Hydrogen bonding of keto-carboxylic acids in the catemer and dimer motifs

Markos M. Papadakis[*,1] and Roger A. Lalancette[1]
[1]Department of Chemistry,
Rutgers University, Newark New Jersey 07102

[*]Rutgers Undergraduate Research Fellow

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Abstract

We have examined the x-ray structures of more than 60 organic keto-carboxylic acids in our laboratory to determine the nature of the hydrogen bonding between the molecules in the solid state. *Keto-carboxylic acids*, besides having a ketone function as part of the acid group, contain a second ketone elsewhere in the molecule. As these organic acids contain only one donor (the acidic H atom) and two possible acceptors (the carboxyl ketone, and the second functionality, another ketone), there are five different possibilities for hydrogen bonding: acid-to-acid dimer formation, acid-to-ketone catemer formation, intramolecular H bonding, acid-to-acid catemer formation and acid-to-ketone dimer formation. There is no way of predicting *a priori* which of these possible hydrogen bonding schemes a previously unstudied keto-carboxylic acid molecule will adopt. We have used single crystal x-ray structure analysis to find out which hydrogen bonding mode prevails in each molecule. Secondly, we also have used the CSD (Cambridge Structural Database) to analyze and compare all the other known *keto-carboxylic acid* structures in the literature.

Introduction

Keto-carboxylic acids provide a useful model system to study simple hydrogen bonding. As each of these molecules contains one donor (the H atom) and two possible acceptors (the carboxyl C=O of the acid and the carbonyl C=O of the ketone), there are five different possible H-bonding motifs. Examples of these motifs are shown in Figures 1-5. Types 1 and 2 are the most common: 71 dimers (type-1) and 30 catemers (type-2) can be found in the literature. Types 3-5 are relatively rare. The structure of 1'-acetylferrocene-1-carboxylic acid, an example of the fifth type of H-bonding (acid-to-ketone dimer), has been completed in our laboratory recently[7]. We present correlation data showing the differences between the two most common types of H-bonding through a comparison of the 71 dimers with the 30 catemers (from the Cambridge Structural Database)[1].

Figure 1. A representation of type 1 (acid-to-acid) hydrogen bonding in the (±)-3-oxocyclohexaneacetic acid[2] dimer. Hydrogen bonds are indicated by dotted lines. The "R" notation in this figure and the corresponding notations in later figures refer to graph-set analysis of the H-bonding patterns in organic crystals[3,4].

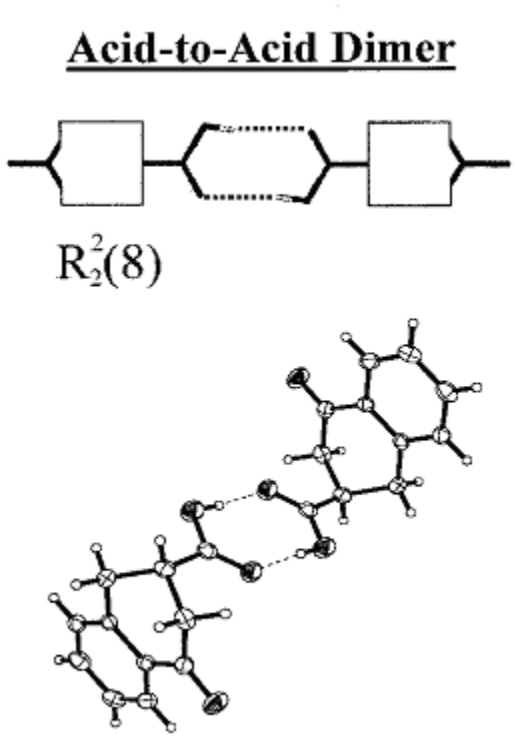


Figure 2. A representation of type 2 (acid-to-ketone) H bonding in the (±)-3-oxocyclohexanecarboxylic acid catemer[2]

