatively, when they are fitted totally by least squares (Fig. 7), then $I_i(21^*) = 42\%$ agrees well with $I_i(21) = 41\%$, indicating that the least-squares fit of the stereoisomers is identical with the observed packing.

(*f*) *Generation* (*or elimination*) *of chiral carbon.* Saturation of the C(4)=C(5) double bond in scill-

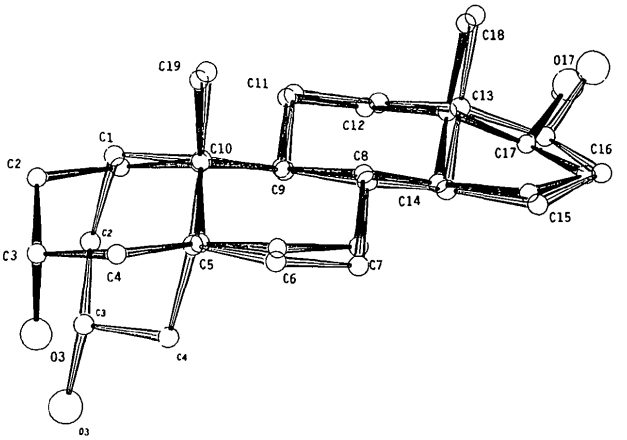


Fig. 6. Least-squares superposition of rings *B*, *C* and *D* for 5α- and 5β-androstane-3α,17β-diols, showing the relevant difference in their 'approximate molecular isomorphism' (Kitaigorodskii, 1961).

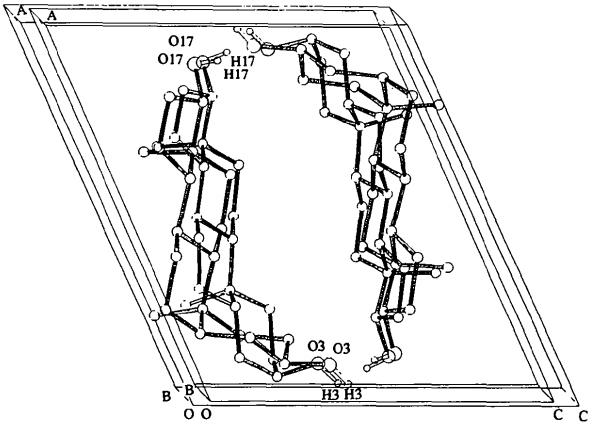


Fig. 7. Least-squares fit of the whole 5α- and 5β-androstane-3α,17β-diol skeletons, which allocates the molecules close to their positions assumed in the unit cells projected perpendicularly onto the polar *b* axis in space group $P2_1$.

arenin (Ribár, Argay, Kálmán, Vladimirov & Zivanov-Stakić, 1983) gives rise to bufalin (Rohrer, Fullerton, Kitatsuji, Nambara & Yoshii, 1982), while C(5) gains chirality (α). Simultaneously, the conformation of ring *A* is turned from half chair to chair, which accounts for the rapid decrease in the $I_i(n)$ function (curve 8 in Fig. 1).

6. Homeostructural crystal pairs

If substitution involves more than one atom on the surface of isometric molecules, then the identical packing arrays in general disappear. For example, the homodisubstituted derivatives of *R*—C_6H_4—CH=N—C_6H_4—*R* (MeMe), (ClCl) and (BrBr), although they have different polymorphs, do not form isostructural pairs with each other (Table 2) (Bernstein, Bar & Christensen, 1976; Bar & Bernstein, 1977, 1982; Bernstein & Schmidt, 1972; Bernstein & Izak, 1975, 1976). Nevertheless, there are pairs termed homeostructural that do display some sort of packing similarity. The variety of the homeostructural relationships is illustrated by a few characteristic examples below.

