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Relationship between Symmetry in Hydrogen-Bonded Benzoic Acids and the Formation of Acentric Crystal Structures

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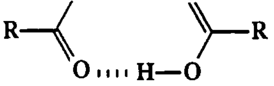
Using a data set of 139 benzoic acids extracted from the Cambridge Crystallographic Data File, a relationship is shown to exist between inversion in hydrogen-bonded aggregates of benzoic acid derivatives and inversion symmetry in their crystal structures. Benzoic acids that aggregate in acentric chains tend to crystallize in acentric space groups. Ortho-substituted benzoic acids are shown to be more likely to organize in hydrogen-bonded chains than meta- or para-substituted benzoic acids. This demonstrates that ortho substitution can indirectly promote the formation of acentric benzoic acid crystals. This information is of practical importance for designing new nonlinear optical materials, because only acentric crystals can exhibit second-order nonlinear optical properties.

Introduction

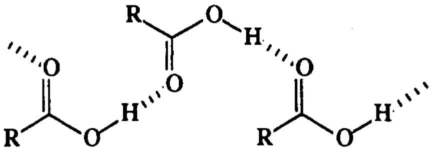
Understanding how intermolecular interactions direct the organization of molecules in condensed matter is a topic of increasing concern. Many studies have focused on correlating molecular structure with crystal structure.[1] A new approach involves relating a single type of intermolecular interaction, such as an electrostatic interaction,[2] a charge-transfer interaction,[3] or a hydrogen-bond interaction,[4] to a substructure within a crystal structure. One type of substructure is a molecular aggregate whose connectivity pattern is dictated by specific noncovalent interactions. In this paper, we demonstrate that a relationship exists between inversion symmetry in hydrogen-bonded aggregates of benzoic acid derivatives and inversion symmetry in their crystal structures, using data retrieved from the Cambridge Crystallographic Data File (CCDF). Specific features of the molecular structure that promote the formation of acentric aggregates will be discussed. By establishing a relationship between molecular structure and the inversion symmetry in an aggregate, we have also established an indirect correlation between molecular structure and inversion symmetry in crystals. This information is of practical importance for designing new nonlinear optical materials, since only acentric crystals can exhibit second-order nonlinear optical properties.[5]

Specifically, the correlations presented here deal with a method of choosing benzoic acids that are likely to crystallize in acentric space groups. Resolved chiral molecules necessarily crystallize in acentric space groups. Only achiral benzoic acids were used for this study, so that correlations between molecular structure and crystal inversion symmetry could be made.

Benzoic acid structures were divided into two sets based on the symmetry of their aggregate patterns. For benzoic acids, their centric patterns are always dimers (I). Some benzoic acids also aggregate in acentric chains[6] resulting from the formation of hydrogen bonds to two or more neighboring benzoic acids (II). One benzoic acid, tetrafluorophthalic acid, was found to aggregate in both chains and dimers.[7] The presence of the dimer introduces inversion symmetry into this hydrogen-bond pattern and so tetrafluorophthalic acid was included in the dimer group.



I



II

Experimental Section

Version II (current to January 1991) of the VAX-compatible CCDF[8] was used for structural searching[9] and plotting structures.

The following criteria were used to screen structures:[10]

1. Only compounds with ≤ 16 carbons were included in order to limit the size of the data set.

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† Alfred P. Sloan Fellow 1989–1991.

(1) Desiraju, G. R. *Prog. Solid State Chem.* 1987, *17*, 295–353.

(2) (a) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* 1989, *111*, 1698–1719. (b) Ward, M. D.; Fagan, P. J.; Calabrese, J. C.; Johnson, D. C. *Ibid.* 1989, *111*, 1719–1732.

(3) Herbstien, F. H. In *Perspectives in Structural Chemistry*, Dunitz, J. D., Ibers, J. A. Eds.; Wiley and Sons: New York, 1971; Vol. 4, pp 166–395.

(4) (a) Etter, M. C. *J. Am. Chem. Soc.* 1982, *104*, 1095–1096. (b) Etter, M. C. *Isr. J. Chem.* 1985, *25*, 312–319. (c) Panunto, T. W.; Urbańczyk-Lipkowska, Z.; Johnson, R.; Etter, M. C. *J. Am. Chem. Soc.* 1986, *106*, 7786–7797. (d) Etter, M. C.; Frankenbach, G. M. *Mater. Chem.* 1989, *1*, 10–12. (e) Etter, M. C.; Frankenbach, G. M.; Adsmond, D. A. *Mol. Cryst. Liq. Cryst.* 1990, *187*, 25–39.

(5) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* 1984, *23*, 690–703.

(6) Leiserowitz, L. *Acta Crystallogr.* 1976, *B32*, 775–802. Leiserowitz refers to carboxylic acid chains as catemers.

(7) Gowda, D. S. S.; Rudman, R. *Acta Crystallogr.* 1983, *C39*, 250–253.

(8) (a) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr.* 1979, *B35*, 2331–2339. (b) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* 1983, *16*, 146–153.