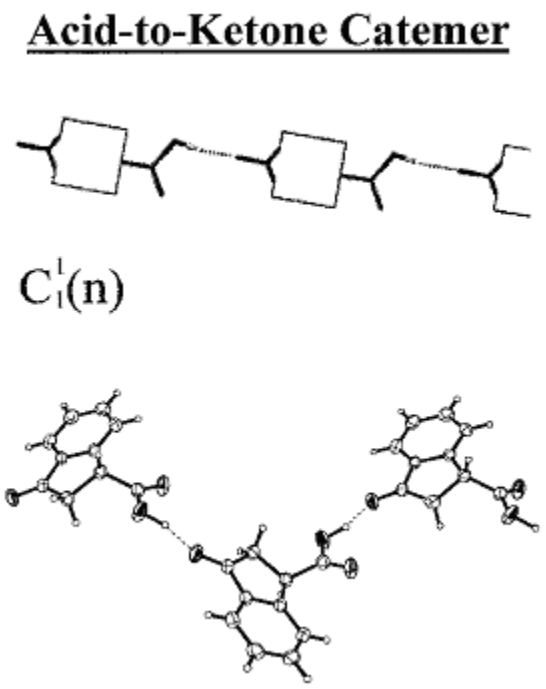


Figure 3. A representation of intramolecular H bonding in1-carboxyfluorenone[5]

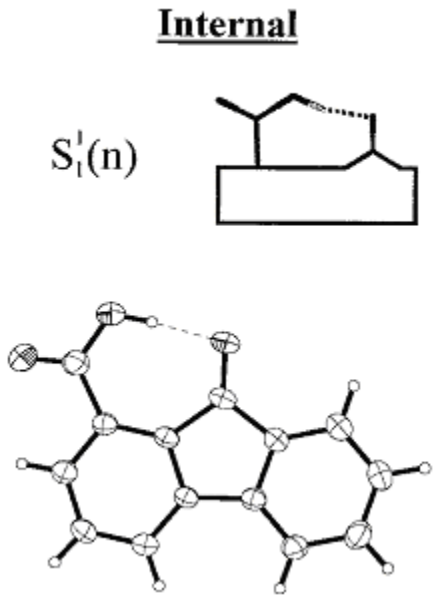


Figure 4. A representation of the H bonding in the acid-to-acid catemer (+)-3-oxo-23,24-dinor-5-cholan-22-oic acid[6]

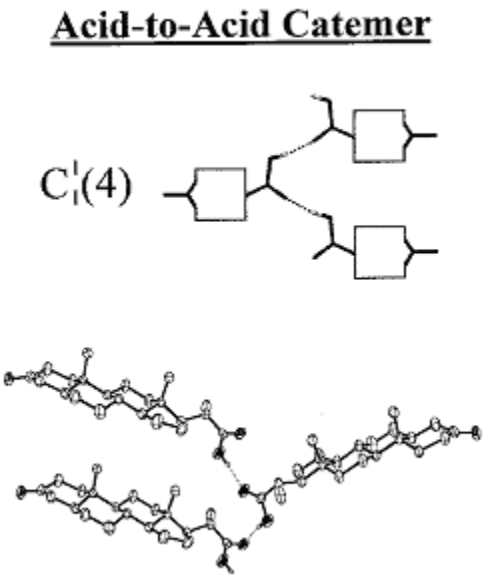
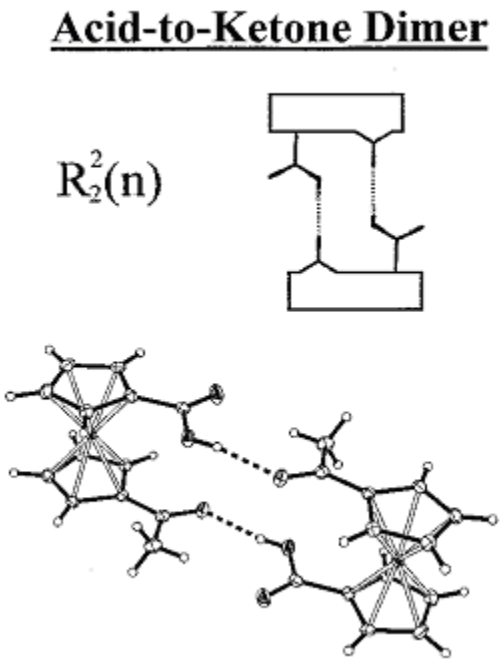


Figure 5. A representation of the H bonding in the acid-to-ketone dimer system 1'-acetylferrocene-1-carboxylic acid[7]



Parameters:

The following parameters relevant to hydrogen bonding in keto-carboxylic acids were extracted using ConQuest, a standard software package in the Cambridge Structural Database (CSD)[1].

