Unexpected Hydrogen Bonding in the Crystal Structure of (4-Chlorophenyl)propiolic Acid. Role of C-H···O Hydrogen Bonds in Determining O-H···O Networks

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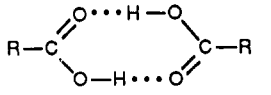
There is a very strong tendency for carboxylic acids to form centrosymmetric, hydrogen-bonded dimers in the solid state, and recent studies have attempted to use this dimeric building block in the crystal engineering of molecular solids. However, hydrogen-bonded molecules of (4-chlorophenyl)propiolic acid, p-$ClC_6H_4C{\equiv}CCO_2H$, do not pack in the crystal according to the predicted dimer motif but, in an unusual manner for this category of molecule, in the catemer arrangement. Crystals of this compound are triclinic, space group $P\bar{1}$, $Z = 2$, $a = 6.120$ (4) Å, $b = 17.323$ (13) Å, $c = 3.944$ (2) Å, $\alpha = 90.47$ (6)°, $\beta = 92.70$ (5)°, $\gamma = 102.26$ (6)°, $R = 0.065$, $R_w = 0.071$, with 831 nonzero reflections. The catemer arrangement observed in this case might have been anticipated for some other carboxylic acids, but it is unexpected here and could arise due to the inability of the molecules to form C-H···O hydrogen bonds. This study shows that weak C-H···O hydrogen bonds need to be considered as important contributors in the formation of hydrogen-bond patterns and that their presence or absence could well determine the manner of networking of stronger O-H···O hydrogen bonds in molecular crystals. Consequently, an ability to predict hydrogen bond patterns could be improved by a better understanding of C-H···O interactions.

Introduction

The supposed predictability of the connectivity of strong hydrogen bonds such as O-H···O and N-H···O has motivated several efforts aimed at rationalizing, predicting, and ultimately designing the crystal structures of hydrogen-bonded organic solids[1-14] such as those that may have useful nonlinear optical properties.[15,16] One of the commonest and most easily predicted of hydrogen-bond networks is the centrosymmetric dimer motif (1) for carboxylic



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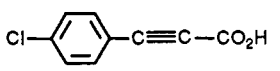

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acids.[9,11,14] In certain acids, the absence of the dimer motif is easily anticipated. It has been pointed out,[9] for example, that a chiral acid cannot form a centrosymmetric dimer; likewise, the formation of a dimer may also be difficult in sterically hindered acids such as 2,6-disubstituted benzoic acids because the mean planes of the aromatic rings and the central hydrogen-bonded ring would be inclined, thus leading to a nonplanar (and consequently less compact) dimer. However, achiral, sterically unhindered carboxylic acids show an overwhelming preference for motif 1 since the considerable stability of the motif is largely unaffected by the nature of the substituent, R. In the crystal, this dimer motif acts as the basic building block, packing according to the directional requirements of the atoms in the R substituent. It is therefore surprising that the crystal structure of (4-chlorophenyl)propiolic acid p-$ClC_6H_4C{\equiv}CCO_2H$, displays a catemer hydrogen-bond pattern, which does not incorporate motif 1. This catemer pattern is

Table I. Summary of the Crystallographic Information for Acid 2

formula	$C_9H_5ClO_2$	γ, deg	102.26 (6)
formula wt	180.5	V, Å^3	408.1
cryst method	ethanol solution	T, °C	25
color	colorless	Z	2
size, mm	0.06 × 0.11 × 0.45	data coll	1192
cryst syst	triclinic	σ cutoff	2
space group	$P\bar{1}$	unique data	831
a, Å	6.120 (4)	2θ range, deg	2-45
b, Å	17.323 (13)	R, R_w	0.065, 0.071
c, Å	3.944 (2)	solved with	SHELS-86[25]
α, deg	90.47 (6)	refined with	SHELX-76[26]
β, deg	92.70 (5)		

