

Structure and NMR Spectra of Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic Acid and its Anhydride

R. Alan Aitken,* Fiona M. Fotherby and Alexandra M. Z. Slawin

EaStCHEM School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, United Kingdom

* raa@st-and.ac.uk

Abstract

Two of the three published sets of ^1H and ^{13}C NMR data for bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride have been found to actually be those of the corresponding diacid. The NMR spectroscopic distinction between these two compounds is clarified and $^1J_{\text{C-H}}$ values are reported for the anhydride, the diacid and a related diester. The X-ray structure of the diacid has been determined and features chains of molecules involving both intra- and inter-molecular hydrogen bonding.

Keywords: ^1H NMR; ^{13}C NMR; one-bond spin-spin coupling constant; X-ray structure; hydrogen bonding

Introduction

In the course of recent work we required the strained tricyclic anhydride of norbornadiene-2,3-dicarboxylic acid **1**. Although the diacid **2** was reported as early as 1931 in the classic work of Diels and Alder [1], it was not until 1968 that its dehydration using the unusual dehydrating agent ethoxyacetylene to give the anhydride **1** was described by a group at du Pont [2]. Although that first report did show a (correct) ^1H NMR spectrum at 60 MHz, subsequent papers give contradictory and erroneous data for both

^1H and ^{13}C NMR spectra of anhydride **1** which in most cases actually relate to the diacid **2**. We have now reinvestigated this problem and present authentic NMR spectra for both **1** and **2**. We also present $^1J_{\text{C-H}}$ data for **1**, **2** and the diethyl ester **4** as well as the X-ray structure for the diacid **2**.

Experimental

Melting points were determined using a Reichert hot-stage microscope and are uncorrected. NMR spectra were recorded using a Bruker AV instrument at 300 MHz (^1H) and 75.458 MHz (^{13}C) or a Bruker AVIII instrument at 125 MHz (^{13}C) in CDCl_3 with chemical shifts given with respect to Me_4Si and coupling constants in Hz. HRMS measurements were made using a Thermo Exactive Orbitrap instrument using electrospray ionisation.

Preparation of dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate 3

Freshly cracked cyclopenta-1,3-diene (8.5 g, 0.13 mol) was stirred at 0 °C while dimethyl acetylenedicarboxylate (14.2 g, 12.3 cm³, 0.10 mol) was added dropwise over a period of 0.5 h. After the addition the mixture was maintained at 0 °C for a further 1.5 h and then warmed to RT and submitted to Kugelrohr distillation under reduced pressure. The first fraction (4.51 g), bp 115 °C at 20 Torr, consisted of dicyclopentadiene and unreacted DMAD. The second fraction proved to be the title product **3** (13.28 g, 64 %) as a colourless liquid, bp 160 °C at 20 Torr (lit. [1] 134–135 °C at 10–11 Torr). ^1H NMR: δ_{H} 6.92 (2H, m, H-5,6), 3.94 (2H, m, H-1,4), 3.78 (6H, s, 2 x OMe), 2.28 and 2.10 (2H, AB pattern of t, J 7, 2, H-7) [good agreement with lit. [3]].

Preparation of bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid 2 from 3

A solution of dimethyl ester **3** (2.08 g, 10 mmol) and lithium hydroxide (0.60 g, 25 mmol) in 50 % aqueous THF (20 cm³) was stirred at 50 °C for 5 h. The water layer was then separated and acidified to pH 1 using 1 M HCl and extracted with EtOAc (3 x 25 cm³). The combined organic extracts were dried over MgSO_4 , and solvent removed *in vacuo* to give the title product

2 (1.04 g, 57 %) as a colourless solid, mp 165–170 °C (lit. [4] mp 160–161 °C). For spectroscopic data see below.