(9) The test questions used are deposited as supplementary material (see the paragraph at the end of the paper).

(10) A list of refcodes for benzoic acids used in this study is deposited as supplementary material.

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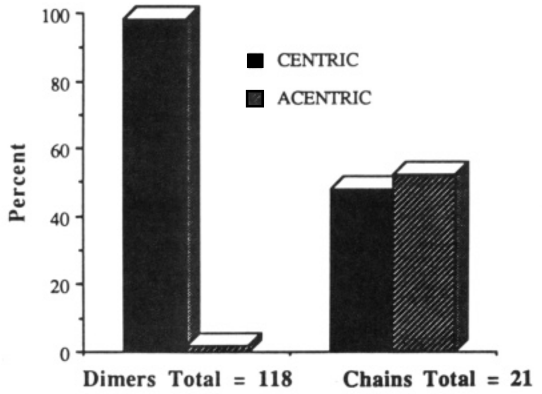

Figure 1. Set of benzoic acid crystals divided into two groups based on the hydrogen-bond pattern of the aggregate within the crystal. These two groups were subdivided into centric or acentric sets.

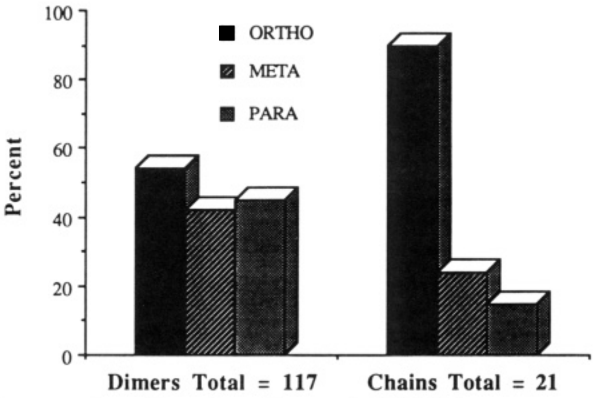

Figure 2. Set of benzoic acid crystals divided into two groups based on the hydrogen-bond pattern of the aggregate within the crystal. These two groups were subdivided based on the intramolecular substitution pattern. (The sum of the percentages of ortho, meta, and para substituents is greater than 100% because a benzoic acid may have more than one substituent.)

2. Salts were excluded to eliminate competition between ionic interactions and hydrogen bonds.[11]

3. Structures containing two different molecules (cocrystals, solvates, and complexes) were excluded.

4. Only achiral compounds were included in the data set because chiral compounds necessarily crystallize in acentric space groups.

5. Benzoic acids with more than two carboxy groups were not allowed.

6. Compounds that form only intramolecular hydrogen bonds[12] were excluded because these compounds do not form aggregates.

7. No crystal structure was excluded from this set on the basis of the size of the *R* factor because the presence of acid dimers or chains was clearly evident even in structures with poor *R* factors. The highest *R* factor was 17%. An *R* factor ≥10% occurred for 22% of the structures.

The final data set contained 139 benzoic acid structures.

Results

To illustrate the correlation between the centric aggregate and the centric crystal, the data set was first divided into a set of crystals containing dimers and a set of crystals containing chains. Each of these sets was subdivided into sets of centric and acentric crystals. The results are reported graphically in Figure 1.

A clear correlation exists between the presence of hydrogen-bonded dimers and the formation of centric crystals and between the presence of hydrogen-bonded chains and the formation of acentric crystals. Of the 118 crystals that contain dimers,[13] 98% crystallize in a centric space group.[14] Of the 21 crystals that contain chains,[15] 52% crystallize in an acentric space group.

Most benzoic acids that form chains have at least one substituent ortho to the carboxy group. The frequency of ortho, meta, and para substitution is shown for chain and dimer aggregates, Figure 2. Of the 21 benzoic acids that form chains, 90% have an ortho substituent, while no preference for ortho, meta, or para substitution was found for dimers.

Chain formation in di-ortho-substituted benzoic acids is related to the degree of rotation between the carboxy group and benzene ring, as shown in Table I. Only two benzoic acids with torsion angles greater than 60° failed to form chains.

Discussion

Benzoic acid molecules are known to aggregate in solution, so it may be that these aggregates initiate crystal nucleation (eq 1) and that the symmetry of the solution

$$\text{molecule} \rightleftharpoons \text{aggregate} \rightleftharpoons \text{crystal} \qquad (1)$$

aggregate biases the final symmetry of the nucleation site. Rather than thinking of crystallization as a stacking of individual molecules, this study indicates that for molecules forming hydrogen bonds, the process of crystallization may be better represented as pairs or chains of molecules arranging themselves into an energetically suitable packing pattern. The packing pattern will be dictated by aggregate properties such as the charge distribution, shape and symmetry of the aggregate. The features that are predictable from knowledge of hydrogen-bond patterns are the connectivity patterns and the symmetry of the hydrogen-bonded sets.