Bond angles: The bond angles theta and phi are defined as follows (Figure 6):

> theta is the angle between the H-bond acceptor carbonyl and the hydrogen to which it is bonded. phi is the angle between the average plane of the H-bond accepting carbonyl and the hydrogen to which it is bonded.

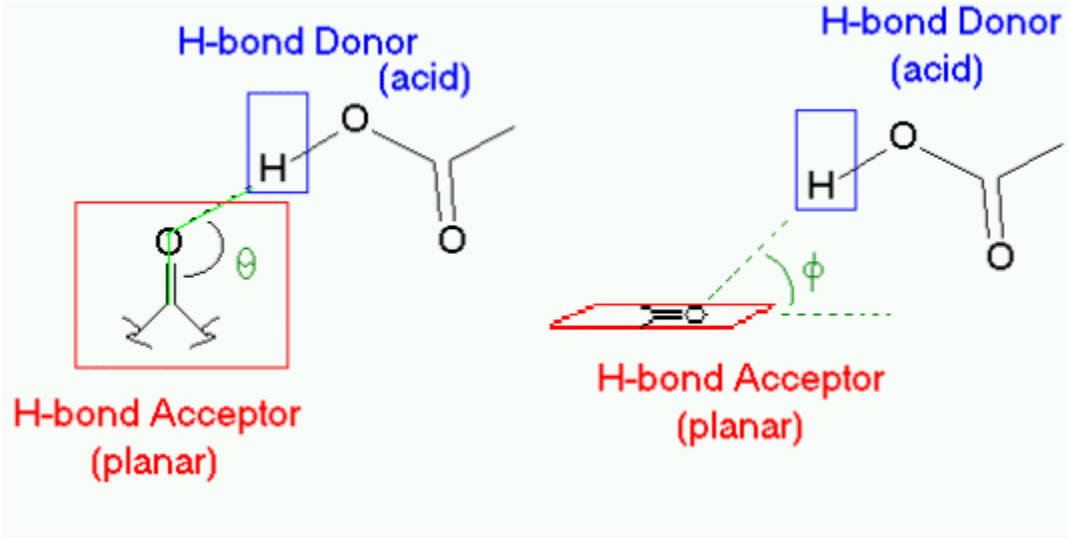
These angles together specify the location of the hydrogen in relation to the oxygen to which it is bound.

Bond distances: The following bond distances were obtained in Angstroms:

> Donor-hydrogen to oxygen-acceptor distance.
> Oxygen-to-oxygen distance (which is the H-bond).

Distance along the normal of hydrogen from the average plane of the carbonyl acceptor.

Figure 6. Hydrogen bonds are defined with respect to two angles: theta, which is the C=O···H or H-bond planar acceptor angle (in the plane); and phi, which is the O-H···O or H-bond acceptor angle (out-of-plane).



The results of the CSD1 search are summarized here and tabulated below (Table 1).

A scatter plot (Figure 7) of angles theta vs. phi for all 71 dimers and 30 catemers shows that the values for dimers are clustered around means of theta = 113(7)° and phi = 5(5)°; for the catemers, the means are theta = 132(12)° and phi of 8(8)°, respectively. Some statistics for the data set are shown in Table 1. These results indicate that the hydrogen bonding in the dimers is more closely aligned to the ideal values of theta = 120° and phi = 0° than are those of the catemers.

Figure 7. Hydrogen bond angles theta and phi for the 71 dimers and 30 catemers compiled.

