

RESEARCH ARTICLE

X-ray crystal structure analysis of 4,7-dioxononanoic acid

A.M. Abeysekera*, C. Padumadasa and S.M.V.D. Mala

Department of Chemistry, Faculty of Applied Sciences, University of Sri Jayewardenepura, Gangodawila, Nugegoda.

Revised: 21 May 2013; Accepted: 19 July 2013

Abstract : The structure of 4,7- dioxononanoic acid previously assigned on the basis of its NMR spectra, was confirmed by X-ray crystallography. The compound exhibits only one sharp peak in its solid state IR spectrum at 1685 cm^{-1} for its three carbonyl groups. A plausible explanation for this anomaly is provided by X-ray crystallography on the basis of crystal packing and dipole-dipole interactions in aligned arrays of carbonyl groups. This alignment is found in the carboxylic acid group as well, so that the hydrogen bonded interactions of the two carboxylic acid groups found normally in the "dimeric" structures of carboxylic acids in the solid state are not present in the title compound.

Keywords: Crystal packing, dioxocarboxylic acids, dipole-dipole interactions, hydrogen bonding, IR spectroscopy, X-ray crystallography.

INTRODUCTION

4,7-Dioxocarboxylic acids are useful intermediates in the synthesis of γ -lactones. For instance, they can be reduced by zinc amalgam and concentrated hydrochloric acid to give 4-alkyl- γ -lactones, some of which are important as fragrance and flavour compounds (Terai & Tanaka, 1956). They can also be reduced to 7-hydroxy- γ -lactones with sodium borohydride, where the 7-hydroxy group provides a convenient handle for the modification of the side chain (Abeysekera *et al.*, 2008). Due to the presence of two keto carbonyl groups in a 1,4-relationship as well as a carboxyl carbonyl group and keto carbonyl group in a 1,4-relationship, the 4,7-dioxocarboxylic acids are potentially good precursors for the synthesis of 5- and 6-membered heterocyclic and fused heterocyclic compounds (Katritzky & Rees, 1984).

While the synthesis of 4,7-dioxo acids have been known for over a hundred years, our group recently

reported for the first time their ^1H and ^{13}C NMR spectroscopic data including that of 4,7-dioxononanoic acid (4) (Abeysekera *et al.*, 1991, 2008). The solid state IR spectra of 4,7-dioxocarboxylic acids are anomalous in that only a single sharp absorption band for carbonyl stretching is observed at 1685 cm^{-1} . In order to confirm that the synthesized compound identified as 4,7-dioxononanoic acid had the structure (4), a single crystal X-ray structure analysis was carried out. The results presented here, not only confirmed the structure, but also provided a plausible explanation for its anomalous IR spectrum.

METHODS AND MATERIALS

Instrumentation

X-ray crystallography was carried out using a Rigaku R-AXIS RAPID diffractometer. IR spectra were recorded on a Thermo Nicolet iS10 mid IR FT-IR spectrometer.

Synthesis of 4,7-dioxononanoic acid (4)

4,7-Dioxononanoic acid (4) was synthesized according to the procedures reported previously (Midorikawa, 1953; Abeysekera *et al.*, 1991, 2008). The pure product (4) was obtained as white triangular plates in 10.3 % yield.

X-ray crystallography

The slow evaporation of a hexane and ethyl acetate solution of compound (4) yielded crystals suitable for single crystal X-ray structure determination. A colourless block crystal having approximate dimensions of $0.40 \times 0.30 \times 0.10\text{ mm}^3$ was mounted on a glass fiber.

* Corresponding author (ajitabey@gmail.com)

Diffraction measurements were made on a Rigaku R-AXIS RAPID imaging plate area detector with graphite monochromated Mo-K α radiation at a temperature of -50 ± 1 °C to a maximum 2θ value of 54.9° . Intensity data were corrected for Lorentz and polarization effects. The structure was solved using the direct methods programme SIR92 and expanded using Fourier techniques (Altomare *et al.*, 1994; Beurskens *et al.*, 1999). The non-hydrogen atoms were refined anisotropically and the hydrogen atoms using the riding model. Subsequent full-matrix least squares refinement was carried out using the Crystal Structure Crystallographic software package (Carruthers *et al.*, 1999; Rigaku & Rigaku, 2000 - 2007).