The idea that the symmetry of constituents may bias the symmetry of the crystal structure is not new. Kitai-

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(11) *o*-Anthranilic acid was taken as an exception to this rule because neutral as well as ionic molecules were found in this structure and the hydrogen-bond pattern of this form of *o*-anthranilic acid was not found to be very different from the hydrogen-bond pattern of the totally neutral form of *o*-anthranilic acid (Brown, C. J. *Proc. R. Soc. London, A* **1968**, *302*, 185–199).

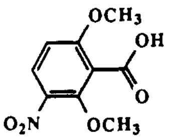
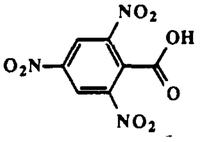
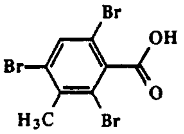
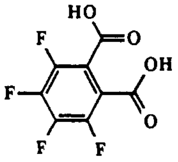
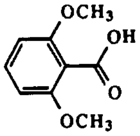
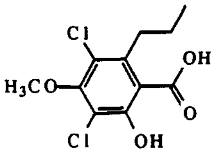
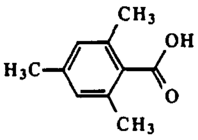
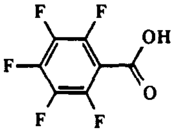
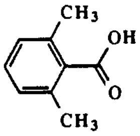
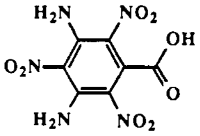
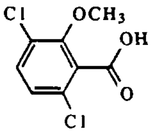
(12) Only 2-ethoxybenzoic acid (Gopalakrishna E. M.; Cartz, L. *Acta Crystallogr.* **1972**, *B28*, 2917–2924) and 4-(dimethylamino)azobenzene-2′-carboxylic acid (Moreiras, D.; Solans, J.; Solans, X.; Miravitlles, C.; Germain, G.; Declercq, J. P. *Cryst. Struct. Commun.* **1980**, *9*, 921–924) were found to form exclusively intramolecular hydrogen bonds.

(13) The molecule 3-(2-carboxyphenyl)-1-phenyltriazene 1-oxide does not crystallize in the typical eight-member hydrogen-bonded dimer; however, it does form a centric 18-member ring and therefore it is included in this data set (Sarkar, S. B.; Khalil, M.; Saha, S. C.; Talpatra, S. K. *Acta Crystallogr.* **1983**, *C39*, 1075–1076).

(14) The three compounds which form dimers and then crystallize in acentric space groups are 2,5-dihydroxybenzoic acid (Haisa, M.; Kahino, S.; Hanada, S.-I.; Tanaka, K.; Okazaki, S.; Shibagaki, M. *Acta Crystallogr.* **1982**, *B38*, 1480–1485), *p*-*n*-pentoxybenzoic acid (Bryan, R. F.; Hartley, P. *Mol. Cryst. Liq. Cryst.* **1980**, *62*, 259–280), and (4-carboxyphenyl)diethylarsine sulfide (Bel'skii, V. K.; Zavodnik, V. E.; Galyametdinov, Yu. G. *Dokl. Phys. Chem.* (*Engl. Transl.*) **1983**, *271*, 526–528).

(15) (a) Only the unit cell parameters have been determined for 2-(3-chloro-2-hydroxybenzoyl)benzoic acid (Skzrat, Z. *Pol. J. Chem.* **1972**, *46*, 143–144. Skzrat, Z. *Pol. J. Chem.* **1971**, *45*, 1933–1937). The unit cell parameters of this compound indicate it is isostructural with 2-(3-bromo-2-hydroxybenzoyl)benzoic acid for which a structure has been determined (Skzrat, Z.; Donitz, A. *Pol. J. Chem.* **1980**, *54*, 1029–1034). Because compound 2-(3-bromo-2-hydroxybenzoyl)benzoic acid forms chains, 2-(3-chlorohydroxybenzoyl)benzoic acid is also assumed to form chains. (b) A few of the benzoic acids which form hydrogen-bonded chains were found independent of the CCDF investigation. These structures include 2,6-dimethoxy-3-nitrobenzoic acid (Frankenbach, G. M.; Etter, M. C.; Britton, J. D. *Acta Crystallogr.* **1991**, *C47*, 553–555), 2,4,6-trinitrobenzoic acid (Rheingold, A. L.; Baldacchini, C. J.; Grote, C. W. *J. Cryst. Spectrosc. Res.* **1989**, *19*, 25–37), 2-(5-phenyl-1,3,4-oxadiazol-2-yl)-benzoic acid (Smith, G.; Kennard, C. H. L.; Katekar, G. F. *Aust. J. Chem.* **1983**, *36*, 2455–2463), and 2-carboxybenzanilide (Bocelli, G.; Rizzoli, C.; Ori, O. *Z. Kristallogr.* **1989**, *189*, 301–316).