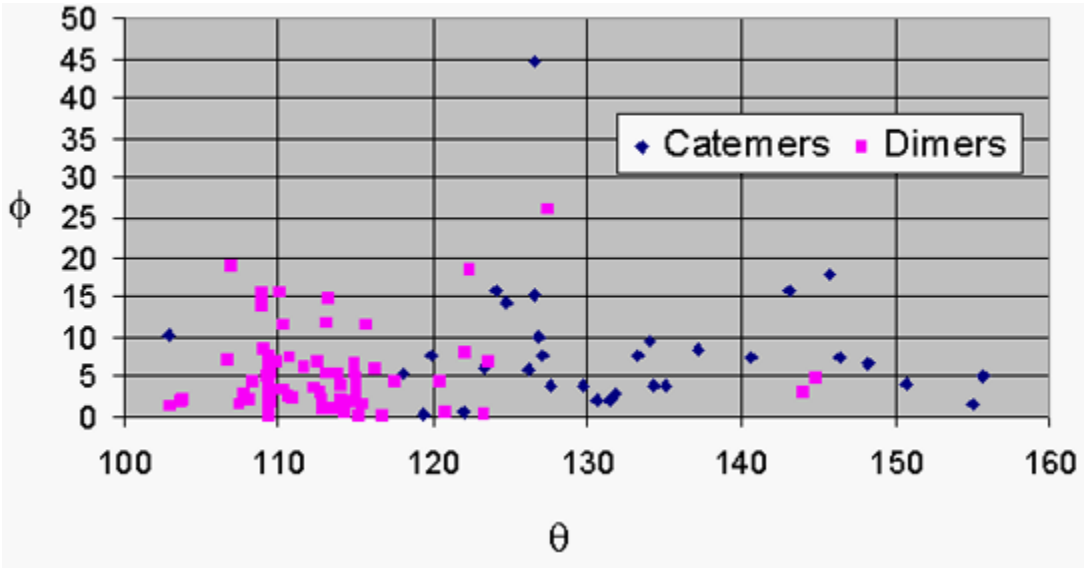


Table 1. Statistical properties of hydrogen bond angle data for the 71 dimers and the 30 catemers compiled.

	Catemers		**Dimers**	
	theta	phi	theta	phi
Mean	132	8	113	5
Max	156	45	145	26
Min	103	0	103	0
SD	12	8	7	5
N	30	30	71	71

The donor-hydrogen to oxygen-acceptor distances for the dimers and the catemers are shown in Figures 8 and 9, respectively. The mean value for the dimers is 1.73(15)Å and that for the catemers is 1.85(12)Å.

Figure 8. Donor-H to O-acceptor distance in acid-to-acid dimer motif. Each of the 71 dimers is represented by a bar, and its H···O distance is given on the y-axis

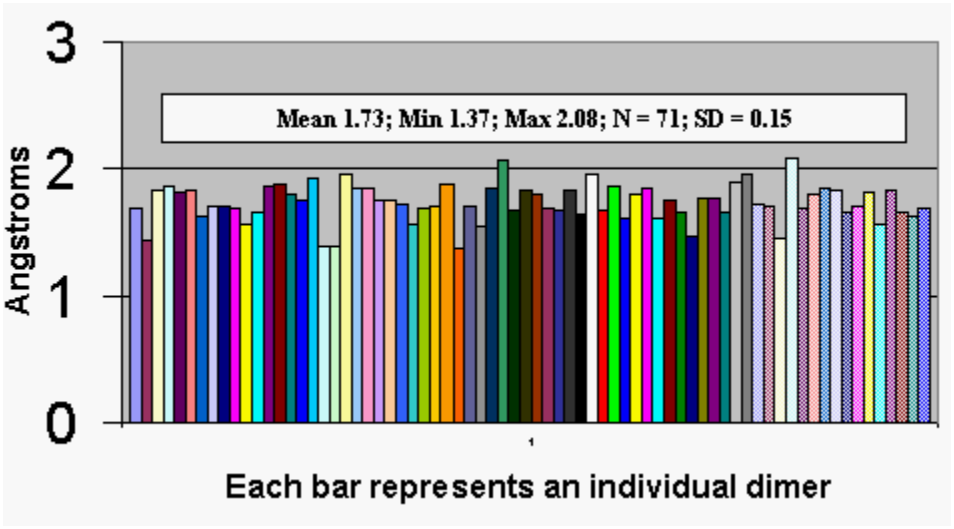
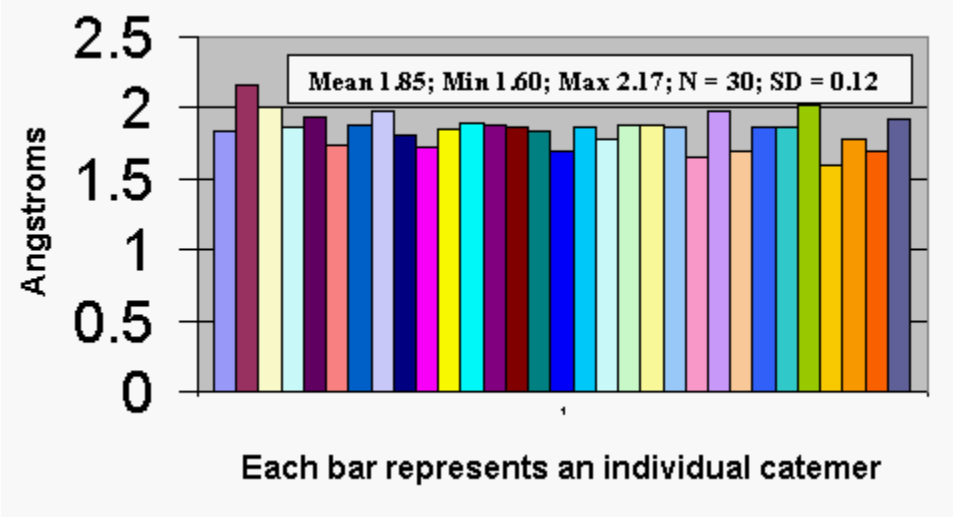


