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HYDROGEN BONDING AND CONFORMATION OF 5-SUBSTITUTED DIPYRRROMETHANES – A SOLID STATE STUDY

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Abstract – A crystallographic study of nine different meso-substituted dipyrromethanes identifies the main types of intra- and intermolecular hydrogen bonding pattern in this class of porphyrin building blocks. Most compounds form similar hydrogen-bonded dimers in the crystal but distinct differences in the dipyrromethane conformations are observed in dependence on the type of the meso substituent.

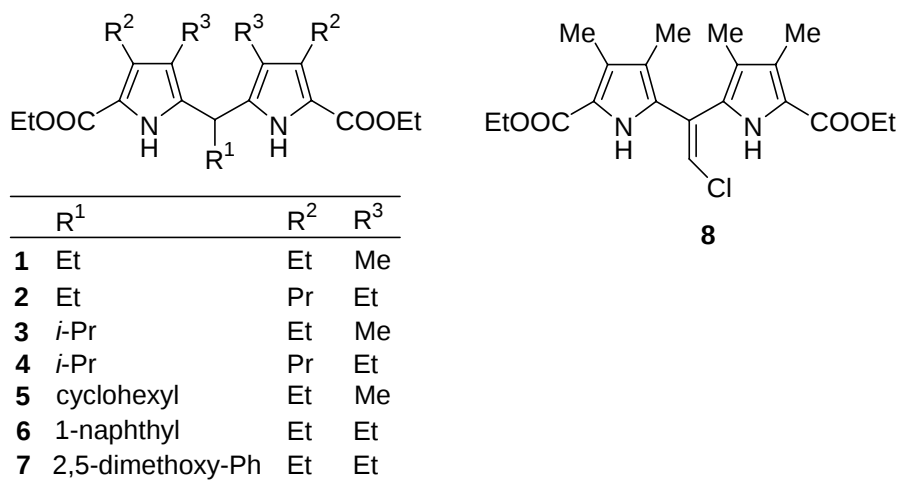
INTRODUCTION

Dipyrromethanes are amongst the most important building blocks used for laboratory porphyrin synthesis. Often they are used as key components for so-called [2+2] condensation reactions.¹ The biosynthesis of porphyrins involves attachment of pyrrole units to a dipyrromethane cofactor of porphobilinogen deaminase.² Additional dipyrromethane units are structural components of many hybrid (oligo)pyrrole macrocycles with only partial conjugation, e.g. calixphyrins,³ in the well known porpho(di)methenes⁴ and in many bilanes.⁵ Compared to the number of structural studies on bilanes, calixpyrroles, calixphyrins and so on, or the use of dipyrromethanes as solid state synthons,⁶ the number of structural studies on isolated dipyrromethanes is rather small. Bonnett's structure of a meso unsubstituted dipyrromethane remains the classical study in this area.⁷ More recent studies almost exclusively targeted α -unsubstituted dipyrromethanes.^{8,9} No broad range investigations on the interrelationship of hydrogen bonding pattern and conformational aspects has been published.

In order to take a closer look at solid state structural features of dipyrromethanes a series of compounds (**1-8**) containing both various meso substituents and α -ester groups was chosen. Such compounds serve as standard starting materials for [2+2] condensations to yield porphyrins with both meso and β -substituents.^{1,10-12} Such porphyrins exhibit conformational distortion as a result of the meso- β -substituent interactions.^{10,12,13} The present study complements our ongoing studies on the anion binding and hydrogen bonding in porphyrins¹⁴ and pyrrole derivatives.¹⁵

RESULTS AND DISCUSSION

The dipyrromethanes (**1–8**) were crystallized by liquid diffusion of a concentrated solution of the dipyrromethane in dichloromethane into *n*-hexane or methanol. The compounds generally crystallize quite well and within days gave crystals suitable for analysis. The molecular structures of the individual compounds are shown in Figure 1. Overall, the basic structural parameters, such as bond lengths and angles in the two pyrrole units are comparable to related structures and bilanes.^{5,7} Selected structural parameters are compiled in Table 1.



The structures are characterized by a ‘roof-type’ arrangement of the two pyrrole units with the meso carbon (C5) on top. In the meso alkyl series (**1–5**) the pyrrole hydrogen vectors point towards the same side of the molecules. In fact, the pyrrole tilt angles and structural parameters for the C4–C5–C6 unit are comparable in all these structures. The crystal structure of **1** exemplifies most of the salient features encountered in the present study. The molecular arrangement in the crystal is characterized by the formation of hydrogen-bonded dimers (Figure 2). Like in Bonnett’s structure⁷ of a meso-unsubstituted dipyrromethane only one of the two ester carbonyl groups (O1) acts as a hydrogen bond acceptor for the two N–H donor groups. Thus, the dimers are held together by four classical NH $\cdots$ O hydrogen bonds. A search for weaker C–H $\cdots$ O interactions using the criteria put forward by Steiner¹⁶ (with $\angle_{D-H\cdots A} = 110^\circ$ as cutoff) reveals that the other carbonyl group (O3) is used for linking the dimers together by CH₂ $\cdots$ O interactions. In addition, the hydrogen-bonded dimers are further stabilized by very weak CH₃ $\cdots$ O1 interactions. Full details of the hydrogen bonding pattern, geometrical parameters and symmetry codes involved are listed in Table 2.