Direct preparation of bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid 2

Freshly cracked 1,3-cyclopenta-1,3-diene (1.20 g, 1.5 cm³, 18.15 mmol) was added dropwise to a solution of acetylenedicarboxylic acid (1.0 g, 8.77 mmol) in THF (20 cm³) and the mixture was stirred at RT for 20 h. The solvent was removed *in vacuo* to give the title product **2** (1.55 g, 98 %) as a colourless solid, mp 169–170 °C (lit. [1] 170 °C). ¹H NMR: δ_H 6.94 (2H, m, H-5,6), 4.22 (2H, m, H-1,4) and 2.29 and 2.18 (2H, AB pattern of t, *J* 7, 1.5, H-7); ¹³C NMR: 167.1 (CO), 157.9 (2,3-C), 142.2 (5,6-CH), 73.1 (7-CH₂) and 54.2 (1,4-CH); HRMS (ESI): Calcd for C₉H₇O₄ (M⁺-H) 179.0344. Found 179.0347.

A portion was recrystallised from water to give crystals suitable for X-ray diffraction and the structure was determined on a Rigaku XtalLAB P200 diffractometer using graphite monochromated Mo Kα radiation λ = 0.71075 Å.

Crystal data for C₉H₈O₄, *M* = 180.16 g mol⁻¹, colourless platelet, crystal dimensions 0.10 × 0.10 × 0.02 mm, orthorhombic, space group Pna2₁ (No. 33), *a* = 16.453(5), *b* = 7.731(2), *c* = 6.2767(17) Å, α = β = γ = 90.00°, *V* = 798.4(4) Å³, *Z* = 4, *D*_{calc} = 1.499 g cm⁻³, *T* = 93 K, *R*₁ = 0.0440, *R*_w2 = 0.1212 for 1189 reflections with *I* > 2σ(*I*), and 126 variables, *R*_{int} 0.0522, Goodness of fit on *F*² 1.104. Data have been deposited at the Cambridge Crystallographic Data Centre as CCDC 2073912. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/getstructures>. The structure was solved by direct methods and refined by full-matrix least-squares against *F*² (SHELXL Version 2018/3 [5]).

Preparation of bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride 1 using ethoxy acetylene

A suspension of diacid **2** (1.0 g, 5.55 mmol) in CH₂Cl₂ (25 cm³) was stirred at 30–35 °C while ethoxyacetylene (60 % in hexane, 1 cm³, 6.26 mmol) was added and the resulting mixture was stirred at 30–35 °C under nitrogen for 18 h. The solution was then reduced to half volume in a

nitrogen stream and filtered to remove a dark oily solid. The filtrate was treated with charcoal, filtered and evaporated *in vacuo* to give the title anhydride **1** (0.51 g, 56 %) as a pale brown solid, mp 70–75 °C, (lit. [2] mp 80–83 °C). ¹H NMR: δ_H 6.99 (2H, m, H-5,6), 4.01 (2H, m, H-1,4) and 2.72 (2H, t, *J* 1.5, H-7); ¹³C NMR: 170.8 (CO), 159.5 (2,3-C), 142.8 (5,6-CH), 78.2 (7-CH₂) and 47.9 (1,4-CH); HRMS (ESI): Calcd for C₉H₇O₃ (M⁺+H) 163.0395. Found 163.0391.

Preparation of bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride 1 using acetic anhydride

The diacid **2** (1.46 g, 8.1 mmol) was stirred in acetic anhydride (50 cm³) at rt for 4 h. The volatile material was removed *in vacuo*, and residue was placed under vacuum in a desiccator containing KOH pellets for 18h, to give a brown liquid and a colourless solid (0.85g, 65 %) which were separated. The latter was shown by NMR to contain mainly anhydride **1** (data as above) but accompanied by traces of residual acetic acid and acetic anhydride which could not be removed.

Preparation of bicyclo [2.2.1] hepta-2,5-diene-2,3-dicarboxylic anhydride 1 using trifluoroacetic anhydride

A solution of diacid **2** (0.31 g, 1.72 mmol) in trifluoroacetic anhydride (4.53 g, 3 cm³, 22.6 mmol) was stirred for 16 h at RT before being evaporated *in vacuo* to yield a white solid. This was placed under vacuum in a desiccator containing KOH pellets for 18h, to give a colourless solid (0.28 g, ca. 100 %) shown by NMR to contain mainly anhydride **1** (data as above). NMR analysis of the same material after 3 days under ambient conditions showed that it had largely hydrolysed back to diacid **2**.