Table I. Calculated Torsion Angles between the Carboxy Group and the Benzene Ring for All 2,6-Di-Ortho-Substituted Benzoic Acids

no.	compound	*R*	torsion angle,[a] deg	aggregate type (hydrogen-bond conformation)	space group	ref[e]
1		0.061	-64.6	chains (syn-anti)	*Pccn*	a
2		0.045	78.8	chains (syn-anti)	$P2_12_12_1$	b
3		0.134	89.8	chains (syn-anti)	*Pbca*	c
4[b]		0.033	-81.8 11.2	chains (syn-anti) and dimers (syn-syn) chains (syn-anti)	$P2_1/n$	d
5[c]		0.035	-54.7	chains (anti-anti)	$P2_12_12_1$	e
6[d]		0.050	10.8 -7.2	dimers (syn-syn) dimers (syn-syn)	$P\bar{1}$	f
7		0.05	-48.7	dimers (syn-syn)	*C*2/*c*	h
8		0.04	-29.2	dimers (syn-syn)	$P\bar{1}$	h
9		0.168	-51.3	dimers (syn-syn)	$P2_1/a$	i
10		0.039	-66.2	dimers (syn-syn)	$P2_1/c$	j
11		0.034	82.0	dimers (syn-syn)	$P\bar{1}$	k

[a] The four atoms used to calculate all torsion angles included the carbonyl moiety on the acid group and the ortho carbon atom in the benzene ring which gave an angle of less than 90°. [b] Tetrafluorophthalic acid has two adjacent carboxy groups, and both aggregate patterns are reported. [c] The compound 2,6-dimethoxybenzoic acid is unique in this group of acids because the carboxy group has adopted the antiplanar conformation. [d] This crystal contains two molecules per asymmetric unit. An intramolecular hydrogen bond is formed between the 2-hydroxy groups and the carboxy group in both asymmetric units (O···O = 2.472 and 2.527 Å) which probably forces the carboxy group to remain in the same plane as the benzene ring despite molecular crowding. [e] References: (a) See ref 15b. (b) See ref 15b. (c) Karloak-Wojciechowska, J.; Wiezorek, M. *Pol. J. Chem.* **1980**, *54*, 301–305. (d) See ref 7. (e) See ref 31. (f) Imimura, Y.; Sakurai, T.; Asahi, K.-I.; Takahashi, N. *Acta Crystallogr.* **1984**, *C40*, 2058–2061. (g) Fronczek, F. R.; Merrill, M. L.; Gandour, R. D. *Acta Crystallogr.* **1982**, *B38*, 1337–1339. (h) Benghiat, V.; Leiserowitz, L. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1778–1785. (i) Anca, R.; Martinez-Carrera, S.; Garcia-Blanco, S. *Acta Crystallogr.* **1967**, *23*, 1010–1016. (j) Ammon, H. L.; Prasad, S. M. *Acta Crystallogr.* **1985**, *C41*, 921–924. (k) Smith, G.; O'Reilly, E. J.; Kennard, C. H. L. *Aust. J. Chem.* **1983**, *36*, 2175–2183.

gorodskii has shown that centric molecules always crystallize in centric space groups.[16] This statement is extreme, but we have shown that as a general rule it also applies to centric benzoic acid aggregates.[17]

No such correlation has been demonstrated between acentric molecules and acentric crystals (other than for chiral molecules). In 1981, the crystal structures of 29 059 organic compounds were surveyed,[18] and 71% were found to crystallize in centric space groups, even though most organic molecules typically have low symmetry and are not themselves centric. Thus, many molecules that are acentric pack in centric structures.

We have found that a correlation does exist between the presence of acentric benzoic acid chains and the formation of acentric crystals. Of the 21 crystals that contain chains, 52% crystallize in an acentric space group. Chains do not topologically preclude the formation of centers between them, so what mechanism could account for the relationship between acentric chains and acentric crystals?

Further study of the benzoic acid chains revealed two types of chains, simple and complex. In simple chains, benzoic acids are bonded to only two other benzoic acids. In complex chains, benzoic acids bond to more than two other acids. Complex chains are composed of simple chains cross-linked by hydrogen bonding resulting in a hydrogen-bonded network. Of the 21 benzoic acid chains studied, 12 are simple and 9 are complex.

The simple benzoic acid chains compiled in Table II were found to include five centric and seven acentric crystals. Of the seven acentric crystals, *all but one* crystallize in the polar, chiral space group $P2_12_12_1$. The prevalence of the polar space group $P2_12_12_1$ is in agreement with Gavezzotti's recent packing analysis of molecules containing carbonyls and nitriles which demonstrated that polar molecules are more likely to crystallize in polar space groups than nonpolar molecules.[19]

We would like to propose an additional reason for the prevalence of the $P2_12_12_1$ space group in this data set. Many of these acids have either two ortho groups causing the carboxy group to twist out of the plane of the benzene ring or two rings twisted with respect to one another. Conformational enantiomerism results from these distortions. These acids can form chains about a screw axis containing only one enantiomer or chains with mirror or glide symmetry containing racemic pairs. The enantiomeric chain and the racemic chain are diastereomers and must differ in energy so that the formation of one is favored depending on the energetics involved in the interaction between the hydrogen-bonded acids. The enantiomeric chains could spontaneously resolve, like crystal conglomerates, resulting in chiral and therefore acentric crystals. In this model, it is the aggregate rather than the molecules that induces packing in a chiral space group.