The triclinic B modification of **2** exhibits an almost identical molecular arrangement in the crystal (not shown). The only differences are somewhat stronger CH₂ $\cdots$ O1 interactions that join the dimers to infinite chains. Nevertheless, some flexibility for different arrangements exists in these compound. The second triclinic modification of **2** (A) overall exhibits a similar hydrogen bonding arrangement, i.e. coordination of the two N–H donors to one C=O acceptor. However, while in all other meso alkyl dipyrromethanes the

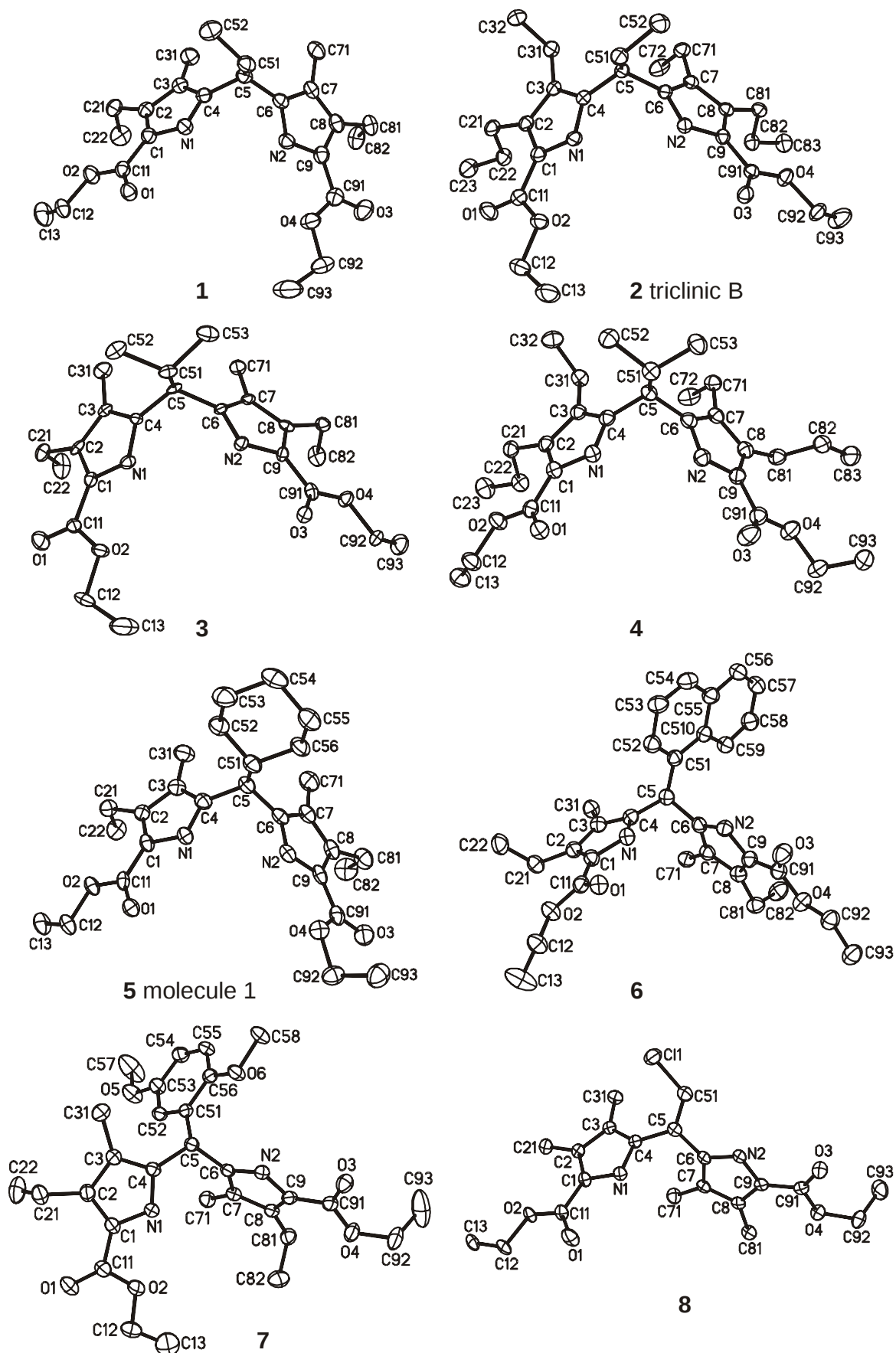


Figure 1 View of the molecular structures of the dipyrromethanes in the crystal. Thermal ellipsoids are drawn for 50 % occupancy. Hydrogen atoms and disordered positions have been omitted for clarity.

