

Article

Solid State Structure and Hydrogen Bonding of Some Cyclic NH Carboximides

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Abstract: Thirteen new crystal structures of cyclic NH carboximides have been determined and are compared with respect to the mode of intermolecular hydrogen bonding observed in the crystal. The structures include a new cyclobutane-fused succinimide, seven new simple bi- and tricyclic succinimides derived from Diels–Alder reactions of maleimide, three methylated glutarimides, a morpholinedione and adipimide, the first seven-membered ring NH carboximide to be structurally characterised. Overall, seven of the compounds adopt a ribbon structure, five show centrosymmetric dimers, and one has bonding between NH and a remote bridging ether oxygen. Halogen bonding was also detected in one case.

Keywords: hydrogen bonding; dimer; ribbon; succinimide; glutarimide; halogen bonding

1. Introduction

In a recent review in this journal [1] we surveyed the published crystal structures of over 300 cyclic NH carboximides containing the CO–NH–CO functional group and this revealed some important trends. In particular, two hydrogen bonded structures, namely, a centrosymmetric dimer **A** and a linear ribbon structure **B** involving two parallel rows of molecules exemplified for a simple monosubstituted succinimide (Figure 1) were by far the most common, accounting respectively for 119 and 74 examples among the total of 311 analysed. A further less common pattern **F** was one involving a chain formed by hydrogen bonding of NH to a remote non-imide oxygen elsewhere in the structure (29 examples). There were also less common modes of bonding such as hydrogen bonding of NH to a remote non-imide nitrogen (11 examples), dimers formed by bonding of imide NH to a remote oxygen (9 examples) or nitrogen (2 examples), hydrogen bonding of NH to imide CO in four molecules leading to a square shape (2 examples) and the equivalent to the centrosymmetric dimer but with bis imides leading to a doubly linked chain (11 examples). In addition, a host of more complex structures involving additional hydrogen bonding interactions with other functional groups were described.

The review also highlighted some notable gaps in previous structural studies. In this paper, we describe the determination of 13 new cyclic NH imide crystal structures and analysis of their hydrogen bonding patterns, including those of seven new simple maleimide Diels–Alder adducts, three methylated glutarimides, and the first seven-membered ring imide adipimide (hexahydroazepine-2,7-dione). The structures 1–13 involved are summarised in Figure 2.



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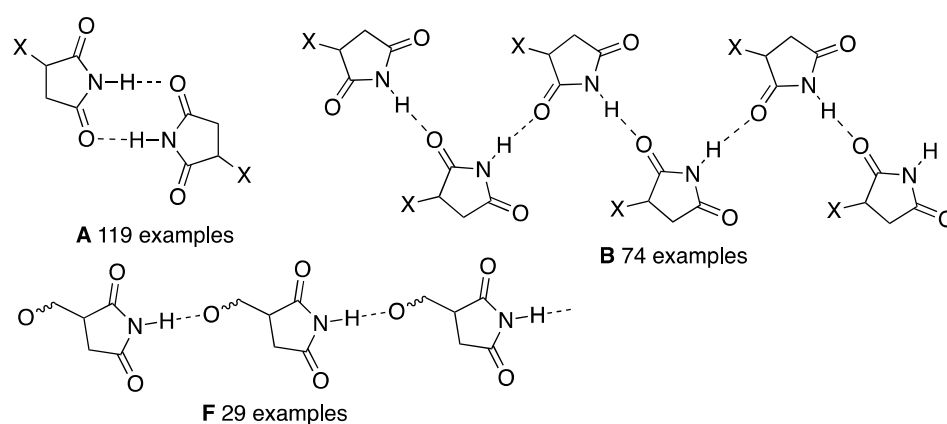


Figure 1. Most common previously reported hydrogen bonding patterns.

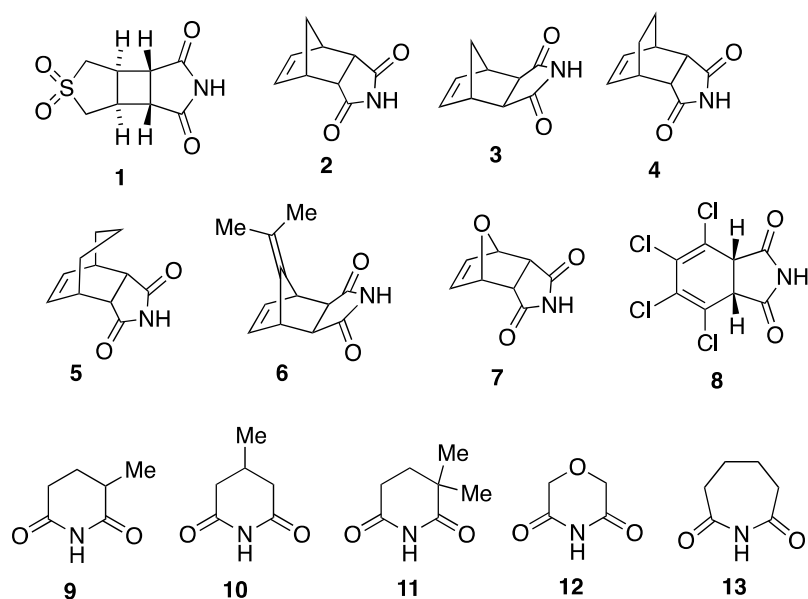


Figure 2. Cyclic NH imides for which structures were determined.