Of the nine complex chains, four were found to crystallize in acentric space groups. With such a small sample, in which each acid has a complex hydrogen-bonding pattern, it is difficult to determine why these acids pack in acentric space groups. However, secondary nitroanilines, which can form complex networks also show a tendency to crystallize in acentric space groups.[4c,e]

It is satisfying to observe that a relationship also exists between chain formation and molecular structure because the hydrogen-bond motif and, to some extent, the crystal inversion symmetry can be predicted based on molecular structure. Most benzoic acids that form chains were found to have at least one ortho substituent. Ortho substituents favor chain formation through the two mechanisms described below.

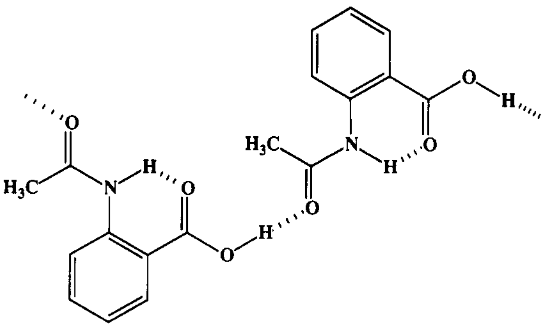


Figure 3. Hydrogen-bonded chains found in the crystal structure of *N*-acetylanthranilic acid.

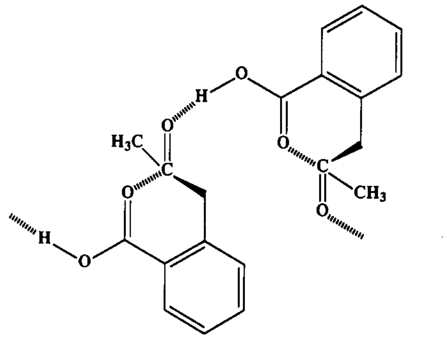


Figure 4. Hydrogen-bonded chains found in the crystal structure of 2-acetonyl-6-methoxybenzoic acid.

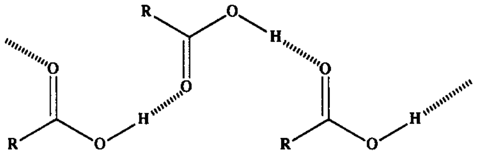


Figure 5. Carboxylic acid with syn–anti stereochemistry about the hydrogen bond.

The formation of an intramolecular interaction between an ortho substituent and the acid group is one mechanism for favoring chain formation. An intramolecular interaction discourages dimer formation by tying up two hydrogen-bonding sites. The remaining free hydrogen-bonding sites are like an extended acid with one carbonyl and one –OH donor, which can form only chains. A good example of such a structure is *N*-acetylanthranilic acid,[20] Figure 3. An intramolecular hydrogen bond forms between the amide hydrogen and the acid carbonyl. The amide carbonyl and the acid hydroxy group form intermolecular hydrogen bonds resulting in chains.

The hydrogen-bond pattern of 2-acetonyl-6-methoxybenzoic acid[21] is analogous to the pattern in *N*-acetylanthranilic acid, Figure 4. In this compound, there is a very short nonbonding contact (C···O = 3.017 Å)[22] between the carbonyl oxygen of the acid and the carbon of the carbonyl group in the acetyl functionality.[23] The re-

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[16] Kitaigorodskii, A. I. *Organic Chemical Crystallography*; Consultants Bureau: New York, 1961; p 102.

[17] Three acids that do not follow this general rule are listed in ref 14.

[18] Mighele, A. D.; Hines, V. L. *Acta Crystallogr.* **1983**, *A39*, 737–740.

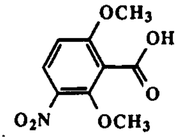
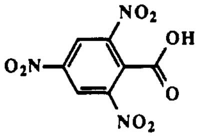
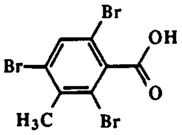
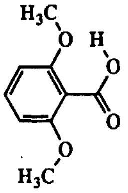
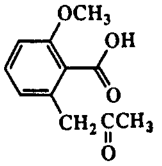
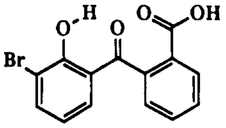
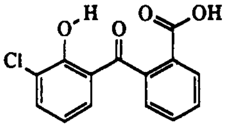
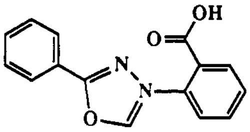
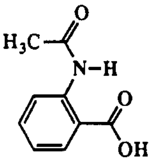
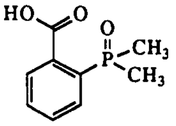
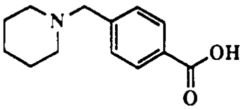
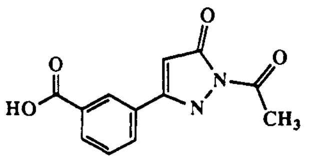
[19] Gavezzotti, A. *J. Phys. Chem.* **1990**, *94*, 4319–4325.