Table 1. Selected structural and geometrical parameters of the structures.

Compound	1	2 tricl. A	2 tricl. B	3	4	5 mol. 1	6	7	8
<i>Bond lengths, Å</i>									
C4-C5	1.503(3)	1.507(7)	1.509(2)	1.506(5)	1.501(4)	1.512(5)	1.503(4)	1.511(4)	1.473(4)
C5-C51	1.546(3)	1.532(7)	1.534(3)	1.550(5)	1.554(4)	1.560(5)	1.535(4)	1.513(4)	1.473(4)
C5-C6	1.507(3)	1.490(7)	1.510(2)	1.505(5)	1.505(4)	1.505(5)	1.513(4)	1.513(4)	1.334(4)
<i>Bond angles, deg</i>									
C4-N1-C1	109.40(16)	110.6(4)	109.35(14)	109.1(3)	109.3(2)	109.6(3)	109.2(2)	109.7(2)	109.3(2)
C6-N2-C9	109.42(16)	110.4(4)	109.50(14)	109.3(3)	109.8(2)	110.0(3)	109.5(2)	110.1(2)	109.7(2)
C4-C5-C6	113.18(15)	111.5(4)	112.68(14)	112.6(3)	111.4(2)	112.5(3)	108.8(2)	112.6(2)	117.2(3)
C4-C5-C51	111.86(16)	112.4(4)	112.71(15)	112.5(3)	112.4(2)	113.5(3)	115.3(2)	113.2(2)	123.8(3)
C6-C5-C51	111.86(16)	112.5(4)	112.07(14)	112.5(3)	113.3(2)	113.5(3)	114.4(2)	110.8(2)	119.0(3)
<i>Torsion angles, deg</i>									
N1-C4-C5-C51	-45.4(2)	62.1(6)	-62.4(2)	-63.8(4)	-56.5(3)	-67.3(4)	-73.9(3)	121.8(3)	-130.0(3)
C3-C4-C5-C51	131.2(2)	-117.7(6)	118.2(2)	113.4(4)	124.5(3)	115.3(4)	113.6(3)	-60.7(4)	56.1(5)
C3-C4-C5-C6	-101.5(2)	114.9(6)	-113.8(2)	-118.1(4)	-107.1(3)	-114.0(4)	-116.4(3)	172.7(4)	-121.0(3)
C51-C5-C6-C7	-110.8(2)	137.8(6)	-130.14(18)	-131.5(4)	-123.5(3)	-118.9(4)	-152.1(3)	-64.7(4)	-145.8(3)
C51-C5-C6-N2	69.4(2)	-39.4(6)	48.1(2)	49.6(5)	58.7(3)	61.0(4)	35.5(3)	115.3(3)	28.9(4)
N1-C4-C5-C6	81.8(2)	-65.4(6)	65.7(2)	64.7(4)	71.8(3)	63.3(4)	56.2(3)	-4.8(4)	52.6(4)
C4-C5-C6-N2	-57.9(2)	87.9(6)	-80.3(2)	-78.9(4)	-69.2(3)	-69.6(4)	-95.0(3)	-116.8(3)	-153.8(3)
Pyrrole tilt	62.90(8)	111.4(1)	64.78(8)	62.8(1)	67.8(1)	63.7(1)	89.11(11)	69.91(10)	72.0(2)

two N-H...O=C have similar lengths and bond angles here one short (N1-H1...O3 = 2.08 Å) and one longer (N2-H2...O3 = 2.23 Å) hydrogen bond are found. This arrangement results in a much “flatter” arrangement of the two pyrrole units with a tilt angle of 111.4(1)°, the largest found in all structures discussed here.

Changing the meso alkyl group to a bulkier *iso*-propyl residue gives rise to small geometrical changes but does not alter the general picture significantly. In fact, the structural parameters of **3** are very similar to those of **1** and **2B** and the hydrogen bonding pattern is similar to **1**. While in **1** or **2** the ipso CH₂ group coordinates weakly to the carbonyl oxygen involved in hydrogen bonding, here the *iso*-propyl CH group is involved in a similar arrangement (Figure 3). However, further increasing the steric interactions by exchanging the β-methyl groups to ethyl does results in significant changes. The N-H...O bond lengths found in **4** are the shortest found in all structures and the D-H...A bond angles become almost linear. In contrast, the C51-H51...O1 interaction is amongst the weakest found in these structures. This trend is continued in structure (**5**) with the bulky cyclohexyl residue. While the overall arrangement of the molecules in the dimer are similar and again the ipso C-H vector points towards the carbonyl oxygen atom involved in the hydrogen bonds, the distance is now 2.85 Å. As shown in Table 2 a number of weak intermolecular contacts are present in this structure.