2. Materials and Methods

2.1. Synthesis of Imides 1–13

The cyclic imides, all previously known compounds, were prepared by reported methods and had physical and spectroscopic data in agreement with literature values. Specifically, **1** was prepared by photochemical [2 + 2]-cycloaddition between 3-sulfolene and maleimide in acetone [2], compounds **2**, **4**, **5**, **6**, **7** and **8** were prepared by Diels–Alder reaction of maleimide with, respectively, cyclopentadiene [3], 1,3-cyclohexadiene [4], 1,3-cycloheptadiene [5], 6,6-dimethylfulvene [6,7], furan [8], and tetrachlorothiophene 1,1-dioxide [9]. In the case of the furan adduct **7** it was essential to avoid undue heating since that resulted in isomerisation to the *exo* isomer whose structure has already been determined (see below). The *exo*-isomer **3** was prepared by reaction of the corresponding *exo*-anhydride with ammonium acetate in acetic acid [10]. Imides **9**–**12** were prepared by treatment of the corresponding dicarboxylic acids with ammonia; specifically, **9** was prepared by treatment of 2-methylglutaric acid with aqueous ammonia followed by evaporation to dryness and distillation [11], **10** was formed by reaction of 3-methylglutaric acid with thionyl chloride then aqueous ammonia followed by evaporation to dryness and distillation [12], **11** was prepared by reaction of 2,2-dimethylglutaric acid with urea at 160 °C [13], and **12** was prepared by treating diglycolic acid with aqueous ammonia followed by evaporation to dryness and distillation [14]. Imide **13** was prepared by treatment of ϵ -caprolactam with ozone in CCl_4 [15].

2.2. Crystallography

Data were collected on either a Rigaku XtaLAB P200 diffractometer (Tokyo, Japan) using graphite-monochromated Mo (1, 3, 6, 7, 8, 10, 11, 12) or Cu (4, 5) radiation or a Rigaku XtaLAB P100 diffractometer using Cu radiation (2, 9, 13). Structures were solved by direct methods and refined by full-matrix least squares against F^2 (SHELXL version 2018/3 [16]). The crystallographic data are summarised in detail in Tables 1–3. The cif files are available in the Supplementary Materials.

Table 1. Summary of crystallographic data obtained for compounds 1–4.

Compound	1	2	3	4
CCDC deposit no.	2225715	2225716	2225713	2225707
Empirical formula	C ₈ H ₉ NO ₄ S	C ₉ H ₉ NO ₂	C ₉ H ₉ NO ₂	C ₁₀ H ₁₁ NO ₂
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /n (No. 14)	P2 ₁ /c (No. 14)	P2 ₁ /c (No. 14)	P2 ₁ /c (No. 14)
Temperature (K)	93	173	93	125
Crystal form	colourless prism	colourless prism	colourless prism	colourless prism
Size (mm)	0.10 × 0.10 × 0.03	0.12 × 0.03 × 0.03	0.20 × 0.10 × 0.10	0.12 × 0.05 × 0.02
Unit cell dimensions (Å, °)	<i>a</i> = 6.0139 (3) <i>b</i> = 14.2212 (6) <i>c</i> = 10.2142 (5) β = 100.804 (5)	<i>a</i> = 11.1131 (3) <i>b</i> = 6.07791 (12) <i>c</i> = 12.2001 (3) β = 100.690 (3)	<i>a</i> = 8.394 (2) Å <i>b</i> = 16.964 (5) <i>c</i> = 10.681 (3) β = 90.818 (7)	<i>a</i> = 10.3980 (2) <i>b</i> = 6.53350 (10) <i>c</i> = 12.8770 (2) β = 105.469 (2)
Volume (Å ³)	858.08 (7)	770.90 (4)	1520.8 (7)	843.11 (3)
Z	4	4	8	4
D _c (g cm ^{−3})	1.666	1.406	1.425	1.396
Absorption coefficient	0.363 mm ^{−1}	0.830 mm ^{−1}	0.102 mm ^{−1}	0.802 mm ^{−1}
Radiation type, wavelength	Mo K α , 0.71073 Å	Cu K α , 1.54184 Å	Mo K α , 0.71075 Å	Cu K α , 1.54184 Å
<i>F</i> ₍₀₀₀₎	448.00	344.00	688.00	376.00
θ range	2.484–28.235°	4.253–68.319°	2.253–25.355°	4.412–75.133°
Limiting indices	−7 ≤ <i>h</i> ≤ 7, −18 ≤ <i>k</i> ≤ 18, −12 ≤ <i>l</i> ≤ 13	−13 ≤ <i>h</i> ≤ 11, −6 ≤ <i>k</i> ≤ 7, −14 ≤ <i>l</i> ≤ 14	−10 ≤ <i>h</i> ≤ 8, −14 ≤ <i>k</i> ≤ 20, −12 ≤ <i>l</i> ≤ 12	−12 ≤ <i>h</i> ≤ 12, −8 ≤ <i>k</i> ≤ 8, −16 ≤ <i>l</i> ≤ 15
Reflns collected/unique	12460/1899	7229/1409	7224/2745	9087/1705
<i>R</i> _{int}	0.0799	0.0216	0.0281	0.0159
Data/restraints/parameters	1899/1/131	1409/1/114	2745/2/226	1705/1/122
Data with <i>I</i> > 2 σ (<i>I</i>)	1659	1385	2584	1672
Goodness of fit on F^2	1.175	1.068	1.048	1.094
<i>R</i> ₁ , <i>wR</i> ₂ (data <i>I</i> > 2 σ (<i>I</i>))	0.0505, 0.1563	0.0781, 0.1697	0.0393, 0.1062	0.0389, 0.1039
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0552, 0.1584	0.0783, 0.1703	0.0410, 0.1075	0.0394, 0.1044
Largest diff. peak/hole (e Å ^{−2})	0.77 and −0.55	0.42 and −0.68	0.48 and −0.26	0.28 and −0.24

Table 2. Summary of crystallographic data obtained for compounds 5–8.