[20] Mascarenhas, Y. P.; de Almeida, V. N.; Lechat, J. R.; Barelli, N. *Acta Crystallogr.* **1980**, *B36*, 502–504.

[21] Kawai, K.-I.; Ito, H.; Nagase, H.; Yamaguchi, R.; Nakajima, S. *Acta Crystallogr.* **1985**, *C41*, 415–417.

[22] The sum of the van der Waals radii for carbon and oxygen is 3.22 Å (Bondi A. *J. Phys. Chem.* **1964**, *68*, 441–451).

Table II. Benzoic Acids That Form Simple Chains and Their Space Groups

no.	compound	sym relationship of hydrogen-bonded neighbors	space group	ref[a]
1		$x, \bar{y} + {}^1/_2, z + {}^1/_2$ glide plane	*Pccn*	a
2		$x + {}^1/_2, \bar{y} + {}^1/_2, \bar{z}$ screw axis	$P2_12_12_1$	b
3		$\bar{x} - {}^1/_2, y - {}^1/_2, z$ glide plane	*Pbca*	c
5		$\bar{x}, y + {}^1/_2, \bar{z} + {}^1/_2$ screw axis	$P2_12_12_1$	d
7		$x + {}^1/_2, \bar{y} + {}^1/_2, \bar{z}$ screw axis	$P2_12_12_1$	e
12		$\bar{x} + {}^1/_2, \bar{y} + 1, z + {}^1/_2$ screw axis	$P2_12_12_1$	f
13		$\bar{x} + {}^1/_2, \bar{y} + 1, z + {}^1/_2$ screw axis	$P2_12_12_1$	g
14		$\bar{x} + {}^1/_2, \bar{y}, z + {}^1/_2$ screw axis	$P2_12_12_1$	h
15		$x - {}^1/_4, \bar{y} + {}^1/_4, z + {}^3/_4$ glide plane	*Fdd*2	i
16		$x, y + 1, z$ translation	$P\bar{1}$	j
17		$x + {}^1/_2, y + {}^1/_2, z$ translation	*C*2/*c*	k
18		$\bar{x}, y + {}^1/_2, \bar{z} + 1$ screw axis	$P2_1/c$	l

[a] (a) See ref 15b. (b) See ref 15b. (c) See ref c from Table I. (d) See ref 31. (e) See ref 21. (f) See ref 15a. (g) See ref 15a. (h) Smith, G.; Kennard, C. H. L.; Katekar, G. F. *Aust. J. Chem.* **1983**, *36*, 2455–2463. (i) See ref 20. (j) Antipin, M. Yu.; Struchkov, Yu. T.; Matrosov, E. I.; Bondarenko, N. A.; Tsvetkov, E. N.; Kabachinik, M. I. *Zh. Struk. Kim.* **1981**, *22*, 100–104. (k) Riddell, F. G.; Murray-Rust, P.; Murray-Rust, J. *Tetrahedron* **1974**, *30*, 1087–1096. (l) Andreetti, G. D.; Bocelli, G.; Cavalca, L.; Sgarbotto, P. *Gazz. Chim. Ital.* **1972**, *102*, 106–116.