6.1. *Phenyl ring(s) replaced by smaller or larger moieties*

(*a*) Brown (1955) reported that phenyl isocyanate dimer was 'isomorphous' with *p*-terphenyl. Baudour, Delugeard & Sanquer (1974) compared the packing of these structures in detail (*cf.* Fig. 2 in that paper). Both types of molecules, with their centre of symmetry fixed at 000, lie in the *ac* plane. The longer *p*-terpenyl molecules stretch over the shorter phenyl isocyanate dimers, permitting only a low degree of isostructurality (*e.g.* $\Pi = 0.04$ is an order of magnitude higher than values observed for highly isostructural crystals).

(*b*) The butterfly-like chiral molecules of diphenyldiacyloxyspirosulfurane (2) (Kálmán, Sasvári & Kapovits, 1973) and its binaphthyl analogue (3) (Kapovits *et al.*, 1993) possess C_2 molecular symmetry on the short twofold axes (Table 5) of the orthorhombic unit cells (space group *Fdd*2). Despite the larger naphthyl rings, the packing array of (3) is quite similar to that of (2) (Fig. 8). Of course, $I_i(n)$ calculation is limited to a few common central atoms, and the large naphthyl groups account for the elongated (by *ca* 25%) *a* axis ($\Pi = 0.077$). Spirosulfuranes (2) and (3) exemplify well Kitaigorodskii's 'homologous isomorphism', described by the lattice parameters (space group $P2_1/a$) of biphenyl, *p*-terphenyl and *p*-quaterphenyl (Kitaigorodskii, 1961).

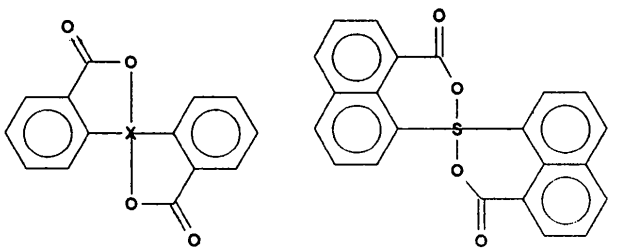
Table 5. *Lattice parameters* (Å) *of two homologous diaryldiacyloxyspirosulfuranes* [(2), (3)] (*space group Fdd*2)

	a	*b*	*c*	Reference
(2)	20.092 (3)	27.764 (3)	4.228 (1)	(*a*)
(3)	25.026 (3)	26.182 (3)	4.883 (1)	(*b*)

References: (*a*) Kálmán *et al.* (1973); (*b*) Kapovits *et al.* (1993).

6.2. *Packing 'similarities' generated by substituent migration*

(*a*) The crystal structures of 2,4- and 3,5-dichloroanilines (Dou, Weiden & Weiss, 1993) exemplify the effects of migration of a small function. The 'mirror' plane of the symmetric 3,5-DA molecule bisecting the NH_2 group assumes a position parallel with the *b* axis of the orthorhombic unit cell (space group $P2_12_12_1$). By using one of its H atoms, the NH_2 group acts simultaneously as donor and acceptor to form infinite —NH···N— hydrogen-bond helices around the screw axes at $\frac{1}{4}$, 0, *z*, *etc.*, while the other H atom is donated to a Cl atom of the molecule related by the screw axis at 0, *y*, $\frac{1}{4}$ (Fig. 9*a*). When the NH_2 group is moved from the 'symmetric' to the 'asymmetric' position, the 2,4-DA molecules assume a new arrangement by rotation through *ca* 30° around the *c* axis. Otherwise, they would collide with each other. These asymmetric 2,4-DA molecules, by visible rotation and additional translation along the *a* axis (Fig. 9*b*), preserve a packing similar to that of the isomer molecules. In both crystal



(2) (*X* = S, Se) (3)

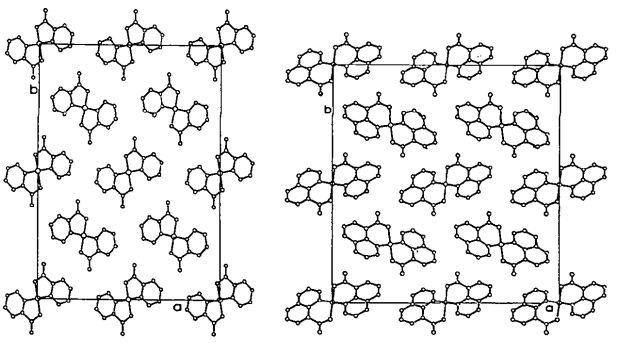


Fig. 8. Perspective views of the full unit cells (perpendicular to the short *c* axis) of two diaryldiacyloxyspirosulfuranes [(2), (3)] crystallized with the polar space group *Fdd*2.