Compound	5	6	7	8
CCDC deposit no.	2225709	2225714	2225712	2225711
Empirical formula	C ₁₁ H ₁₃ NO ₂	C ₁₂ H ₁₃ NO ₂	C ₈ H ₇ NO ₃	C ₈ H ₃ Cl ₄ NO ₂
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	P2 ₁ /c (No. 14)	P2 ₁ /c (No. 14)	P2 ₁ 2 ₁ 2 ₁ (No. 19)	P2 ₁ /c (No. 14)
Temperature (K)	125	173	173	93
Crystal form	colourless plate	colourless prism	colourless prism	colourless plate
Size (mm)	0.12 × 0.04 × 0.01	0.12 × 0.10 × 0.03	0.15 × 0.15 × 0.08	0.10 × 0.10 × 0.02
Unit cell dimensions (Å, °)	<i>a</i> = 11.3039 (4) <i>b</i> = 7.28194 (18) <i>c</i> = 12.3790 (4) β = 113.542 (2)	<i>a</i> = 10.978 (3) <i>b</i> = 11.441 (3) <i>c</i> = 8.122 (2) β = 92.417 (7)	<i>a</i> = 7.0068 (7) <i>b</i> = 8.1073 (8) <i>c</i> = 12.7199 (13)	<i>a</i> = 6.4439 (4) <i>b</i> = 5.8690 (3) <i>c</i> = 26.8276 (19) β = 95.696 (6)
Volume (Å ³)	934.16 (6)	1019.2 (5)	722.57 (13)	1009.59 (11)
Z	4	4	4	4
D _c (g cm ^{−3})	1.360	1.324	1.518	1.888

Table 2. Cont.

Compound	5	6	7	8
Absorption coefficient	0.763 mm ⁻¹	0.090 mm ⁻¹	0.118 mm ⁻¹	1.143 mm ⁻¹
Radiation type, wavelength	Cu K α , 1.54184 Å	Mo K α , 0.71075 Å	Mo K α , 0.71075 Å	Mo K α , 0.71075 Å
$F_{(000)}$	408.00	432.00	344.00	568.00
θ range	4.266–75.347°	1.857–25.361°	2.980–25.375°	3.052–28.139°
Limiting indices	−13 ≤ h ≤ 14,	−13 ≤ h ≤ 13,	−8 ≤ h ≤ 7,	−8 ≤ h ≤ 8,
	−8 ≤ k ≤ 9,	−13 ≤ k ≤ 13,	−9 ≤ k ≤ 9,	−7 ≤ k ≤ 6,
	−15 ≤ l ≤ 15	−9 ≤ l ≤ 9	−15 ≤ l ≤ 14	−32 ≤ l ≤ 32
Refins collected/unique	10,206/1886	11,923/1856	8213/1307	9882/2148
R_{int}	0.0172	0.0286	0.0295	0.0365
Data/restraints/parameters	1886/1/131	1856/0/142	1307/1/113	2148/1/140
Data with $I > 2\sigma(I)$	1845	1743	1296	1972
Goodness of fit on F^2	1.041	1.090	1.022	1.006
R_1, wR_2 (data $I > 2\sigma(I)$)	0.0360, 0.0967	0.0370, 0.0969	0.0267, 0.0815	0.0303, 0.0848
R_1, wR_2 (all data)	0.0364, 0.0970	0.0385, 0.0981	0.0269, 0.0818	0.0324, 0.0862
Largest diff. peak/hole (e Å ²)	0.25 and −0.19	0.21 and −0.20	0.15 and −0.18	0.58 and −0.28

Table 3. Summary of crystallographic data obtained for compounds 9–13.

Compound	9	10	11	12	13
CCDC deposit no.	2225705	2225704	2225708	2225710	2225706
Empirical formula	C ₆ H ₉ NO ₂	C ₆ H ₉ NO ₂	C ₇ H ₁₁ NO ₂	C ₄ H ₅ NO ₃	C ₆ H ₉ NO ₂
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Space group	P2 ₁ /c (No. 14)	P2 ₁ /c (No. 14)	P2 ₁ /n (No. 14)	P-1 (No. 2)	P2 ₁ /n (No. 14)
Temperature (K)	173	93	93	173	173
Crystal form	colourless platelet	colourless prism	colourless prism	colourless prism	colourless prism
Size (mm)	0.10 × 0.10 × 0.01	0.10 × 0.10 × 0.03	0.20 × 0.03 × 0.03	0.15 × 0.05 × 0.05	0.15 × 0.12 × 0.03
Unit cell dimensions (Å, °)	$a = 11.795$ (8) $b = 7.040$ (4) $c = 7.721$ (5) $\beta = 103.355$ (8)	$a = 10.231$ (4) $b = 5.949$ (2) $c = 10.412$ (4) $\beta = 95.784$ (8)	$a = 15.276$ (3) $b = 6.3447$ (11) $c = 15.358$ (3) $\beta = 90.108$ (5)	$a = 3.92406$ (12) $b = 6.67474$ (18) $c = 9.7328$ (3) $\alpha = 76.716$ (2) $\beta = 82.516$ (2) $\gamma = 77.665$ (2)	$a = 10.9883$ (2) $b = 7.18070$ (11) $c = 8.21778$ (18) $\beta = 109.066$ (2)
Volume (Å ³)	623.8 (7)	630.5 (4)	1488.5 (5)	241.489 (13)	612.84 (2)
Z	4	4	8	2	4
Dc (g cm ⁻³)	1.354	1.339	1.260	1.583	1.378
Absorp'n coefficient	0.853 mm ⁻¹	0.101 mm ⁻¹	0.092 mm ⁻¹	0.137 mm ⁻¹	0.868 mm ⁻¹
Radiation type, wavelength	Cu K α , 1.54187 Å	Mo K α , 0.71075 Å	Mo K α , 0.71075 Å	Mo K α , 0.71075 Å	Cu K α , 1.54184 Å
$F_{(000)}$	272.00	272.00	608.00	120.00	272.00
θ range	3.852–67.810°	2.001–25.339°	2.653–25.335°	2.158–28.247°	4.257–68.071°
Limiting indices	−13 ≤ h ≤ 14,	−10 ≤ h ≤ 12,	−18 ≤ h ≤ 18,	−5 ≤ h ≤ 4,	−13 ≤ h ≤ 12,
	−7 ≤ k ≤ 8,	−5 ≤ k ≤ 7,	−7 ≤ k ≤ 7,	−8 ≤ k ≤ 8,	−5 ≤ k ≤ 8,
	−8 ≤ l ≤ 9	−11 ≤ l ≤ 12	−18 ≤ l ≤ 18	−12 ≤ l ≤ 12	−9 ≤ l ≤ 9
Refln total/unique	6167/1122	3953/1145	15821/2699	7485/1052	5849/1111
R_{int}	0.0670	0.0300	0.0399	0.0254	0.0174
Data/restraints /parameters	1122/1/88	1145/1/87	2699/2/194	1052/1/77	1111/187
Data $I > 2\sigma(I)$	1061	1067	2490	965	1100
Goodness of fit F^2	1.081	1.090	1.196	1.076	1.273
R_1, wR_2 ($I > 2\sigma(I)$)	0.0643, 0.1706	0.0461, 0.1488	0.0452, 0.1592	0.0292, 0.0838	0.0664, 0.1431
R_1, wR_2 (all data)	0.0657, 0.1726	0.0615, 0.2137	0.0486, 0.1618	0.0318, 0.0853	0.0666, 0.1433
Largest diff. peak/hole (e Å ²)	0.62 and −0.29	0.49 and −0.62	0.27 and −0.17	0.32 and −0.21	0.40 and −0.65