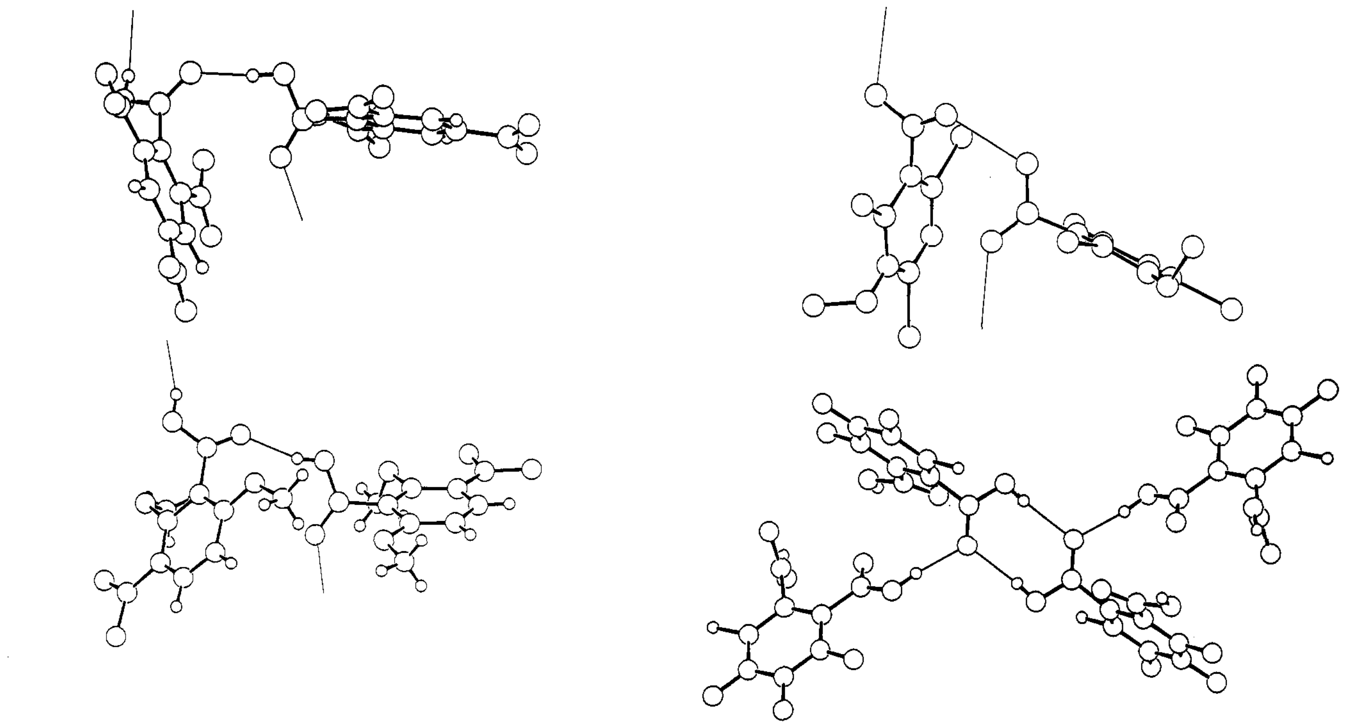


Figure 6. Benzoic acids that crystallize in chains with a syn–anti configuration: (a) 2,4,6-trinitrobenzoic acid (see ref 15b); (b) 2,6-dimethoxy-3-nitrobenzoic acid (see ref 15b); (c) 3-methyl-2,4,6-tribromobenzoic acid (hydrogen positions were not given for this compound: Karloak-Wojciechowska, J.; Wiezorek, M. *Pol. J. Chem.* **1980**, *54*, 301–305); (d) tetrafluorophthalic acid (see ref 7).

maining carbonyl group bonds to an acid hydroxy group on a neighboring molecule, resulting in chain formation. The interaction of the acid carbonyl with the acetyl carbonyl carbon may have weakened the hydrogen-bond-accepting ability of the acid carbonyl, while strengthening the accepting ability of the acetyl carbonyl.[24] The interaction may also simply provide steric hindrance to further association of the oxygen atom.

Chain formation also occurs when two bulky ortho substituents are present. Understanding the relationship between chain formation and the magnitude of the torsion angle of the acid group relates to the stereochemical preferences for an acid hydrogen bond.[25] The stereochemical configuration of the hydrogen bond depends on the conformation of the hydroxyl bond and the orientation of the lone-pair orbital acting as a hydrogen-bond acceptor. The configuration of a hydrogen bond in an acid dimer is syn–syn (see structure I). The first syn refers to the syn-planar conformation of the hydroxyl bond, while the second syn refers to the syn-planar orientation of the lone-pair orbital acting as an acceptor.

Carboxylic acid chains are not constrained to only one hydrogen-bond configuration as are dimers. Leiserowitz showed that carboxylic acids form chains having a syn–anti configuration when the R group is small,[6] Figure 5. Carboxylic acids that aggregate in syn–anti chains include α-oxalic acid (space group = *Pcab*),[26] formic acid (space group = $Pna2_1$),[27] acetic acid (space group = $Pna2_1$),[28] and β-tetrolic acid (space group = $P2_1$).[29] Three of these four acids crystallize with acentric space groups, so the correlation we developed between benzoic acid chains and acentric space groups may apply to other carboxylic acids as well. Force field calculations of carboxylic acid structures show that the syn–anti chains are slightly more stable than the dimers.[30] Both bonding modes incorporate favorable C=O···C=O and OH···OH electrostatic interactions, but in the syn–anti chains there are two such interactions for each acid, as opposed to one in dimers, contributing to the greater stability of the chains.

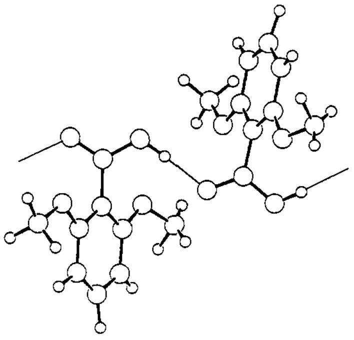


Figure 7. Compound 2,6-dimethoxybenzoic acid (see ref 31), which forms hydroben bonds having the anti–anti configuration.