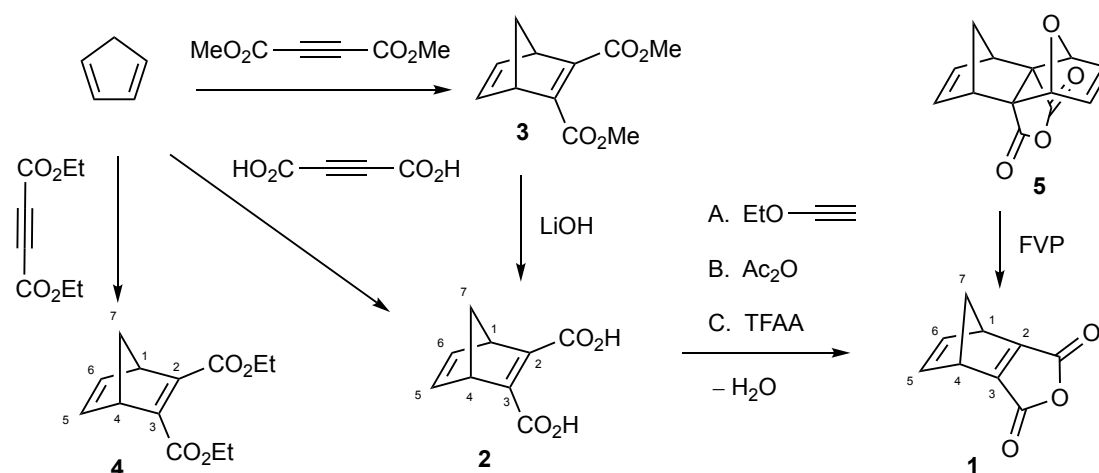
Preparation of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate 4

Freshly cracked cyclopenta-1,3-diene (8.5 g, 0.13 mol) was stirred at 0 °C while diethyl acetylenedicarboxylate (17.0 g, 16.0 cm³, 0.10 mol) was added dropwise over a period of 0.5 h. After the addition the mixture was maintained at 0 °C for a further 1.5 h and then warmed to RT and submitted to Kugelrohr distillation under reduced pressure. The first fraction consisted of unreacted DEAD. The second fraction was the title product **4** (9.44 g, 40 %) as a colourless

liquid, bp 180 °C at 20 Torr (lit. [6] 97–103 °C at 0.3 Torr). $^1\text{H NMR}$: δ_{H} 6.92 (2H, m, H-5,6), 4.24 (4H, q, J 7.2, 2 x CH_2Me), 3.93 (2H, m, H-1,4), 2.28 and 2.09 (2H, AB pattern of t, J 7, 1.5, H-7) and 1.30 (6H, t, J 7.2, 2 x CH_2CH_3) [good agreement with lit. [3]].

Results

Various literature routes to the anhydride have been described and these are summarised in Scheme 1. As already mentioned, the first preparation involved ethoxyacetylene-mediated dehydration [2] of diacid **2** obtained either by direct cycloaddition of cyclopentadiene and acetylenedicarboxylic acid or cycloaddition of cyclopentadiene with dimethyl acetylenedicarboxylate to give diester **3** followed by hydrolysis [1]. A later publication describes hydrolysis of **3** using lithium hydroxide followed by dehydration of **2** using acetic anhydride [7], and this reagent is also used in the most recent report [8] to dehydrate the acid **2** formed by direct cycloaddition. Finally, a quite different approach was used by Warrenner and coworkers [9], who obtained **1** by retro Diels Alder extrusion of furan from compound **5** under flash vacuum pyrolysis conditions.