Figure 9. Donor-H to O-acceptor distance in acid-to-ketone catemer motif. Each of the 30 catemers is represented by a bar, and its H···O distance is given on the y-axis



The H-bond distances (from oxygen-to-oxygen) are shown in Figures 10 and 11: the mean value for the dimers is 2.65(2)Å and that for the catemers is 2.71(6)Å.

Figure 10. H-Bond (oxygen-to-oxygen) distance in the 71 dimers.

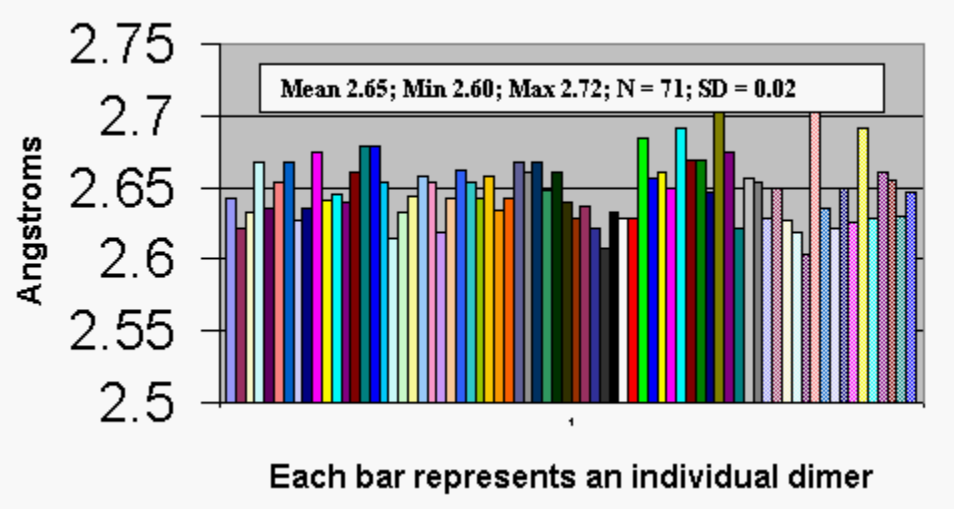
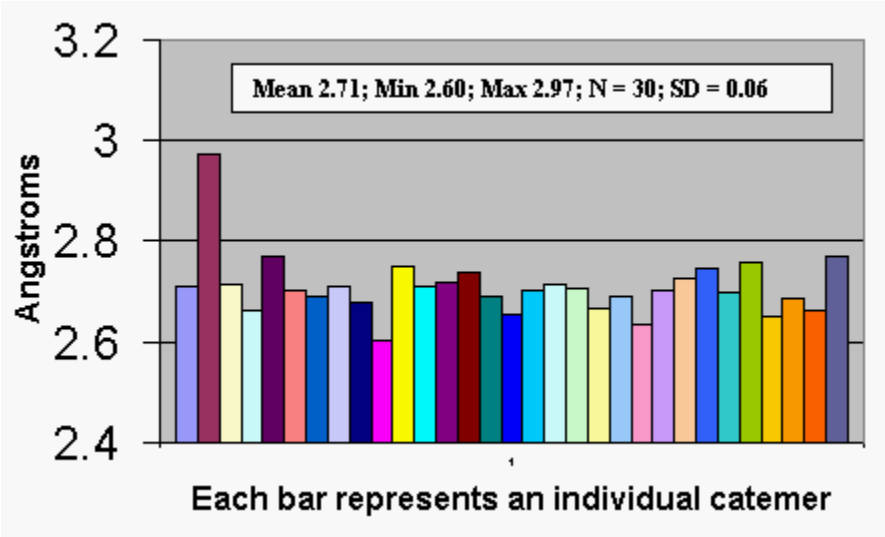