RESULTS AND DISCUSSION

Synthesis

Furfural (1) was condensed with methyl ethyl ketone (2) in alkaline medium to yield furfurylidene ketone (3), which was then subjected to acid catalysed hydrolytic ring cleavage to produce 4,7-dioxononanoic acid (4) as reported previously (Figure I) (Midorikawa, 1953; Abeysekera *et al.*, 1991, 2008).

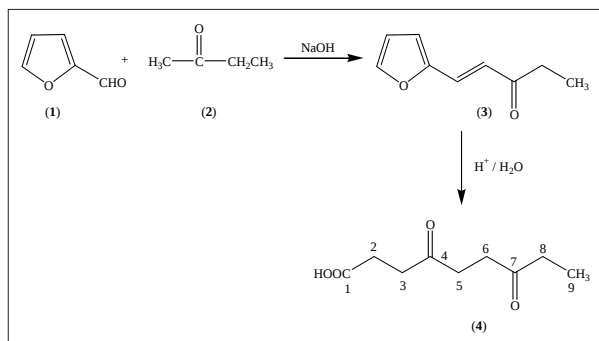


Figure 1: Synthesis of 4,7-dioxononanoic acid (4)

X-ray crystallography

The solid-state molecular structure of compound (4) is shown in Figure 2. X-ray crystallography, which is the most accurate and direct method available for molecular structure determination confirms the structure that was previously proposed for 4,7-dioxononanoic acid (4) using NMR spectral data (Abeysekera *et al.*, 2008).

Compound (4) has crystallized in the monoclinic space group $P2_1/c$ with a two-fold crystallographic axis. Crystal data, details concerning data collection and structure refinement are given in Table 1. In the solid-state, the

molecule adopts a planar, extended conformation. This is likely to be the most stable conformation of the molecule with a staggered anti-conformation for each dimethylene group, and an anti-periplanar arrangement of the 1,4 and 4,7 dicarbonyl groups. Bond lengths and bond angles involving carbon and oxygen are presented in Tables 2 and 3, respectively. Bond lengths for Csp^3-Csp^3 bonds fall within the range of 1.519 - 1.523 Å, while that for

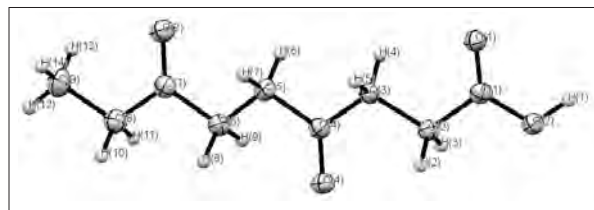


Figure 2: ORTEP view of the molecular structure of 4,7-dioxononanoic acid (4) with atom numbering scheme. Thermal ellipsoids are drawn at the 50 % probability level.

Table 1: Crystal data and details concerning data collection and structure refinement for compound (4)

Empirical formula	$C_9H_{14}O_4$
Formula weight	186.21
Temperature (°C)	- 50
Wavelength (Å)	0.71075
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell parameters	
a (Å)	26.9700 (17)
b (Å)	6.5884 (4)
c (Å)	5.1836 (4)
β (°)	100.3607 (18)
V (Å ³)	906.05 (10)
Z	4
Density (calculated) (g cm ⁻³)	1.365
F_{000}	400.00
Absorption coefficient (cm ⁻¹)	1.067
Crystal size (mm ³)	0.40 x 0.30 x 0.10
$2\theta_{max}$ (°)	54.9
Reflections measured	8592
Unique reflections	2072 ($R_{int} = 0.045$)
Absorption correction	Lorentz-polarization
Structure solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F^2
Residuals : R1 ($I > 2.00 > \sigma(I)$)	0.0482
Residuals : R ($I > 1.00 > \sigma(I)$)	0.0539
Residuals : wR2 ($I > 1.00 > \sigma(I)$)	0.1185
Goodness of fit indicator	1.014
Largest diff. peak and hole (e ⁻ / Å ³)	0.24 and - 0.33

Table 2: Bond lengths involving carbon and oxygen

Bond	Bond distance (Å)
C(2) – C(3)	1.519 (2)
C(5) – C(6)	1.523 (2)
C(8) – C(9)	1.523 (2)
C(1) – C(2)	1.505 (2)
C(3) – C(4)	1.511 (2)
C(4) – C(5)	1.508 (2)
C(6) – C(7)	1.507 (2)
C(7) – C(8)	1.512 (2)
O(1) – C(1)	1.220 (2)
O(4) – C(4)	1.221 (2)
O(3) – C(7)	1.216 (2)
O(2) – C(1)	1.315 (2)