Scheme 1. Synthetic pathways to anhydride **1**

With the exception of the last method, we have repeated all these procedures and can confirm that the anhydride **1** may be obtained from all of them but it is quite susceptible to hydrolysis thus accounting for some of the erroneous spectroscopic data published. In our hands the direct preparation of **2** was best, proceeding in almost quantitative yield, whereas formation of **3** and its hydrolysis using LiOH gave an overall yield of around 40%. Dehydration of **2** to give **1** was best achieved using ethoxyacetylene as originally reported [2], since this method generates only the volatile and easily removed ethyl acetate as byproduct. In contrast we found the use of acetic anhydride to be problematic since it was not possible to completely remove residual traces of acetic acid and acetic anhydride even by prolonged exposure to high vacuum. Not surprisingly, washing a solution of the product with water as described [8] resulted in complete hydrolysis to give only **2**. Given the high cost of ethoxyacetylene, we sought a more satisfactory dehydrating agent and found that trifluoroacetic anhydride gave a high yield in conversion of **2** into **1** and the more volatile byproducts were readily removed under vacuum. Having obtained authentic samples of both **1** and **2**, the NMR spectra were run (see Supporting Material) and our data are compared with all the literature reports presented in chronological order in Table 1.

It is clear that the data for the diacid **2** show a high degree of consistency between the current work and the four previous reports. In contrast, for the anhydride **1**, the current work gives values for the proton spectrum in good agreement with the original preparation [2] and for both proton and carbon spectra in agreement with the data of Warrenner and coworkers for the product made from **5** [9]. However both sets of data for the product made using acetic anhydride are actually those for the diacid **2** [7,8]. The key differences are that the ^1H NMR signals for the alkene protons $\text{H}_{5,6}$ come at δ 6.99–7.14 for the anhydride but at δ 6.90–6.95 for the diacid and, more obviously,

that the CH₂ protons are magnetically equivalent in the anhydride giving rise to a single peak around δ 2.7–2.8 while in the diacid they form an AB pattern with signals centred on δ 2.2 and δ 2.3. These differences are clearly evident in our ¹H NMR spectrum of **1** which contains a small proportion of **2** (see Supporting Material) thus emphasising the differences. In the ¹³C NMR spectra, the most obvious differences are for the bridgehead carbons C_{1,4} which come at δ 47.5–48 for the anhydride but δ 54–55 for the diacid, the CO which has a value of δ 170.5–171 for the anhydride but δ 167–167.5 for the diacid and finally the bridging CH₂ which comes at δ 78.0–78.2 for the anhydride (above CDCl₃) but at δ 73.0–73.3 for the diacid. It should also be mentioned that for the data of entry 5 [8], the authors were unable to locate a signal for C_{2,3} and so assumed it coincided with that for C_{5,6}, and that the text of the paper gives a value of δ 77.99 for C₇ but, on the actual spectrum provided in the supplementary information, the signal is clearly 2-3 ppm below CDCl₃ at 77.0. What is unclear in the two cases where the spectra of the supposed anhydride are actually those of the diacid [7,8], is whether the unwanted hydrolysis has occurred during the synthesis or only on preparation of the samples for NMR. In any case, it is clear that this anhydride is significantly moisture sensitive and quite readily hydrolyses back to the diacid from which it was formed.

Table 1. NMR data for **1** and **2**

Entry	δ_{H}			δ_{C}					solvent	Ref.
	H _{1,4}	H _{5,6}	H ₇	C _{1,4}	C _{2,3}	CO	C _{5,6}	C ₇		
<u>anhydride 1</u>										
1	4.01	6.99	2.72	47.9	159.5	170.8	142.8	78.2	CDCl ₃	(this work)
2	4.08	7.14	2.77	—	—	—	—	—	CDCl ₃	[2]
3	4.01	6.92	2.33/2.15	53.9	153.6	159.8	142.1	73.0	CDCl ₃	[7]
4	4.08	7.14	2.77	47.7	159.3	170.6	142.6	78.0	CDCl ₃	[9]
5	4.04	6.95	2.35/2.19	56.51	142.31	168.74	142.31	74–75	CDCl ₃	[8]
<u>diacid 2</u>										
6	4.22	6.94	2.29/2.18	54.2	157.9	167.1	142.2	73.1	CDCl ₃	(this work)
7	4.05-4.20	6.90	2.0-2.4	55.0	157.6	166.5	143.1	73.3	CD ₃ COCD ₃	[10]
8	4.20	6.93	2.28/2.17	54.3	157.9	167.0	142.2	73.1	CDCl ₃	[7]
9	4.19	6.92	2.28/2.16	54.37	157.84	166.84	142.32	73.17	CDCl ₃	[11]
10	4.20	6.93	2.29/2.17	54.3	158.1	167.4	142.3	73.2	CDCl ₃	[4]