3. Results and Discussion

3.1. Cyclobutane-Fused Succinimide 1

The molecular structure of **1** (Figure 3a) clearly confirms the *anti*-arrangement of the two five-membered rings with respect to the central cyclobutane. This is also consistent with that of the corresponding anhydride **14** (Figure 4) whose crystal structure was reported recently [17]. In the crystal the molecules are arranged in centrosymmetric hydrogen bonded dimers (Figure 3b) with parameters within the normal ranges (Table 4). None of the previously reported seven structures for cyclobutane-fused succinimides show this structure, which using the graph set notation developed by Etter and Bernstein [18,19] would be denoted $R^2_2(8)$.

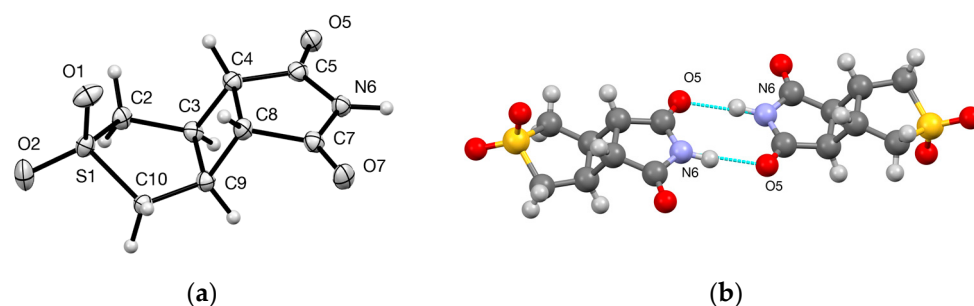


Figure 3. (a) Molecular structure of **1** with numbering system used (50% thermal ellipsoids), (b) hydrogen bonding pattern for **1**.

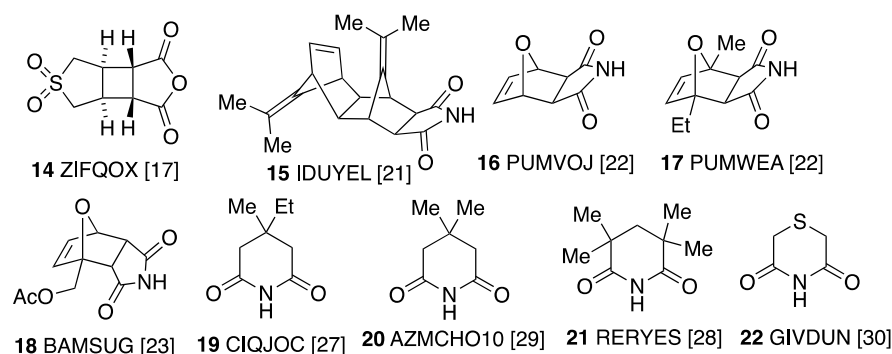


Figure 4. Structure of crystallographically characterised reference compounds **14–22** with CCDC Ref. Codes and literature references.

Table 4. Hydrogen bonding parameters (Å, °).

Compound	D–H ... A	D–A	D–H	H ... A	Angle DHA
1	N(6)–H(6) ... O(5)	2.906(2)	0.97(2)	1.94(2)	170(2)
2	N(1)–H(1) ... O(2)	2.8438(15)	0.977(15)	1.902(15)	160.9(14)
3	N(1)–H(1) ... O(12)	2.9057(16)	0.975(13)	1.946(12)	167.6(14)
	N(11)–H(11) ... O(9)	2.9036(16)	0.972(13)	1.963(12)	162.1(13)
4	N(1)–H(1) ... O(9)	2.8432(12)	0.975(14)	1.878(13)	169.8(13)
5	N(1)–H(1) ... O(9)	2.7991(11)	0.973(11)	1.832(11)	172.4(17)
6	N(1)–H(1) ... O(2)	2.8616(15)	0.880(17)	2.020(17)	159.8(15)
7	N(1)–H(1) ... O(4)	2.8735(19)	0.975(8)	1.909(8)	170.0(19)
8	N(1)–H(1) ... O(9)	2.8576(18)	0.975(16)	1.897(18)	168(2)
9	N(1)–H(1) ... O(6)	2.908(2)	0.978(17)	1.935(18)	173(2)
10	N(1)–H(1) ... O(2)	2.9300(17)	0.973(13)	1.957(13)	177.0(16)
	N(1)–H(1) ... O(6)	2.849(2)	0.977(17)	1.871(17)	179.1(18)
11	N(11)–H(11) ... O(16)	2.883(2)	0.977(19)	1.907(19)	178(2)
12	N(1)–H(1) ... O(2)	2.8872(11)	0.971(11)	1.920(11)	173.3(13)
13	N(1)–H(1) ... O(7)	2.9278(17)	0.975(17)	1.957(17)	173.1(14)