structures, a great helix is formed around the screw axis at $\frac{1}{4}$, $\frac{1}{2}$, z. Each turn is maintained by six molecules *via* eight hydrogen bonds (four single NH···Cl and two double NH···N bonds) developed in the same sequence: (double–single–single–double–single–single). Each molecule takes part in three hydrogen bonds; two of them use only one (NH_2), whereas four of them use two (Cl and NH_2) functions. What differs is their cross section and the orientation of the helices.

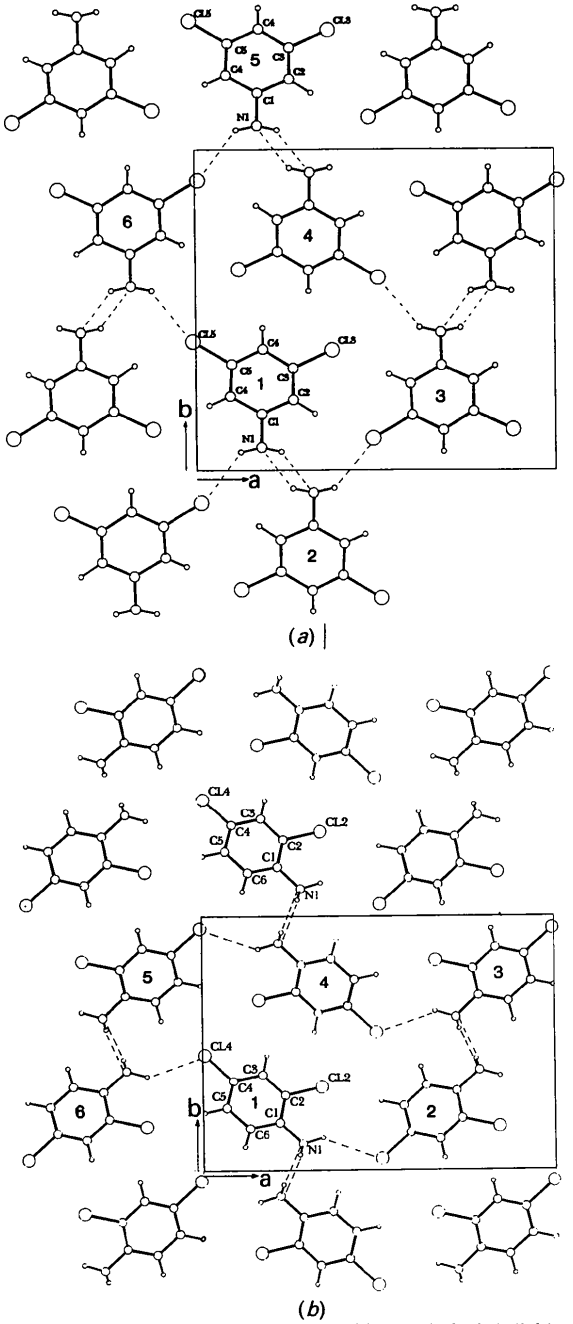


Fig. 9. Projections of (*a*) 3,5-dichloroaniline and (*b*) 2,4-dichloroaniline, showing the similarities in the molecular array perpendicular to the short *c* axis and the dissimilarities in the 'great helices' formed by six molecules (1–6) using four NH···N and four NH···Cl hydrogen bonds. In 3,5-DA there is a 28-membered atomic turn, whereas in isomer 2,4-DA it is 32-membered.