Figure 11. H-Bond (oxygen-to-oxygen) distance in the 30 catemers.



Conclusion

The H-bond differs between the dimers and the catemers. For the 71 dimers, the nominal H-bond distance is 2.65(2) Å and the angles theta and phi are 113(7)° and 5(5)°, respectively; for the 30 catemers, the nominal H-bond distance is 2.71(6) Å and the angles theta and phi are 132(12)° and 8(8)°, respectively.

1. The data show that the H bond is shorter in the dimers than it is in the catemers and suggest that the H bond is stronger and better aligned in the

dimers. It is then no wonder that the dimers make up the majority of all the keto-carboxylic acids whose structures are known.

2. By studying the simple model system of keto-carboxylic acids, we have come to the point where we can predict the mode of H-bonding by choosing molecules that will *not* be able to form the most common type of hydrogen bonding (i.e., the acid-to-acid dimer, Figure 1); we accomplish this by choosing "handed" molecules, which normally crystallize in the acid-to-ketone catemer form, Figure 2.
3. This tendency to engage in one or another type of hydrogen bonding should hold in related systems with other, similar functionalities and so may be useful as a tool for crystal engineering.

References

1. Allen F. H. & Kennard O. (1993). Chemical Design Automation News 8, 1 & 31-37.
2. Barcon, A., Brunskill, A. P. J., Lalancette, R. A. & Thompson, H. W. "(±)-3-Oxocyclohexanecarboxylic and -Acetic Acids: Contrasting Hydrogen-Bonding Patterns in Two Homologous Keto Acids." (2002). Acta Cryst. C58, 154-156.
3. Etter, M. C., MacDonald, J. C. & Bernstein, J. "Graph-Set Analysis of Hydrogen-Bond Patterns in Organic Crystals." (1990). Acta Cryst. B46, 256-262.
4. Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. "Patterns in Hydrogen Bonding: Functionality and Graph Set Analysis in Crystals." (1995). Angew. Chem. Int. Ed. Engl. 34, 1555-1573.
5. Coté, M. L., Lalancette, R. A. & Thompson, H. W. "1-Carboxyfluorenone: an Intramolecularly Hydrogen-Bonded Keto Acid." (1996). Acta Cryst. C52, 1535-1537.
6. Lalancette, R. A., Thompson, H. W. & Brunskill, A. P. J. "(+)-3-Oxo-23,24-Dinor-5 -Cholan-22-oic Acid: Hydrogen-Bonding Patterns in a Steroidal Keto Acid and its Monohydrate." (1998). Acta Cryst. C54, 421-424.
7. Newman, J. M., Papadakis, M. M., Thompson, H. W. & Lalancette, R. A. "1'-Acetylferrocene-1-Carboxylic acid: an Instance of Hydrogen Bonding in the Rare Dimeric Acid-to-Ketone Mode." (2002). Acta Cryst. C58, 89-91.