Table II. Atomic Fractional Coordinates of Acid 2 (Esd's Given in Parentheses)

atom	x/a	y/b	z/c
C(1)	0.4916 (8)	0.2546 (5)	0.474 (1)
C(2)	0.3918 (9)	0.1757 (5)	0.503 (1)
C(3)	0.4971 (9)	0.1177 (3)	0.389 (1)
C(4)	0.7034 (9)	0.1405 (8)	0.250 (1)
C(5)	0.8064 (9)	0.2192 (8)	0.218 (1)
C(6)	0.6982 (9)	0.2760 (7)	0.330 (1)
C(7)	0.3823 (8)	0.3149 (3)	0.591 (1)
C(8)	0.2995 (9)	0.3678 (3)	0.681 (1)
C(9)	0.2211 (9)	0.4375 (3)	0.768 (1)
O(1)	0.3261 (7)	0.5033 (2)	0.670 (1)
O(2)	0.0477 (7)	0.4299 (2)	0.939 (1)
Cl(1)	0.8398 (3)	0.0682 (1)	0.1090 (4)
H(2)	0.256 (8)	0.156 (3)	0.589 (6)
H(3)	0.435 (11)	0.071 (4)	0.400 (5)
H(5)	0.941 (8)	0.240 (3)	0.121 (6)
H(6)	0.752 (9)	0.323 (3)	0.295 (6)

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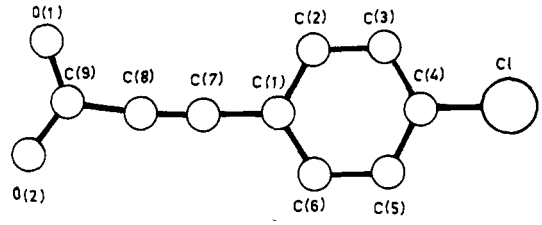


Figure 1. Atom-numbering scheme for acid **2**.

Table III. Bond Lengths and Angles for Acid 2 (Esd's Given in Parentheses)

C(1)–C(2)	1.38 (1)	C(8)–C(9)	1.44 (1)
C(2)–C(3)	1.39 (1)	C(9)–O(1)	1.26 (1)
C(3)–C(4)	1.38 (1)	C(9)–O(2)	1.27 (1)
C(4)–C(5)	1.39 (1)	C(4)–Cl(1)	1.75 (1)
C(5)–C(6)	1.38 (1)	C(2)–H(2)	0.91 (5)
C(6)–C(1)	1.39 (1)	C(3)–H(3)	0.83 (6)
C(1)–C(7)	1.44 (1)	C(5)–H(5)	0.93 (5)
C(7)–C(8)	1.20 (1)	C(6)–H(6)	0.83 (5)
C(2)–C(1)–C(6)	120.0 (5)	C(5)–C(6)–C(1)	120.8 (6)
C(2)–C(1)–C(7)	120.3 (5)	C(1)–C(7)–C(8)	176.7 (5)
C(6)–C(1)–C(7)	119.8 (5)	C(7)–C(8)–C(9)	173.0 (6)
C(1)–C(2)–C(3)	120.2 (6)	C(8)–C(9)–O(1)	118.8 (5)
C(2)–C(3)–C(4)	118.6 (6)	C(8)–C(9)–O(2)	118.4 (6)
C(3)–C(4)–C(5)	122.3 (5)	O(1)–C(9)–O(2)	122.8 (5)
C(3)–C(4)–Cl(1)	119.3 (4)		
C(5)–C(4)–Cl(1)	118.5 (4)		
C(4)–C(5)–C(6)	118.1 (6)		

unusual for this category of compound and exhibits certain features that are hitherto unreported.

Experimental Section

Acid **2** was prepared from 4-chlorobenzaldehyde by methods described elsewhere.[17] Fine needle-shaped crystals suitable for X-ray work were obtained by slow cooling from EtOH. Data were collected on a Syntex P1 diffractometer at the Department of Chemistry, Ben Gurion University. Details of the crystal structure determination are given in Table I and Figure 1. Carbon and oxygen atoms were refined anisotropically and hydrogens isotropically, but the acid hydrogen atom could not be located.