(*b*) The crystal structures of 5- and 7-chloroindol-3-ylacetic acids (5- and 7-Cl-IAA) (Kojić-Prodić *et al.*, 1992) exhibit a somewhat greater difference. Although 7-Cl-IAA has lattice parameters quite similar to those of its substitutional isomer 5-Cl-IAA (see §4.2 above), their packing motifs differ. However, a close inspection of these molecular arrays (the atomic coordinates were also kindly provided by Dr Kojić-Prodić) reveals that they are related by non-crystallographic symmetries (Fig. 10): if the monoclinic unit cells (space group $P2_1/c$) are orthogonalized, then it can be seen that a good overlap of the packing motifs can be established by an additional mirror plane perpendicular to the *c* axis.

6.3. *Elimination of a hydrogen-bond donor*

Partial oxidation of the aforementioned (Figs. 6 and 7) 5α-androstane-3α,17β-diol (Précigoux *et al.*, 1972) terminates the donor function of the 17-oxo group in the novel 5α-androstan-3α-ol-17-one (High & Kraut, 1966). The new helical packing of the molecules occurs along the polar 2_1 axes in a monoclinic unit cell, which is similar to that of the parent compound (space group $P2_1$). Nevertheless, the new and the old packing arrays are related by a non-crystallographic twofold axis almost parallel to the *c* axis of the 5α-androstane-3α,17β-diol crystal.

6.4. *Superposition of different forms of disorder*

Replacement of either substituent of *p*-Me—C_6H_4—CH=N—C_6H_4—Me and *p*-Cl—C_6H_4—CH=N—C_6H_4—Cl (Table 2) by the opposite function invariably results in almost identical crystals of *p*-Cl—C_6H_4—CH=N—C_6H_4—Me and *p*-Me—C_6H_4—CH=N—C_6H_4—Cl (Bar & Bernstein, 1983);

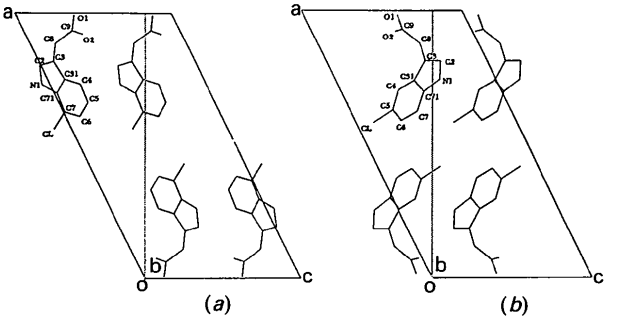


Fig. 10. Projections of 5Cl-IAA (*a*) and 7Cl-IAA (*b*) molecules perpendicular to the monoclinic *b* axis, showing the similarity of the packing motifs related by non-crystallographic symmetries.

the volumes of their unit cells differ by only 2.5 Å^3. While they differ from those of the five 'polymorphs' of the parent (MeMe and ClCl) compounds, these crystals are homeostructural by the superposition of orientational, positional and substitutional disorders. They jointly generate non-crystallographic symmetry relationships (twofold axis, centre of symmetry) between all of these substitutional isomers. *Mutatis mutandis*, *p*-Br—C_6H_4—CH=N—C_6H_4—Me and *p*-Me—C_6H_4—CH=N—C_6H_4—Br are homeostructural with the ClMe and MeCl pair (Bar & Bernstein, 1987).

7. Isostructurality of molecular associates (*A*/*B*)

The similar packing of binary systems is of particular importance since they help to map out the voids formed by the host molecules in respect of the distribution of dispersion forces. Molecular associates can be regarded as supramolecular systems in which one 'large substituent' (the guest molecule) is replaced by another. If this substitution does not change the packing array of the 'host compound', we may speak about a novel class of isostructurality.

This phenomenon is well exemplified by Weber, Csöregh, Stensland & Czugler (1984). Of the five different alcohol clathrates of 1,1′-binaphthyl-2,2′-dicarboxylic acid (studied by X-ray diffraction), two exhibit visible packing similarity in the monoclinic space group $C2/c$. As shown by the relatively high $I_i(13) = 88\%$ calculated for the atoms of 1,1′-binaphthyl-2,2′-dicarboxylic acid, the voids in the crystal lattices accommodate ethanol and isopropanol without a substantial change in the packing array of the host molecule. When the positions of the disordered alcohol molecules are also taken into account $I_i(17)$ is diminished only to 70%, which indicates a high form of isostructurality.