3.2. Bi- and Tricyclic Diels–Alder Adducts of Maleimide 2–8

The Diels–Alder reaction of maleimide has been well investigated and at least 50 previous bicyclo[2.2.1] and [2.2.2] adducts derived in this way have been crystallographically characterised [1]. However, it is notable that these do not include many of the very simplest examples, such as the *endo* cyclopentadiene adduct **2** first reported as early as 1944 [20]. We report here the structure of both *endo* and *exo* cyclopentadiene adducts **2** and **3**, the *endo* adducts from 1,3-cyclohexadiene and 1,3-cycloheptadiene **4** and **5**, the *exo* dimethylfulvene adduct **6**, the *endo* furan adduct **7** and the *cis* tetrachlorocyclohexadiene-fused compound **8** formed by cycloaddition with tetrachlorothiophene 1,1-dioxide followed by extrusion of SO₂. The molecular structures (Figure 5) confirm the *exo/endo* configuration in each case. It is perhaps surprising that the C(11) bridge in **5** is oriented towards the apparently more hindered imide function rather than the double bond. It should be noted here that in a previous publication [21], the structure of a 2:1 adduct of dimethylfulvene with maleimide **15** was determined (Figure 4) which clearly results from a further diene addition onto the initial *exo* adduct **6**. Despite this, the 1:1 adduct also obtained was shown with the *endo* configuration [21] which is clearly an error as now confirmed by the structure of **6**.

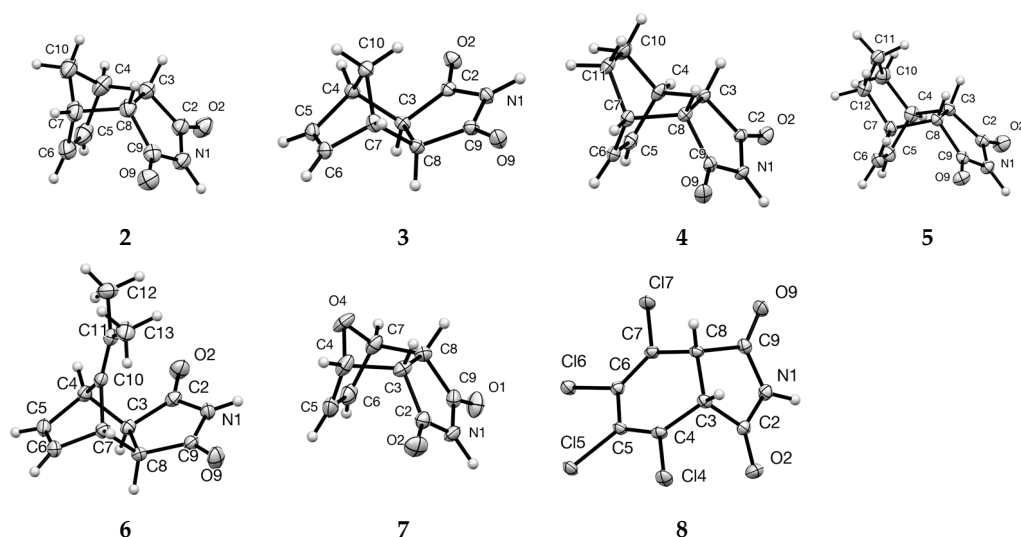


Figure 5. Molecular structures for Diels–Alder derived compounds **2–8** showing numbering systems used (50% probability ellipsoids).

All the molecular structures **2–8** show fairly conventional bond lengths and angles but when we come to the mode of hydrogen bonding an interesting pattern emerges. Only the *endo* cyclopentadiene adduct **2** forms the centrosymmetric $R^2_2(8)$ structure (Figure 6) while its *exo* isomer **3** as well as the higher homologues **4** and **5** and compounds **6** and **8** all form the $C(4)$ ribbon structure (Figure 7). The hydrogen bonding parameters (Table 4) are standard. It should be noted that for compound **3** there are two independent molecules and these alternate in the hydrogen bonding pattern.

In our review [1], fifty Diels–Alder derived tricyclic succinimides were covered and fifteen of these show the centrosymmetric $R^2_2(8)$ dimer structure **A** while twenty show the linear $C(4)$ ribbon structure **B**. The factors that favour one of these as opposed to the other are subtle and there seems to be a fine balance. The *endo* furan adduct **7** was of particular interest since the *exo* isomer **16** (Figure 4) was previously found to form the centrosymmetric dimer structure [22] but, by way of contrast, compound **7** adopts the linear $C(6)$ structure (Figure 7) with NH hydrogen bonding to the bridging oxygen of the next molecule. It is worth noting that this is the structure also observed for several simple substituted derivatives such as **17** in the *exo* series [22] and **18** in the *endo* series [23] (Figure 4).

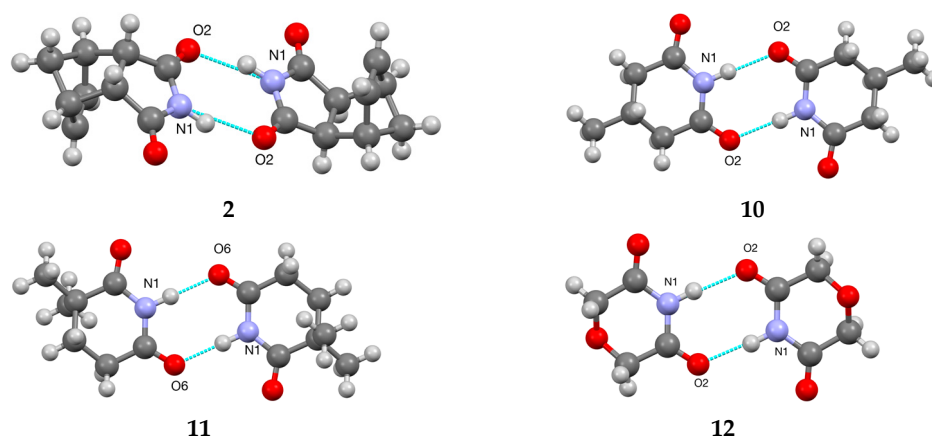


Figure 6. Hydrogen bonded $R^2_2(8)$ dimer structures for 2, 10, 11 and 12.