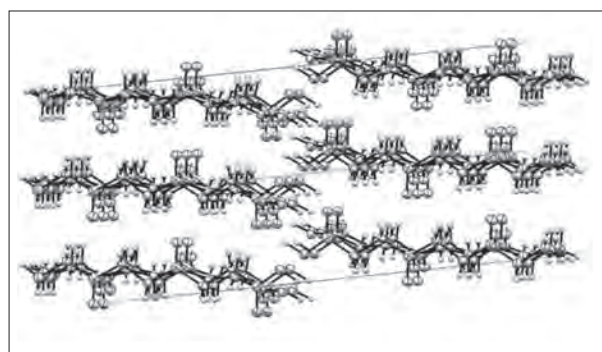
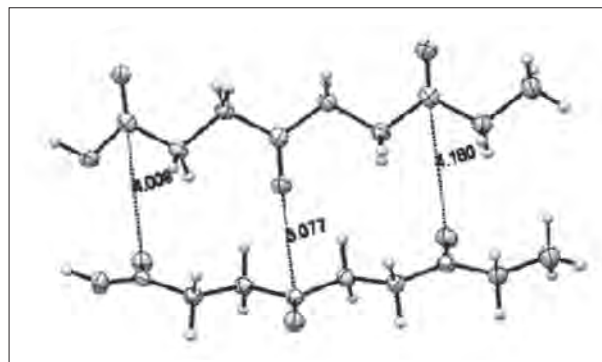
Table 3: Bond angles involving carbon and oxygen

Bond	Bond angle (°)
O(1) – C(1) – O(2)	124.34 (14)
O(2) – C(1) – C(2)	111.86 (15)
O(1) – C(1) – C(2)	123.80 (15)
C(1) – C(2) – C(3)	113.26 (14)
C(2) – C(3) – C(4)	113.43 (14)
O(4) – C(4) – C(3)	121.90 (15)
O(4) – C(4) – C(5)	122.50 (13)
C(3) – C(4) – C(5)	115.58 (15)
C(4) – C(5) – C(6)	113.87 (15)
C(5) – C(6) – C(7)	113.78 (15)
O(3) – C(7) – C(6)	122.57 (15)
O(3) – C(7) – C(8)	122.19 (17)
C(6) – C(7) – C(8)	115.21 (15)
C(7) – C(8) – C(9)	114.46 (16)

$Csp^3 - Csp^2$ bonds are slightly lower and fall within the range of 1.505 - 1.512 Å. The lowest range for bond lengths is observed for $Csp^2 - O$ bonds of keto and carboxyl carbonyl groups and they are within the range of 1.216 - 1.221 Å. The bond length for $Csp^2 - O$ bond between carbonyl carbon and hydroxyl oxygen of the carboxylic acid group is 1.315 Å. All these values are in agreement with the published data for other organic compounds determined by X-ray crystallography (Allen *et al.*, 2006). In addition, bond angles show no significant differences with the published data.

Crystal packing of compound (4) is given in Figure 3. The adjacent molecules are linked through electrostatic interactions formed between hydroxyl groups of carboxylic acid groups at one end and van der Waals interactions between alkyl substituents at the other end to form infinite chains along the bc crystallographic plane. These chains in turn stack one below the other infinitely along the ab crystallographic plane and are held together by dipole-dipole interactions between aligned keto and carboxyl carbonyl groups. The solid state intermolecular non-covalent carbonyl distances for compound (4) are given in Figure 4. It seems that dipole-dipole interactions between aligned carbonyl groups of keto and carboxyl carbonyl groups are the primary stabilizing force for the crystal packing of compound (4) in its solid-state. The distances in Figure 4 are of the same magnitude as those reported for the non-covalent attractive interactions between the dipoles of two carbonyls in stabilizing protein conformations as reported in literature (Deane *et al.*, 1999; Improta *et al.*, 2008).

Pure carboxylic acids in the liquid or solid-state exist as dimers held together by hydrogen bonding formed between carbonyl oxygen and hydroxyl hydrogen of the carboxylic acid groups with a linear arrangement of the atoms involved (carbonyl oxygen and hydroxyl hydrogen and oxygen) (Silverstein *et al.*, 1991). However, compound (4) does not exhibit this normal hydrogen bonding interactions between carboxylic acid groups of adjacent molecules, which rather interact by electrostatic interactions between adjacent carboxylic acid hydroxyl groups. It seems that dipole-dipole interactions between aligned carbonyl groups of keto and carboxyl groups of compound (4) in its solid-state is making the carbonyl oxygen of the carboxyl group unavailable for hydrogen bonding.