Although the ^1H and ^{13}C NMR shifts for both **1** and **2** are well documented (with the foregoing clarification), and the pattern of H–H coupling for the diacid **2** has been analysed in detail [12], there have apparently been no reports on the C–H coupling in such systems. In particular it is known that the magnitude of the one-bond spin-spin coupling $^1J_{\text{C-H}}$ gives a good measure of the hybridisation and strain situation at a given carbon [13] and this parameter has been reported for similar bicyclic systems including norbornadiene [14]. Since the measurement is easily made simply by recording the ^{13}C NMR spectrum without ^1H decoupling, we have recorded this data for compounds **1**, **2**, and **4** and this is compared with that for norbornadiene in Table 2. In addition, the signal for C-1/4 took the form of a doublet of quartets allowing assignment of $^2J_{\text{C1-H6/7}} = ^2J_{\text{C4-H5/7}} = 8$ Hz in all three compounds. The marginal increase in all three 1J values on going from **2** and **4** to **1** is consistent with the greater degree of strain in the latter [13].

Table 2. Values of $^1J_{\text{C-H}}$ for norbornadiene-2,3-dicarboxylic acid derivatives (Hz)

Compound	1,4-CH	5,6-CH	7-CH ₂	Ref.
1	157	184	139	this work
2	155	178	137	this work
4	153	178	137	this work
norbornadiene	150	174	134	[14]

Finally in this study, while the structure of anhydride **1** has been determined by X-ray diffraction [15], that of the diacid **2** has not [16] and we report this here. Suitable crystals were obtained by recrystallisation from water and the resulting molecular structure is shown in Figure 1.

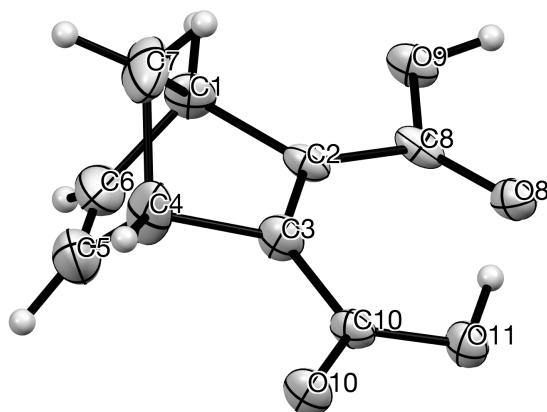


Figure 1. Molecular structure of **2** showing numbering system used with selected bond lengths: C(1)–C(2) 1.540(4), C(2)–C(3) 1.356(4), C(3)–C(4) 1.541(5), C(4)–C(5) 1.449(8), C(5)–C(6) 1.264(7), C(6)–C(1) 1.496(7), C(1)–C(7) 1.590(6), C(4)–C(7) 1.625(5), C(2)–C(8) 1.473(4), C(8)–O(8) 1.230(4), C(8)–O(9) 1.328(3), C(3)–C(10) 1.483(4), C(10)–O(10) 1.233(3), C(10)–O(11) 1.318(3) Å

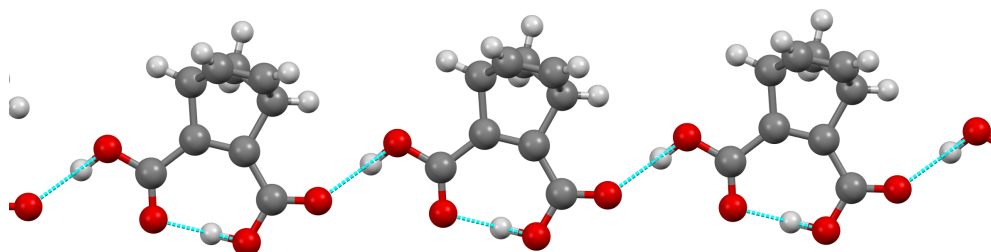


Figure 2. Hydrogen bonding pattern observed for **2**

Such a structure with two carboxylic acid groups rigidly held in close proximity to one another has various options for hydrogen bonding and the structure adopted, as shown in Figure 2, involves both an intramolecular interaction which locks the orientation of the two acid groups in a seven-membered ring and an intermolecular interaction between adjacent molecules, also through seven atoms, leading to infinite chains. Using the graph set notation introduced by Etter and Bernstein [17–19] this would be