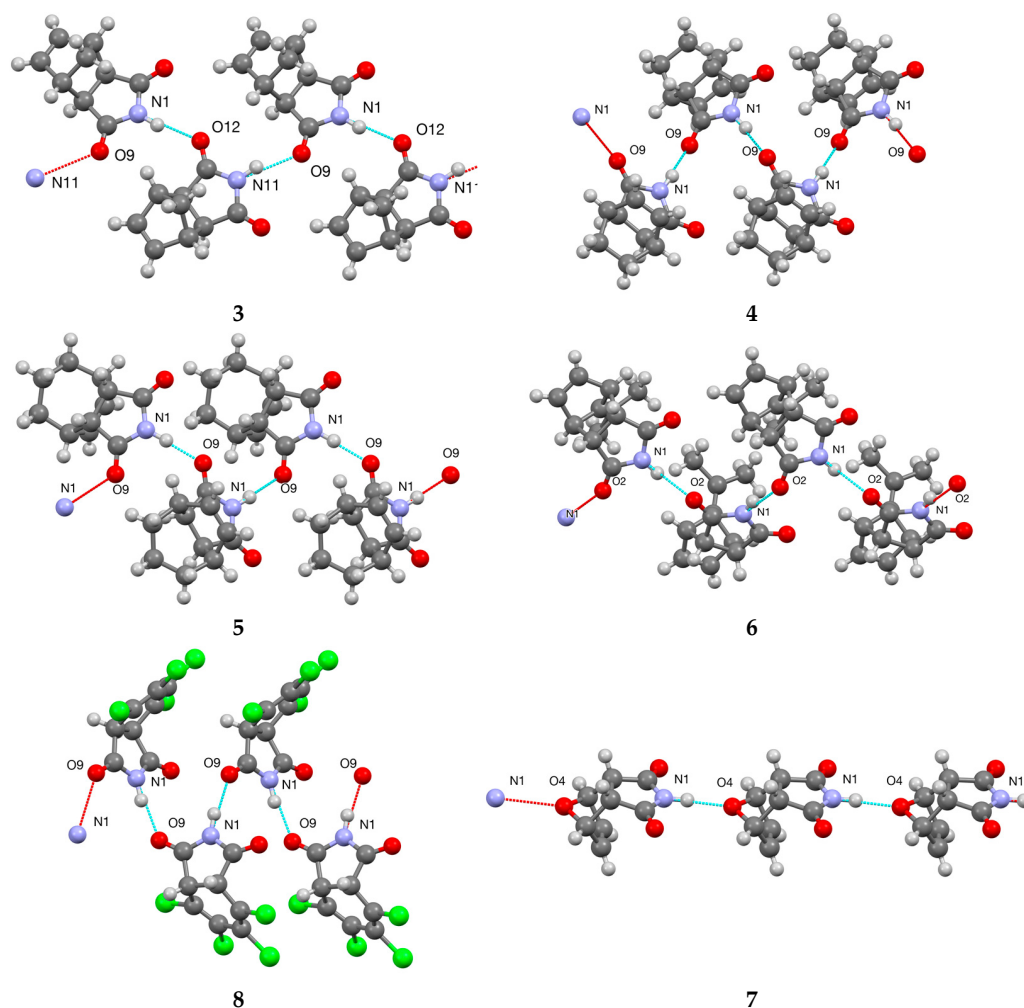


Figure 7. Hydrogen bonded $C(4)$ structures for 3, 4, 5, 6 and 8 and $C(6)$ structure for 7.

A further element of interest was the detection of a strong intermolecular halogen bonding interaction [24] in the structure of 8 between one ring C–Cl bond and the same imide carbonyl as is involved in hydrogen bonding to NH. Since this forms additional chains in a direction perpendicular to those formed by the hydrogen bonding interaction, the overall structure is quite complex and for simplicity the halogen bonding is shown separately (Figure 8). Examples in which a C–Cl halogen bonds to C=O seem to be rather

uncommon but a comparable example is provided by sydnone-containing hydroximoyl chloride compound **23** [25].

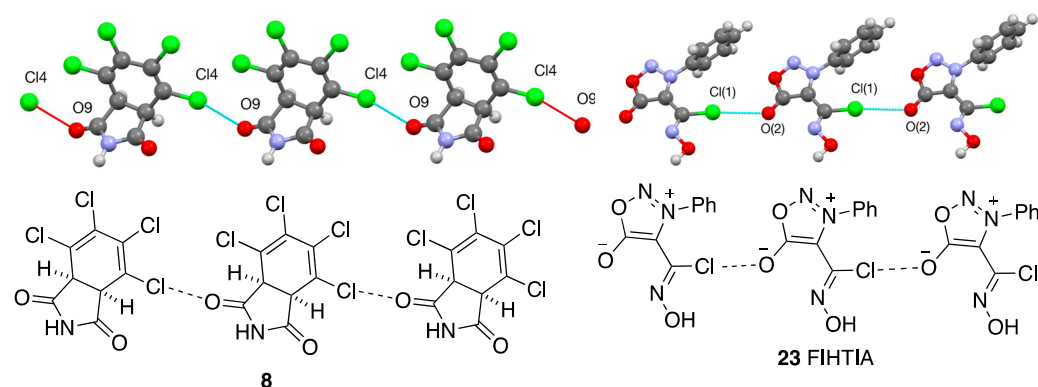


Figure 8. Halogen bonding interaction in structure of **8** [C–Cl ... O parameters: C(4)–Cl(4) 1.722(2), Cl(4) ... O(9) 2.940(1), C(4)–O(9) 4.569(2) Å, angle 156.26(6)°] and for comparison **23** [C–Cl ... O parameters: C(9)–Cl(1) 1.717(2), Cl(1) ... O(2) 3.150(2), C(9)–O(2) 4.861(3) Å, angle 173.57(9)°].