Results and Discussion

The crystal structure of acid **2** was investigated in connection with its solid-state thermal reactivity to form self-Diels–Alder adducts.[17] The crystal structure was solved and refined routinely (see Table I). Table II gives the positional parameters of the atoms (with esd's), and Table III gives the intramolecular bond lengths and angles (with esd's). Figure 1 shows the atom-numbering scheme. A view of the crystal structure of acid **2** looking down the short axis is shown in Figure 2. The carboxyl group is completely disordered (C–O distances 1.26 (1), 1.27 (1) Å), and yet the environments around the two oxygen atoms are quite distinct.[18] The hydrogen-bond network is of the catemer type, the two O···O distances being 2.59 (1) and 2.66 (1) Å. In this unexpected arrangement, one of the O=C–O–H conformations is syn-planar while the other is anti-planar. The syn-planar arrangement is by far the commoner,[9] but the novel feature of this structure is that *both* conformations coexist in the crystal even though the carboxyl group is disordered. The hydrogen-bonded catemers are further linked with short Cl···Cl contacts of 3.50 (1) Å to form molecular sheets. The tertiary or complete

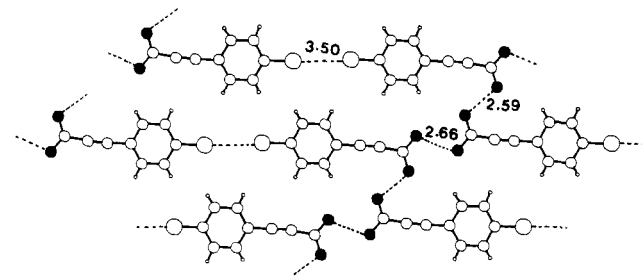
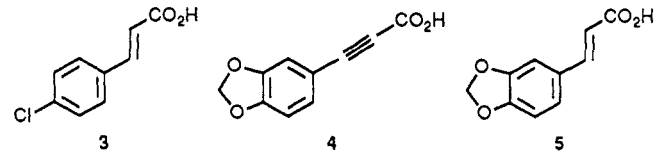


Figure 2. Crystal structure of (4-chlorophenyl)propiolic acid (**2**) down the short axis [001] to show O–H···O hydrogen bonding and Cl···Cl interactions. Oxygen atoms are shaded. Molecular layers such as shown here are stacked along [001] to generate the complete structure.

structure is obtained by a van der Waals stacking of these sheets in the short-axis direction. Such a stacking arrangement permits the thermal Diels–Alder reaction in crystalline **2** referred to above.[17]

Clearly, there would be no steric constraint if acid **2** were to adopt the dimer motif **1**, which is observed not only in the corresponding cinnamic acid **3**[19] but also in the pair of isomorphous methylenedioxy acids **4**[20] and **5**.[17,21] Other



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derivatives such as (4-methoxy-, (3,4-dimethoxy-, and (3,4,5-trimethoxyphenyl)propiolic acids all exhibit motif **1**.[17] In crystal engineering it is perhaps useful to inquire why a particular compound does *not* adopt a particular structure. Accordingly, in the present context, one might ask why molecules of acid **2** do not pack employing the almost exclusively observed motif **1**.

It may be noted that the crystal structures of oxygenated aromatic compounds are stabilized by a large number of weak, yet directional, C–H···O bonds that are seemingly possible within the framework of the supposedly more dominant O–H···O and N–H···O bonds.[3,9,22] In the crystal structures of a number of substituted benzoic and cinnamic acids, for instance, centrosymmetric dimers **1** are further linked through these C–H···O bonds involving carboxyl and other oxygen atoms. In several cases, the alkene–carboxyl conformation is decided by the C–H···O bond arrangement. Acids **4** and **5** are efficiently C–H···O bonded through the heterocyclic groups, while acids **3** and **5** form C–H···O bonds that involve olefinic hydrogen atoms. Although it is not yet possible to precisely quantify these weak interactions, their strength and frequency of occurrence seem to depend on the number and donor–acceptor abilities of the hydrogen and oxygen atoms in the molecular structure.[22,23] By this token, acid **2** is a poor candidate for C–H···O bonding. There are no oxygen atoms other than those in the carboxyl group, and furthermore olefinic hydrogens (in contrast to acids **3** and **5**) are absent. The observed crystal structure in fact does not exhibit any pronounced C–H···O bonding. It is suggested accordingly