described as $C^1_1(7)$ [S(7)]. The hydrogen bonding parameters (Table 3) are within normal ranges.

Table 3. Hydrogen bonding parameters for **2** (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O(9)—H(9)...O(10)	0.98(3)	1.72(3)	2.629(3)	153(3)
O(11)—H(11)...O(8)	0.98(2)	1.60(3)	2.560(3)	164(5)

A limited number of similar cyclic and bicyclic 1,2-diacids have been structurally characterised and three main hydrogen bonding patterns occur, denoted A–C and shown schematically in Figure 3. The hydrogen bonding patterns for diacids **6–15** (Figure 4) are summarised in Table 4.

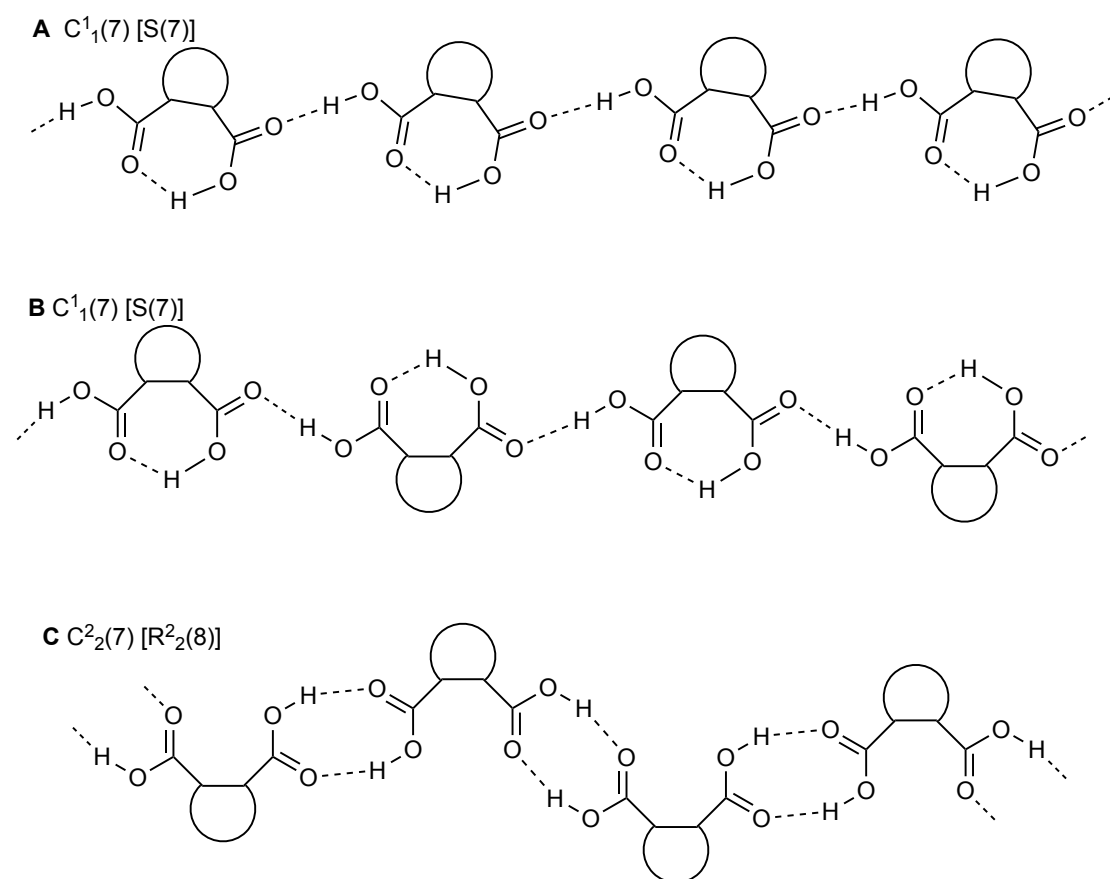


Figure 3. Common hydrogen bonding patterns observed for 1,2-diacids

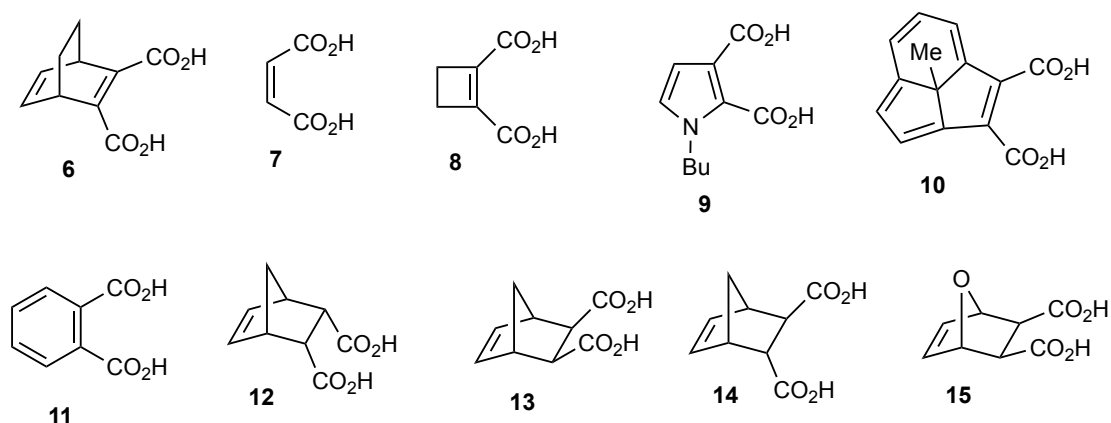


Figure 4. A selection of crystallographically characterised 1,2-diacids

Table 4. Hydrogen bonding patterns in diacids **2** and **6–15**

Compd	CSD RefCode	H-bonding pattern	Ref.
2	—	A	this work
6	BCOCD	A	[20]
7	MALIAC11	A	[21]
7	MALIAC13	A	[22]
8	CBUDCX	B	[23]
8	CBUDCX02	B	[24]
9	BICYER	B	[25]
10	MCINDE	B	[26]
11	PHTHAC02	C	[27]
12	NBENDC02	C	[28]
13	AHENIK	C	[29]
14	HUMGUR	C	[30]
15	TUNNEY	C	[31]

The first pattern (A), observed for our diacid **2** also occurs for the homologous bicyclo[2.2.2] compound **6** and for the acyclic maleic acid **7** and involves chains of molecules all aligned in the same way. Closely related to this, the second form (B) is

identical in terms of atom connectivity (and thus has the same graph set designation) but differs in the alignment of the molecules, with these now alternating in a zig-zag arrangement with the diacid functions directed inwards and the cyclic part to the outside. This is observed for cyclobutene-1,2-dicarboxylic acid **8** where the polar structure has been used to explain the observation of ferroelectric properties [24], as well as in the pyrrole-2,3-diacid **9** and the [10]-annulene diacid **10**. The third major pattern (C) has no intramolecular hydrogen bonding and instead involves only intermolecular $R^2_2(8)$ interactions leading to a chain of alternately oriented doubly hydrogen bonded units. This is the form adopted by phthalic acid **11**, all three stereoisomers **12–14** of the 2,3-dihydro analogue of **2**, as well as the oxygen-bridged analogue **15**. This last compound has recently been used to direct supramolecular assembly [31], and the relative orientation of adjacent carboxylic acid groups can have other important implications as shown in an early study [32] which established a correlation between dissociation constants pK_1 , pK_2 and the solution structure of 1,2-diacids including **2**, **7**, **8** and **11**.

Supplementary Materials

Supplementary material associated with this article can be found, in the online version, at doi:

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