The compound crystallized with two independent molecules in the unit cell; structural differences between the two molecules were minor. Thus, while the overall pattern of the hydrogen-bonded dimers remains similar, different steric interactions between the meso and β-substituents mainly affect the weaker C-H...O interactions.

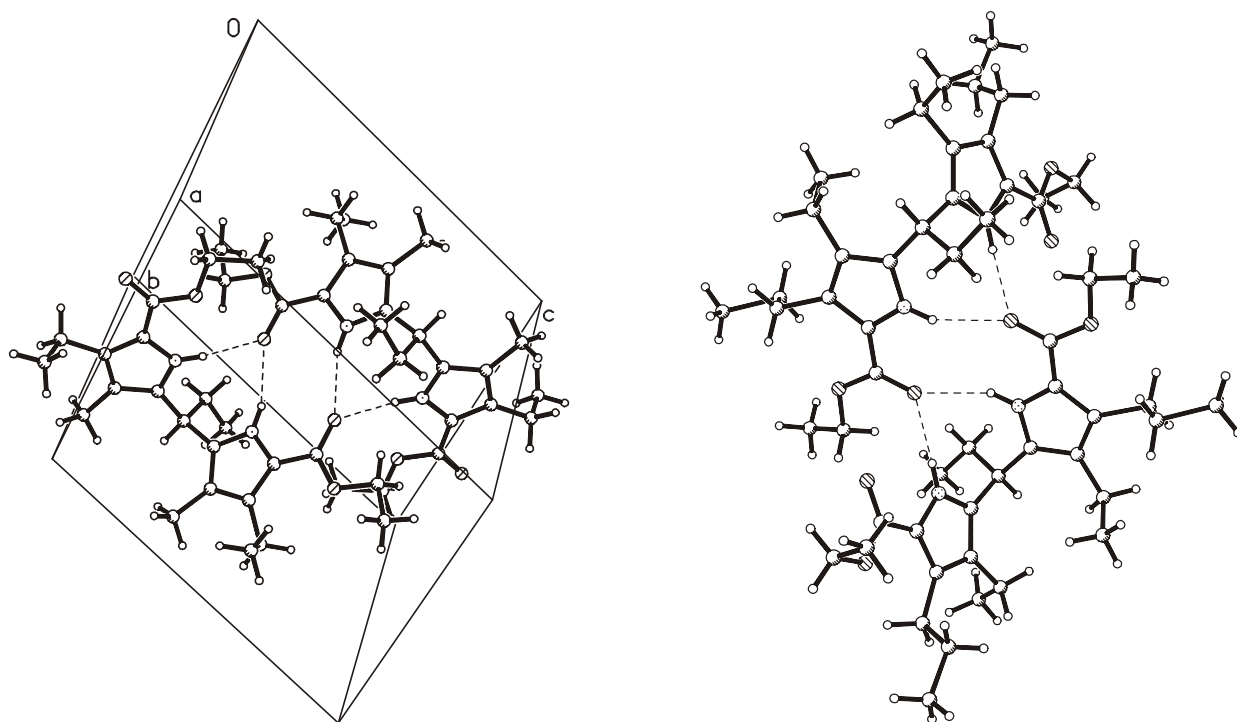


Figure 2 View of the hydrogen-bonded dimers formed by **1** (left) and **2A** (right) in the crystal. Dashed lines indicate classical hydrogen bonds.

Switching the meso substituent to aryl residues, e.g., a naphthalene residue in **6** gives rise to more elaborate differences in crystal packing. Nevertheless, the most prominent feature is again the formation of hydrogen-bonded dimers involving coordination of two N–H donors to one carbonyl acceptor (Figure 4). The two hydrogen bonds differ significantly in their bond lengths and angles and the two pyrrole rings are oriented almost orthogonal to each other. The structure exhibits several close intermolecular contacts. The ester group not involved in classic hydrogen bonding is coordinated by the C21 CH₂ group, albeit with an angle (110.3°) at the low limit for bonding interactions. A somewhat stronger intermolecular interaction involves orientation of the C8 methylene group towards O4 (2.38 Å). Additionally, one of the