3.3. Ring-Methylated Glutarimides **9–11** and Morpholine Analogue **12**

The structure of glutarimide (piperidine-2,6-dione) was determined at an early stage and it exhibits the C(4) ribbon structure **B** [26]. Very few simple derivatives have been structurally characterised so far and we describe here the structures of the 3- and 4-methyl derivatives **9** and **10** as well as the 3,3-dimethyl compound **11** (Figure 9). The morpholine-3,5-dione structure **12** is also included.

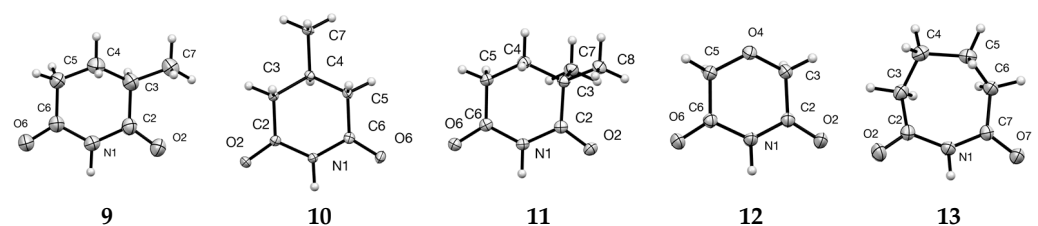


Figure 9. Molecular structures for glutarimides **9–11**, morpholine analogue **12** and adipamide **13** showing numbering systems used (50% probability ellipsoids).

Among these four compounds only one, the 3-methylglutarimide **9**, shows a C(4) ribbon structure (Figure 10) while the remaining three all adopt the centrosymmetric $R^2_2(8)$ dimer structure (Figure 6). Comparison with the few similar structures reported previously (Figure 4) shows that while the 4-ethyl-4-methyl compound **19** [27] and the 3,3,5,5-tetramethyl compound **21** [28] both have dimeric structures similar to **10** and **11**, the 4,4-dimethyl compound **20** [29] forms a C(4) ribbon similar to **9**. The dimer observed for **12** also contrasts with the ribbon structure reported for the thiomorpholine analogue **22** [30].

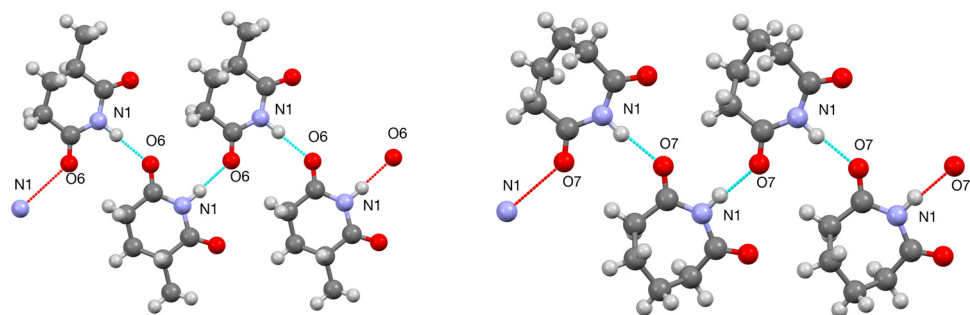


Figure 10. Hydrogen bonded C(4) structures for **9** and **13**.

3.4. Adipimide 13

Although X-ray structures of five- and six-membered cyclic NH imides are very common and there are a few structures of eight- and nine-membered rings [1], no previous examples of a seven-membered ring have been reported as far as we are aware. The molecular structure of the first such example, adipimide or hexahydroazepine-2,7-dione **13**, showed a bent structure with C(4) and C(5) above the plane formed by the approximately coplanar remaining five ring atoms (Figure 9). This compound again adopted a C(4) ribbon structure (Figure 10).

4. Conclusions

In this paper we have filled in obvious gaps in the structural characterisation of cyclic NH carboximides. The observed hydrogen bonding patterns among the 13 structures fall mainly into the two commonest types for this class of compounds with seven adopting a C(4) ribbon structure and five exhibiting $R^2_2(8)$ centrosymmetric dimers. The remaining example has a less common C(6) structure with NH bonding to the bridging ether oxygen of the next molecule. Overall it is clear that there is a fine balance between the different possible hydrogen binding modes with closely similar compounds often giving different results.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13010150/s1>, cif and checkcif files for **1–13**.

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References

1. Aitken, R.A.; Sonecha, D.K. The solid state structures of cyclic NH carboximides. *Crystals* **2020**, *10*, 606. [CrossRef]
2. Shaikhrazieva, V.S.; Tolstikov, G.A.; Enikeev, R.S. Photoinitiated addition of maleic anhydride and its derivatives to 3-sulfolene. *Zh. Org. Khim* **1972**, *8*, 377–382.
3. Michaelis, S.; Blechert, S. Ring-opening cross-metathesis (ROCM) as a novel tool for the ligation of peptides. *Chem. Eur. J.* **2007**, *13*, 2358–2368. [CrossRef]
4. Fujimoto, M.; Okabe, K. Nouvelle méthode de synthèse des dérivés d'ethano-4,7-polyhydroisindoline. *Chem. Pharm. Bull.* **1962**, *10*, 714–719. [CrossRef]
5. Abou-Gharbia, M.; Patel, U.R.; Webb, M.B.; Moyer, J.A.; Andree, T.H.; Muth, E.A. Polycyclic aryl- and heteroaryl piperazinyl imides as 5-HT_{1A} receptor ligands and potential anxiolytic agents: Synthesis and structure–activity relationship studies. *J. Med. Chem.* **1988**, *31*, 1382–1392. [CrossRef] [PubMed]
6. Poos, G.I.; Lehman, M.M.; Landis, E.B.; Rosenau, J.D. Bicyclic bases. IV. Aryl substituted bridged hydroisindolines. *J. Med. Chem.* **1962**, *5*, 883–896. [CrossRef] [PubMed]
7. Graham, B.; Fayter, A.E.R.; Houston, J.E.; Evans, R.C.; Gibson, M.I. Facially amphipathic glycopolymers inhibit ice recrystallization. *J. Am. Chem. Soc.* **2018**, *140*, 5682–5685. [CrossRef]
8. Kwart, H.; Burchuk, I. Isomerism and adduct stability in the Diels–Alder reaction. I. The adducts of furan and maleimide. *J. Am. Chem. Soc.* **1952**, *74*, 3094–3097. [CrossRef]
9. Raasch, M.S. Annulations with tetrachlorothiophene 1,1-dioxide. *J. Org. Chem.* **1980**, *45*, 856–867. [CrossRef]
10. Kreituss, I.; Chen, K.-Y.; Eitel, S.H.; Adam, J.-M.; Wuitschik, G.; Fettes, A.; Bode, J.W. A robust, recyclable resin for decagram scale resolution of (±)-mefloquine and other chiral N-heterocycles. *Angew. Chem. Int. Ed.* **2016**, *55*, 1553–1556. [CrossRef]
11. Aitken, R.A.; Farrell, D.M.M.; Kirton, E.H.M. Synthesis and pyrolysis of tetrahydro-1,4-oxazine-3,5-diones and tetrahydro-1,4-thiazine-3,5-diones. *Chem. Heterocycl. Compd.* **2001**, *37*, 1526–1531. [CrossRef]
12. Sircar, S.S.G. The influence of groups and associated rings on the stability of certain heterocyclic ring systems. Part 1. The substituted glutarimides. *J. Chem. Soc.* **1927**, 600–605. [CrossRef]