Rotation of the acid group out of the plane of the benzene ring reduces steric hindrance to syn–anti chain formation. Of the four benzoic acids that crystallize with syn–anti chains (Figure 6), 2,6-dimethoxy-3-nitrobenzoic acid has the smallest torsion angle, −64.6°. Benzoic acids, having smaller torsion angles, except for 2,6-dimethoxybenzoic acid, form dimers.

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(23) The molecule is poised for reaction to the lactol–hydroxy tautomer. (a) Chadwick, D. J.; Dunitz, J. D. *J. Chem. Soc., Perkin Trans. 2* **1979**, 276–284. (b) Burgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153–151 and references therein.

(24) The compound 3-oxo-*cis*-bicyclo[4.4.0]decane-1-carboxylic acid also forms an intramolecular contact between the acid carbonyl and the carbonyl carbon (O···C = 2.912 Å and hydrogen-bonded chains O···O = 2.654 Å (Chadwick, D. J.; Dunitz, J. D. *J. Chem. Soc., Perkin Trans 2* **1979**, 276–284)).

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Chem. Mater. **1992**, *4*, 278–284

Two acids with torsion angles greater than 60°, 2,5-dichloro-6-methoxybenzoic acid (82.0°) and 2,4,6-triamino-3,5-dinitrobenzoic acid (−66.2°), crystallize as dimers rather than chains. In the structure of 2,5-dichloro-6-methoxybenzoic acid, the methoxy group is rotated nearly perpendicular to the plane of the benzene ring and it is on the same side of the benzene ring as the carbonyl group. The methoxy group sterically hinders the anti lone-pair orbital. The reason for dimer formation in 2,4,6-triamino-3,5-dinitrobenzoic acid is not as obvious. The nitro and amino groups, however, form an extensive hydrogen-bond network that may interfere with the formation of benzoic acid chains.

The torsion angle in 2,6-dimethoxybenzoic acid (−54.7°) is smaller than in the four benzoic acids with syn–anti hydrogen bonds. The structure of this acid is unique because it is the only acid in this study with an anti–anti hydrogen-bond configuration, Figure 7.[31] The anti–anti hydrogen-bond configuration in 2,6-dimethoxybenzoic acid is stabilized by an intramolecular hydrogen bond between the –OH group of the acid and the oxygen of the methoxy group ($O\cdots O = 2.853$ Å, $O–H\cdots O = 105.3°$).

Conclusions

A correlation has been established between aggregate inversion symmetry and crystal inversion symmetry, suggesting that hydrogen-bonded aggregates formed in solution direct the crystal growth process. Consequently, acentric aggregate structures promote the formation of acentric crystal structures.

A second correlation has been established between the formation of acentric hydrogen-bonded chains and the presence of ortho substituents on benzoic acids. An ortho substituent that forms intramolecular hydrogen bonds reduces the likelihood of acid dimer formation. Alternatively, two bulky ortho substituents cause the acid group to rotate out of the plane of the benzene ring, so that it is sterically more accessible for chain formation.

These results show that predictions about the symmetry of benzoic acid crystals and the structure of the hydrogen-bonded aggregates can be derived from their molecular structures. It also shows that ortho substitution on a benzoic acid ring can indirectly promote formation of acentric crystals.

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Supplementary Material Available: Test questions and refcodes from the CCDF (3 pages). Ordering information is given on any current masthead page.

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Radiation-Induced Chemistry of Poly(4-[(*tert*-butoxycarbonyl)oxy]styrene-*co*-sulfur dioxide)

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Copolymers of 4-[(*tert*-butoxycarbonyl)oxy]styrene (TBS) and sulfur dioxide (SO_2) have been found to act as sensitive X-ray ($\lambda = 14$ Å) single-component, chemically amplified, aqueous-base-soluble positive-acting resists. The X-ray response of these materials was a function of copolymer composition and independent of molecular weight. It was observed that increasing the SO_2 content enhanced the resist sensitivity. Initial investigation into the radiation-induced reaction mechanism provided evidence that acid formation occurs via polymer main-chain scission. It is proposed that at the scission sites radical species are produced which in turn are responsible for the formation of the acidic moieties. Heat treatment of resist films after exposure converted copolymers to poly(4-hydroxystyrene sulfone) and permitted exposed film areas to be developed in an aqueous base solution. Preliminary lithographic evaluation has resolved 0.5-μm line and space patterns in 0.65-μm-thick 1.75/1 TBS/SO_2 resist films using an X-ray dose of 10 mJ/cm^2. No change in X-ray dose was required to resolve the same width feature in the same resist having a film thickness of 1.0 μm.

Introduction

Resist systems based on chemical amplification have provided materials which exhibit both high sensitivity and resolution when used in conjunction with photon and electron-beam lithography.[1-3] To date, these resist systems are multicomponent materials, and the radiation-induced chemistry is substantially different from that which occurs in standard novolac–diazonaphthoquinone photoresist formulations. Central to each chemically amplified resist formulation is an acid-generating species (AGS) which can be ionic or nonionic in nature and is the component that initially responds to the radiation that is used to expose the resist.[1,4] Additional components act

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