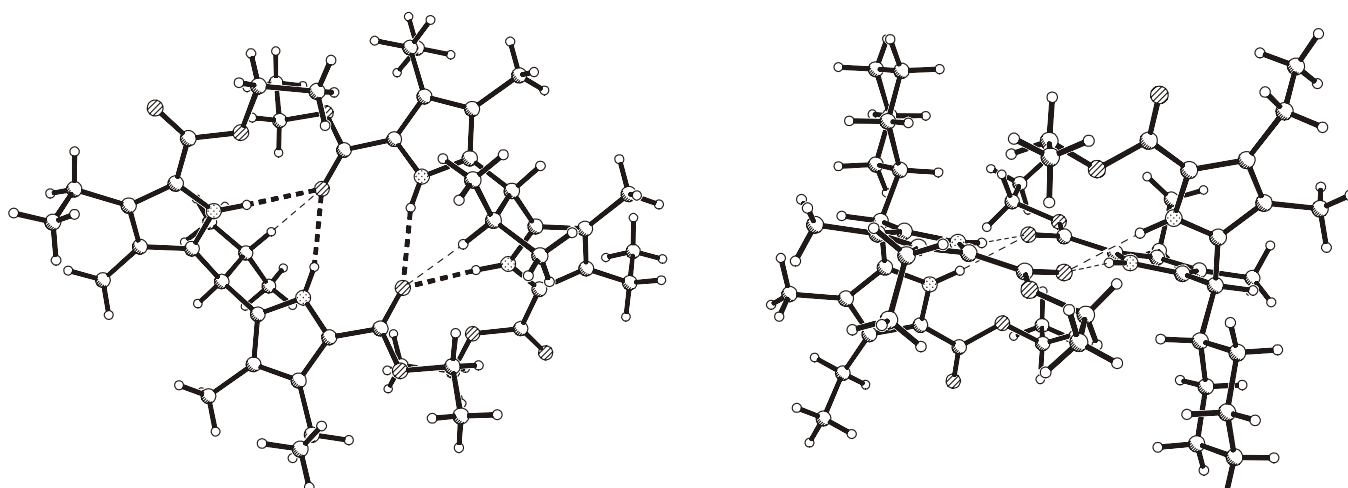


Figure 3 View of the hydrogen-bonded dimers formed by **3** (left) and a side view of one of the dimers formed by **5** (right) in the crystal. Dashed lines indicate classical hydrogen bonds, weak dashed lines in the left panel indicate C–H...O interactions.

Table 2. List of hydrogen bonds and interactions in the crystal structures (Å, deg).

#	D-H-A	D-H (Å)	H...A	D...A	D-H...A	symmetry code
1	N1-H1-O1	0.88	2.13	2.971(2)	159.0	1-x, 1-y, 1-z
	N2-H2-O1	0.88	2.11	2.942(2)	157.0	1-x, 1-y, 1-z
	C12-H12A-O3	0.99	2.57	3.237(3)	125.0	x, y, -1+z
	C51-H51A-O1	0.99	2.60	3.506(3)	153.0	1-x, 1-y, 1-z
	C81-H81A-O3	0.99	2.55	3.102(3)	115.0	—
2A	N1-H1-O3	0.88	2.08	2.952(5)	168.4	-x, -y, -z+1
	N2-H2-O3	0.88	2.23	3.034(5)	147.5	-x, -y, -z+1
2B	N1-H1-O3	0.88	2.15	3.010(3)	167.1	-x+1, -y+1, -z
	N2-H2-O3	0.88	2.14	2.989(2)	162.8	-x+1, -y+1, -z
	C12-H12B-O1	0.99	2.45	3.391(3)	157.0	-x+1, -y+1, -z+1
	C22-H22B-O1	0.99	2.59	3.180(3)	117.9	—
	C51-H51B-O3	0.99	2.59	3.511(3)	155.3	-x+1, -y+1, -z
3	N1-H1-O3	0.88	2.15	3.002(4)	162.2	-x, -y, 1-z
	N2-H2-O3	0.88	2.11	2.964(4)	163.9	-x, -y, 1-z
	C21-H21B-O1	0.99	2.48	3.125(6)	122.2	—
	C51-H51-O3	1.00	2.56	3.498(5)	155.3	-x, -y, 1-z
	C92-H92B-O1	0.99	2.39	3.148(5)	133.4	x, -y, 1+
4	N1-H1-O1	0.88	2.07	2.947(3)	172.2	1-x, 1-y, 1-z
	N2-H2-O1	0.88	2.09	2.970(3)	173.5	1-x, 1-y, 1-z
	C51-H51-O1	1.00	2.68	3.605(3)	153.3	1-x, 1-y, 1-z
	C22-H22B-O2	0.99	2.59	3.159(4)	116.9	—
	C32-H32A-O3	0.98	2.56	3.496(4)	159.2	x, -1+y, z
5	N1-H1-O1	0.88	2.10	2.967(4)	170.8	-x+1, -y+1, -z+1
	N2-H2-O1	0.88	2.09	2.968(4)	171.9	-x+1, -y+1, -z+1
	N1A-H1A-O3A	0.88	2.14	3.005(4)	166.6	-x+1, -y+1, z
	N2A-H2A-O3A	0.88	2.08	2.934(4)	161.8	-x+1, -y+1, z
	C12-H12B-O1A	0.99	2.59	3.377(5)	136.5	—
	C21-H21B-O2	0.99	2.45	2.959(5)	111.4	—
	C21A-H21D-O2A	0.99	2.46	2.958(5)	110.7	—
	C81-H81A-O3	0.99	2.42	3.120(5)	126.8	—
6	N1-H1-O1	0.88	2.17	3.032(3)	165.0	1-x, -y, 1-z
	N2-H2-O1	0.88	2.26	2.912(3)	130.5	1-x, -y, 1-z
	C21-H21A-O2	0.99	2.50	2.996(3)	110.3	—
	C52-H52-N1	0.95	2.57	3.211(3)	125.5	—
	C81-H81B-O4	0.99	2.38	3.071(4)	126.0	—
7	N2-H2A-O3	0.88	2.05	2.898(3)	162.9	1-x, 1-y, 1-z
	C57-H57A-N1	0.98	2.59	3.331(5)	132.9	-1+x, y, z
	C81-H81A-O4	0.99	2.47	3.030(4)	115.3	—
8	N1-H1-O1	0.88	2.01	2.872(3)	168.1	2-x, 1-y, 1-z
	N2-H2A-O3	0.88	2.10	2.975(3)	171.9	1-x, 1-y, -z
	C81-H81A-O4	0.98	2.43	2.924(4)	110.7	—
	C92-H92B-Cl1	0.99	2.83	3.676(4)	144.2	1-x, 1-y, -z