Alternatively, the three clathrates of 5-methoxysulfadiazine with the guest molecules dioxane, tetrahydrofuran and chloroform, reported recently by Caira & Mohamed (1992), exhibit both main forms of isostructurality. Whereas dioxane and tetrahydrofuran are chemically and topologically similar, chloroform differs from them. Consequently, the clathrates of dioxane and tetrahydrofuran are isostructural, while that of chloroform is only homeostructural with them.

Similarly as for scillarenin and bufalin, the generation (or elimination) of a novel chiral carbon establishes an isostructural relationship between 5-androstene-3β,17β-diol (Kálmán *et al.*, 1992) and 5α-androstane-3β,17β-diol (Précigoux & Fornies-Marquina, 1973), with a low unit-cell similarity index, $\Pi = 0.004$. However, these isostructural crystals are formed with the active participation of water molecules. As indicated by the limited fall in the $I_i(n)$ (curve 6 in Fig. 1) to a final 76%, in these binary crystals the common guest molecules forming three intermolecular hydrogen bonds stabilize the closely related packing motifs.

The search for further isostructural crystals of clathrates, *etc.* is in progress.

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Cyclooctatetraene Formation in the Photolyses of Dibenzobarrelene Diesters

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Abstract

A study of cyclooctatetraenes (COTs) derived from the photolyses of dibenzobarrelene derivatives indicates the formation of two types of COT with different substitution patterns; the structures of one example of each type have been determined by X-ray crystal analyses. Crystal data: $T = 294$ K, Cu $K\alpha$, $\lambda = 1.5418$ Å. (1), dimethyl 6-methyldibenzo[*a*,*e*]-cyclooctatetraene-5,11-dicarboxylate, $C_{21}H_{18}O_4$, $M_r = 334.37$, orthorhombic, $Pna2_1$, $a = 18.364$ (4), $b = 10.485$ (3), $c = 9.031$ (4) Å, $V = 1739$ (2) Å^3, $Z = 4$, $D_x = 1.28$ g cm^{-3}, $F(000) = 704$, $\mu = 6.8$ cm^{-1}, $R = 0.054$ for 1303 reflexions. (2), 11-methyl 5-(2-propyl) dibenzo[*a*,*e*]cyclooctatetraene-5,11-dicarboxylate, $C_{22}H_{20}O_4$, $M_r = 348.40$, monoclinic, $P2_1/n$, $a = 9.121$ (1), $b = 20.486$ (1), $c = 10.028$ (1) Å, $\beta = 100.91$ (1)°, $V = 1839.9$ (3) Å^3, $Z = 4$, $D_x = 1.26$ g cm^{-3}, $F(000) = 736$, $\mu = 6.6$ cm^{-1}, $R = 0.043$ for 2688 reflections. COT (2) has a structure consistent with formation *via* a normal $[2\pi + 2\pi]$ intramolecular cycloaddition, while formation of (1) provides another example of abnormal behaviour, with reaction *via* fragmentation of a bis-benzylic 1,4-biradical. The difference in reaction pathways probably results from intramolecular steric effects, which are more severe in the dibenzobarrelene from which (1) is derived (three substituents), in comparison with the formation of (2) (two substituents).

Introduction

Bridgehead-substituted dibenzobarrelene diesters have been found to react *via* their S_1 states to give cyclooctatetraenes (COTs) with substitution patterns different from those obtained in previous studies on benzo- and naphthobarrelenes (Pokkuluri, Scheffer & Trotter, 1993*a*). It is, therefore, intriguing to ask whether all dibenzobarrelenes behave similarly, or is the 'abnormal' behaviour specific to some cases. To answer this question, two COTs have been re-examined, which were earlier characterized assuming 'normal' structures based on a [2 + 2] mechanism; the two COTs (1) and (2) are obtained by photolyses of the 9-methyl-11,12-dimethoxycarbonyl and 9-isopropoxycarbonyl-12-methoxycarbonyl diesters,