**Figure 3:** Crystal packing of 4,7-dioxononanoic acid (4)**Figure 4:** Solid-state intermolecular non-covalent carbonyl distances (Å) for 4,7-dioxononanoic acid (4)

IR spectroscopy

Solid-state IR spectrum of compound (4) showed a single sharp carbonyl (C=O) stretching absorption frequency at 1685 cm^{-1} for the keto carbonyl groups and for the carboxyl carbonyl group (Figure 5). The typical keto carbonyl stretching absorption frequency is observed at 1715 cm^{-1} (Silverstein *et al.*, 1991). In this case, however,

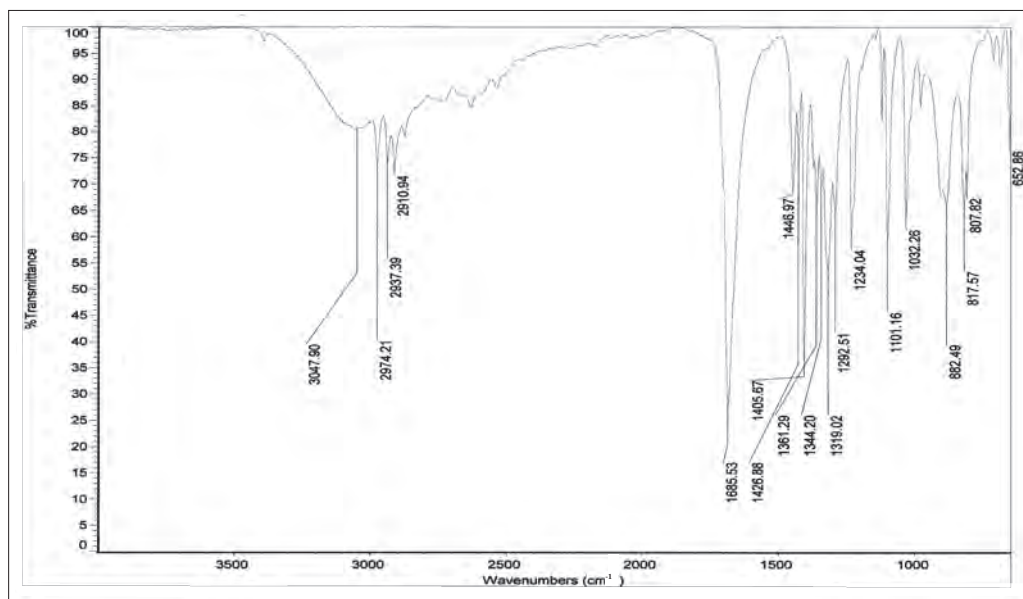


Figure 5: Solid-state IR spectrum of 4,7-dioxononanoic acid (4)

it has been lowered by 30 cm^{-1} , which may be due to dipole-dipole interactions between aligned keto carbonyl groups. Usually, hydrogen bonding reduces carboxylic acid carbonyl stretching absorption frequency from 1760 cm^{-1} to $1720 - 1706\text{ cm}^{-1}$ (Silverstein *et al.*, 1991). The observed reduction up to 1685 cm^{-1} in this case is primarily due to dipole-dipole interactions between aligned carboxyl carbonyl groups.

Lowering of IR carbonyl stretching absorption frequencies in the solid-state due to strengthened electrostatic interactions as a consequence of crystal packing has been documented (Etter, 1976; Painter *et al.*, 2000). Although keto carbonyl groups and the carboxyl carbonyl groups interact independently of each other and should give two distinct stretching absorption frequencies in the IR spectrum, there appears to be a fortuitous overlap of the two stretching absorption frequencies. This interpretation of the solid-state IR spectrum of compound (4) is further supported by the observation of two stretching absorption frequencies, one at 1715 cm^{-1} for the keto carbonyl group and one at 1705 cm^{-1} for the carboxyl carbonyl group arising from the hydrogen bonded dimer in a 0.02 M solution of this compound in CCl_4 .

CONCLUSION

The molecular structure of 4,7-dioxononanoic acid (4), which was previously supported by NMR spectroscopic data has been confirmed by single crystal X-ray structure analysis. The solid-state crystal packing of this

compound, which indicates intermolecular dipole-dipole interactions, also provides a plausible explanation for its anomalous IR spectrum.