pyrrole nitrogen atoms (N1) exhibits a close intermolecular contact with an aromatic C–H donor (H52). A novel feature of this structure is a CH₂... π -aryl contact. H12 is located over one of the benzene rings of the naphthalene unit (C51, C52, C53, C54, C55, C59) with a separation of 2.83 Å. Note, that α unsubstituted dipyrromethanes exhibit N–H...pyrrole interactions as the most prominent feature of the crystal packing.⁸

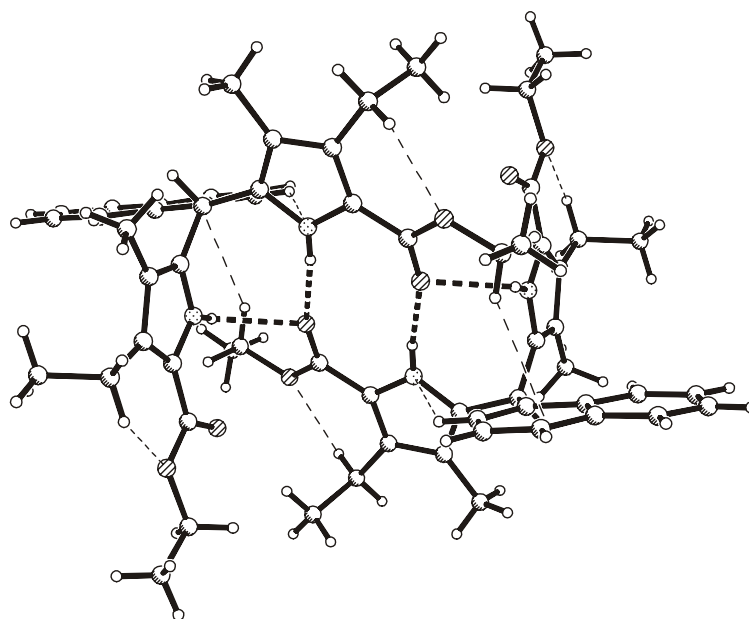


Figure 4 View of the hydrogen-bonded dimers formed by **6** in the crystal. Heavy dashed lines indicate classical hydrogen bonds, weak dashed lines indicate putative C-H...O and C-H...aryl interactions.