13. Dabrowski, Z.; Cybulski, J. Structure and stereochemistry of lactams and cyclic imides. V. Mass spectrometry of substituted glutarimides. *Bull. Acad. Pol. Sci.-Chim.* **1981**, *29*, 11–16.
14. Mizuno, H.; Manabe, A. Pyrimidine Compounds and Pests Controlling Composition Containing the Same. WO2004/99160 A1, 18 November 2004.
15. Alekseeva, O.; Konstantinova, M.; Rasumovskii, S. Efficient method of cyclic imides synthesis under ozone influence by the example of ϵ -caprolactam oxidation reaction. *Heteroatom Chem.* **2008**, *19*, 661–666. [\[CrossRef\]](#)
16. Sheldrick, G.M. A short history of SHELXL. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122. [\[CrossRef\]](#)
17. Chen, T.-G.; Barton, L.M.; Lin, Y.; Tsien, J.; Kossler, D.; Bastida, I.; Asai, S.; Bi, C.; Chen, J.S.; Shan, M.; et al. Building C(sp³)-rich complexity by combining cycloaddition and C–C cross-coupling reactions. *Nature* **2018**, *560*, 350–354. [\[CrossRef\]](#)
18. Etter, M.C. Encoding and decoding hydrogen-bond patterns of organic compounds. *Acc. Chem. Res.* **1990**, *23*, 120–126. [\[CrossRef\]](#)
19. Etter, M.C.; MacDonald, J.C.; Bernstein, J. Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr. Sect. B* **1990**, *46*, 256–262. [\[CrossRef\]](#)
20. Morgan, M.S.; Tipson, R.S.; Lowy, A.; Baldwin, W.E. Some derivatives of *cis*-3,6-endomethylene- Δ^4 -tetrahydrophthalic acid. *J. Am. Chem. Soc.* **1944**, *66*, 404–407. [\[CrossRef\]](#)
21. Hong, B.-C.; Shr, Y.-J.; Liao, J.-H. Unprecedented microwave effects on the cycloaddition of fulvenes. A new approach to the construction of polycyclic ring systems. *Org. Lett.* **2002**, *4*, 663–666. [\[CrossRef\]](#)
22. Struga, M.; Mirosław, B.; Pakosińska-Parys, M.; Drzewiecka, A.; Borowski, P.; Kossakowski, J.; Koziol, A.E. Synthesis, characterization and supramolecular synthons in crystals of new derivatives of 10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione. *J. Mol. Struct.* **2010**, *965*, 23–30. [\[CrossRef\]](#)
23. Bennett, G.D.; Spengler, A.O.; Wheeler, K.A. *CSD Communication*; Cambridge Crystallographic Data Centre: Cambridge, UK, 2016; BAMSUG.
24. Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. The halogen bond. *Chem. Rev.* **2016**, *116*, 2478–2601. [\[CrossRef\]](#) [\[PubMed\]](#)
25. Shih, M.-H.; Yeh, M.-Y.; Lee, M.-J.; Su, Y.-S. Efficient syntheses of 3-(3-arylsynon-4-yl)triazole derivatives. *Synthesis* **2004**, 2877–2885. [\[CrossRef\]](#)
26. Petersen, C.S. The crystal structure of glutarimide. *Acta Chem. Scand.* **1971**, *25*, 379. [\[CrossRef\]](#)
27. Tutughamiarso, M.; Bolte, M. 4-Ethyl-4-methyl piperidine-2,6-dione. *Acta Crystallogr. Sect. E* **2007**, *63*, o4743. [\[CrossRef\]](#)
28. Maurin, J.K.; Czarnocki, Z.; Paluchowska, B.; Winnicka-Maurin, M. Conformation-related reaction efficiency of glutarimides with phenyllithium. Structures of 3,3,5,5-tetramethylglutarimide and 2-hydroxy-2-phenyl-3,3,5,5-tetramethyl-6-piperidone. X-ray and theoretical study. *Acta Crystallogr. Sect. B* **1997**, *53*, 719–725. [\[CrossRef\]](#)
29. Bocelli, G.; Grenier-Loustalot, M.F. The structure of 4,4-dimethylazacyclohexane-2,6-dione (4,4-dimethyl-2,6-piperidinedione). *Acta Crystallogr. Sect. B* **1981**, *37*, 1302–1304. [\[CrossRef\]](#)
30. Aitken, R.A.; Slawin, A.M.Z.; Yeh, P.-P. Tetrahydro-1,4-thiazine-3,5-dione. *Molbank* **2018**, *2018*, M1036. [\[CrossRef\]](#)

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