Acknowledgement

We thank the University of Sri Jayewardenepura for the Research Grant 2010/16 and Dr. S.D. Atula Sandanayaka of the Advanced Institute of Science and Technology, Ishikawa, Japan for X-ray crystallographic services.

REFERENCES

1. Abeysekera A.M., Amaratunge S., Grimshaw J., Jayaweera N. & Senanayake G. (1991). 4,7-Dioxooctonoic acid from the acid catalyzed reaction of (E)-4-(2-furyl)but-3-enone. Electrochemical hydrogenation of some furan derivatives. *Journal of the Chemical Society Perkin Transactions I*: 2021 – 2025.
DOI: <http://dx.doi.org/10.1039/p19910002021>
2. Abeysekera A.M., Mahatantila C. & Sajeevani J.R.D.M. (2008). Synthesis of 7-functionalized γ -lactones from furfural. *Journal of the National Science Foundation of Sri Lanka* **36**(3): 185 – 190.
DOI: <http://dx.doi.org/10.4038/jnsfsv36i3.153>
3. Allen F.H., Watson D.G., Brammer L., Orpen A.G. & Taylor R. (2006). Typical interatomic distances: organic compounds. *International Tables for Crystallography*, volume C, chapter 9.5, pp. 790 – 811. John Wiley & Sons, New York, USA.
DOI: <http://dx.doi.org/10.1107/978095536020600000621>
4. Altomare A., Cascarano G., Giacovazzo C., Guagliardi A., Burla M., Polidori G. & Camalli M. (1994).

- SIR92-a program for automatic solution of crystal structures by direct methods. *Journal of Applied Crystallography* **27**: 435.
5. Beurskens T.P., Admiraal G., Beurskens G., Bosman W.P., de Gelder R., Israel R. & Smits J.M.M. (1999). The DIRDIF-99 program system. *Technical Report of the Crystallography Laboratory*. University of Nijmegen, The Netherlands.
 6. Carruthers J.R., Rollett J.S., Betteridge P.W., Kinna D., Pearce L., Larsen A. & Gabe E. (1999). *Crystals*: crystallographic software package. Chemical Crystallography Laboratory, Oxford, UK.
 7. Deane C.M., Allen F.H., Taylor R. & Blundell T. (1999). Carbonyl–carbonyl interactions stabilize the partially allowed Ramachandran conformations of asparagine and aspartic acid. *Protein Engineering* **12**(12): 1025 – 1028. DOI: <http://dx.doi.org/10.1093/protein/12.12.1025>
 8. Etter M.C. (1976). Solid-state chemistry of organic polyvalent iodine compounds. VII. The relationship between crystal packing modes, solid-state intermolecular interactions, and infrared spectra of benzoxiodole compounds. *Journal of Solid State Chemistry* **16**: 399 – 411.
 9. Improta R., Berisio R. & Vitagliano L. (2008). Contribution of dipole–dipole interactions to the stability of the collagen triple helix. *Protein Science* **17**(15): 955 – 961. DOI: <http://dx.doi.org/10.1110/ps.073301908>
 10. Katritzky A.R. & Rees C.W. (eds). (1984). The structure, reactions, synthesis of heterocyclic compounds. *Comprehensive Heterocyclic Chemistry*, volume 3, pp. 40 – 197. Pergamon Press, Oxford, UK.
 11. Midorikawa H. (1953). On the ring-opening reactions of the furan compounds. III. on the condensation of furfural with methyl ethyl ketone by alkali. *Bulletin of the Chemical Society of Japan* **26**(8): 460 – 463. DOI: <http://dx.doi.org/10.1246/bcsj.26.460>
 12. Painter P., Cleveland C. & Coleman M. (2000). An infrared spectroscopic study of *p*-n-alkoxybenzoic acids. *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals* **348**(1): 269 – 293. DOI: <http://dx.doi.org/10.1080/10587250008024811>
 13. Rigaku & Rigaku A. (2000-2007). *Crystal Structure 3.8*: crystal structure analysis package. Woodlands, USA.
 14. Silverstein R.M., Bassler G.C. & Morrill T.C. (1991). *Spectrometric Identification of Organic Compounds*, 5th edition, pp. 113 – 118. John Wiley & Sons, New York, USA.
 15. Terai Y. & Tanaka T. (1956). A synthesis of γ -alkylbutyrolactones from furfural and a lower group of methyl ketones. *Bulletin of the Chemical Society of Japan* **29**(7): 822 – 824. DOI: <http://dx.doi.org/10.1246/bcsj.29.822>