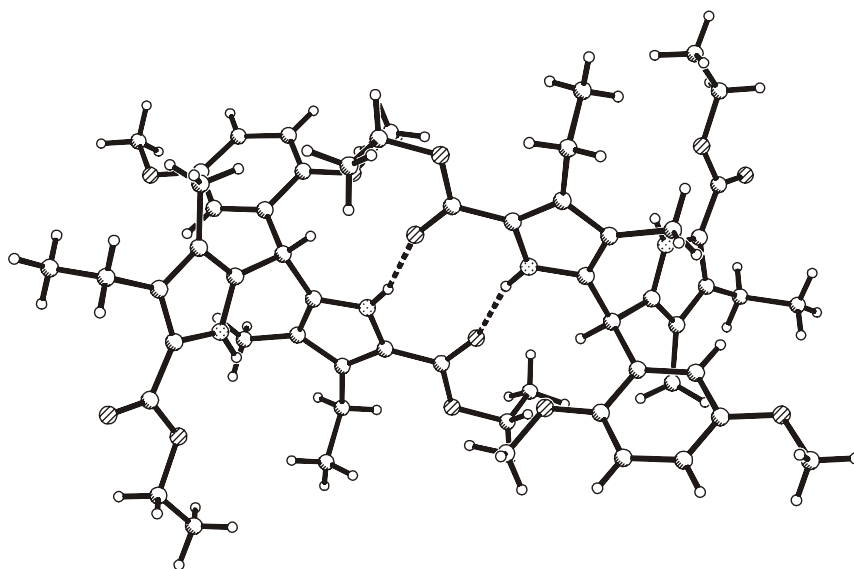


Figure 5 View of the hydrogen-bonded dimers (dashes) formed by **7** in the crystal. Weaker interactions and solvent molecules have been omitted for clarity.

The structure of the second meso aryl derivative (**7**), exhibits a completely different arrangement in the crystal. Again, dimers are formed by classical hydrogen bonds, however, involving only one N–H donor (N2) being coordinated to one carbonyl acceptor (O3) (Figure 5). The second NH (N1) is involved in a weak interaction with an aryl methoxy group (C57), additionally a weak intermolecular contact between the C81 methylene group and O4 is observed. The ester group not involved in bonding to the N–H donor is utilized for intramolecular hydrogen bonds involving a methanol of solvation. O1 is separated from O1S by 2.873 Å, which in turn is loosely bound by the C93 methyl group (H93A...O1S = 2.52 Å).

The structure of the dipyrromethane (**8**) with a meso C=CCl unit was determined for comparison. The structural parameters of the meso bridge are comparable to related compounds¹⁷ and the pyrrole tilt is

similar to that in other structures reported here. However, here the N–H vectors point in opposite directions resulting in the formation of polymers in the crystal (Figure 6). Presumably a $\uparrow\uparrow$ orientation in conjunction with the sp^2 hybridized meso center is of higher energy than the structure realized by rotation about the C5–C6 bond. Each N–H donor forms a hydrogen bond with one carbonyl acceptor group. In addition, a weak intermolecular contact involving O4 is observed (see Table 2), as is an intramolecular $CH_2\cdots Cl$ contact.

In retrospect, all meso alkyl dipyrromethanes and the aryl derivative (**6**) exhibit 3-center hydrogen bonds involving two N–H donors and one C=O acceptor as the major feature. Surprisingly, the effect of different meso and β -substituent combinations, i.e., different degrees of steric interactions is rather small. Effects are mainly noticed in the type and strength of secondary C–H $\cdots$ O interactions and in individual torsion angles (Table 1). A noticeable feature is that all meso alkyl derivatives exhibit crystalline modifications in which a ipso C–H unit is oriented in a way to form at least weak interactions with the carbonyl oxygen atoms involved in classic hydrogen bonds.

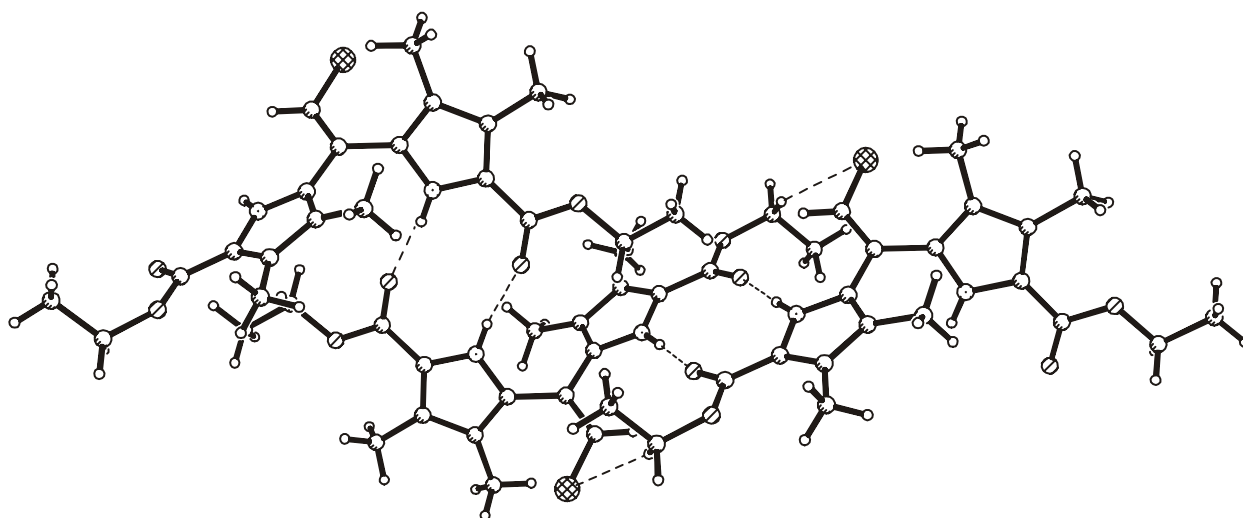


Figure 6 View of the molecular arrangement of **8** in the crystal. Dashed lines indicate hydrogen bonds and C–H $\cdots$ Cl interactions.