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that C–H···O bonds, far from being passive bystanders, may actually discriminate between alternative O–H···O networks which, though geometrically reasonable, are structurally quite distinct. In the present context, it could be possible that the manifestation of C–H···O bonds would lead to the dimer motif and their absence to the catemer. Such a conclusion is in agreement with calculations that show that the isolated catemer is slightly more stable than the dimer.[9,11]

In spite of its greater stability, the catemer is far more sensitive than the dimer to steric factors. Therefore, a possible auxiliary reason for the adoption of the catemer by the title compound could be the lack of substituents adjacent to the carbonyl group or even an interaction of the acidic proton with the alkyne bond. However, the five other phenylpropiolic acids with known crystal structures[17] adopt the dimer motif, and the lack of more detailed structural information on this family of compounds makes further discussion speculative.

As in several other planar chloroaromatic compounds, the crystal structure of acid **2** is characterized by short Cl···Cl contacts (which lead incidentally to the adoption of a 4-Å short axis[22]), and a pertinent question is whether the catemer motif is forced on the structure because of the optimization of these Cl···Cl interactions. However, these short contacts are also found in 4-chlorobenzoic acid (3.44 Å)[14] and 4-chlorocinnamic acid (3.79 Å),[19] and yet both of these acids display the centrosymmetric dimer motif with the dimer units being linked by C–H···O bonds. It would appear then that Cl···Cl interactions are not incompatible with the dimer motif.

It could also be argued that the absence of significant C–H···O bonding ability in acid **2** is correlated with an awkward molecular shape; inspection of Figure 2 shows that there is a close packing of carboxylic and alkynic residues in neighboring molecules that seems to decide the hydrogen bond geometry. However, these are post facto rationalizations, and the manifestation of crystal structures such as those of compound **2** shows that the prediction of hydrogen-bonded structures is still a complex and tricky issue.[1,24]

In spite of these difficulties, it is suggested that materials chemists will find it worthwhile to consider *all* interactions, strong and weak, while attempting to understand novel and unexpected hydrogen-bond arrangements. Only through such understanding would it be possible to advance confidently to the next step of structure prediction and design.

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Registry No. **2**, 3240-10-6.

Supplementary Material Available: Table of thermal parameters (1 page); listing of F_o/F_c values for acid **2** (4 pages). Ordering information is given on any current masthead page.

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Adsorption of Nitric Oxide, Nitrous Oxide, and Oxygen on Ion-Bombarded Gallium Arsenide(100)

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Chemically cleaned (1:1 HCl(conc)/H_2O) GaAs(100) was ion bombarded with 3-keV Ne^+ and Xe^+ at 10^{17} ions/cm^2 and subsequently exposed to NO in the range 10^6–10^8 langmuirs and N_2O in the range 10^7–10^{11} langmuirs. Ion-bombarded GaAs exposed to N_2O yields only Ga_2O_3. However, when ion-bombarded GaAs is exposed to NO, both gallium and arsenic oxides are formed, with Ga_2O_3 being the major component. The extent of oxidation for ion-bombarded GaAs exposed to a series of gases is NO > O_2 > N_2O. The ion-bombarded surface is composed of defects consisting of singly occupied Ga bonds, Ga–Ga bonds, and As vacancies. The limited reaction of N_2O and the greater reactivities of O_2 and NO with ion-bombarded GaAs are due to the interaction of each of these molecules with the defects on the ion-bombarded GaAs surface.

Introduction

The experiments of Bertness et al.[1] for N_2O and O_2 adsorption and Bermudez et al.[2] for NO and O_2 adsorption on GaAs(110) suggest that dissociative adsorption is dependent upon the bond energies of the molecules. Nitrous oxide, with the weakest (N–O) bond energy, shows the greatest reactivity with GaAs(110).[1] Bermudez et al.[2] also observed that NO reacts more slowly than O_2 with GaAs in the exposure range 10^4–10^7 langmuir (1 langmuir = 1.33 × 10^{-4} Pa·s). Defects are thought to play an important role in the dissociation process on cleaved or annealed material.

Ion-bombarded GaAs(100) exhibits increased reactivity compared to chemically cleaned GaAs(100) upon exposure to O_2 or H_2O at 10^7–10^{13} langmuirs. The quantity of gallium and arsenic oxides increased with increasing en-

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