EXPERIMENTAL

The compounds were synthesized as described in the literature.^{10,11,17} Crystals were handled as described by Hope¹⁸ and experimental details for the data collections and structure refinements are compiled in Table 3. The structures were typically solved using Direct Methods of SHELXS,¹⁹ for **6** SIR92²⁰ and for **7** SHELXD²¹ was used. The structures were refined against $|F^2|$ using SHELXL,²² absorption and extinction effects were typically disregarded. Only for structure (**8**) an absorption correction was performed using the XABS2 program.²³ Hydrogen atoms were located in difference maps and refined using a standard riding model. The program PLATON was used for analysis of some of the inter- and intramolecular packing effects.²⁴

Table 3. Summary of crystal data, data collection and refinement for the crystal structure determinations.

Compound	1	2 tricl. A	2 tricl. B	3	4
chemical formula	C ₂₃ H ₃₄ N ₂ O ₄	C ₂₇ H ₄₂ N ₂ O ₄	C ₂₇ H ₄₂ N ₂ O ₄	C ₂₄ H ₃₆ N ₂ O ₄	C ₂₈ H ₄₄ N ₂ O ₄
mol. wt.	402.52	458.63	458.63	416.55	472.65
color	colorless	colorless	colorless	colorless	colorless
habit	block	cube	plate	cube	plate
crystal size (mm)	0.65×0.25×0.1	0.15×0.15×0.15	0.5×0.13×0.12	0.23×0.23 ×0.23	0.36×0.19×0.05
lattice type	triclinic	triclinic	triclinic	triclinic	triclinic
space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
<i>a</i> (Å)	8.666(2)	6.829(2)	8.970(5)	8.791(2)	8.6638(17)
<i>b</i> (Å)	11.099(2)	12.991(4)	10.811(5)	11.107(2)	11.492(2)
<i>c</i> (Å)	12.634(4)	15.224(4)	14.008(6)	12.684(3)	15.186(3)
α (°)	73.31(2)	90.28(3)	73.99(4)	79.42(2)	69.69(3)
β (°)	79.38(2)	98.18(2)	80.98(4)	79.99(2)	79.76(3)
γ (°)	81.42(2)	94.43(2)	83.16(4)	83.64(2)	69.67(3)
<i>V</i> (Å ³)	1138.1(5)	1332.7(7)	1285.5(11)	1194.5(5)	1326.9(6)
<i>Z</i>	2	2	2	2	2
<i>d</i> _{calc} (Mg m ⁻³)	1.175	1.143	1.185	1.158	1.183
radiation	Mo K α	Cu K α	Mo K α	Cu K α	Cu K α
λ (Å)	0.71073	1.54178	0.71073	1.54178	1.54178
μ (mm ⁻¹)	0.080	0.603	0.079	0.627	0.619
<i>T</i> (K)	130	130	126	130	126
θ_{max} (°)	27.54	57.04	27.5	57.03	57.26
collec. reflections	5389	3971	6277	3475	3896
indep. reflections	5126	3606	5905	3226	3593
reflections	3382	2526	4136	2495	3120
<i>F</i> > 4.0 σ (<i>F</i>)					
<i>R</i> _{int}	0.0251	0.0743	0.0395	0.0547	0.092
Parameters	269	306	305	279	307
Δ/ρ_{max} (e Å ⁻³)	0.005	0.000	0.000	0.000	0.000
<i>S</i>	0.975	1.035	1.020	1.025	1.053
<i>R</i> 1 [<i>F</i> > 4.0 σ (<i>F</i>)]	0.0569	0.0966	0.0525	0.0836	0.0664
<i>wR</i> 2 (all data)	0.1624	0.2534	0.1288	0.2385	0.1930

Crystals were obtained by liquid diffusion from CH₂Cl₂/*n*-hexane; triclinic **2A** and **7** was obtained from CH₂Cl₂/CH₃OH. In structure (**1**) the methyl group (C93) of the ester not involved in a classical hydrogen bond showed high thermal libration. The structure of **2A** is of low quality and showed large thermal librational movement for 7-ethyl and 8-propyl group. C83 was refined as disordered over two positions with equal occupancy. Nevertheless, the C-C bond lengths remained unreasonably long. Different disorder models gave no improvement over the present refinement. No search for weak C–H•••O interactions was made for this structure. Compound (**7**) crystallized with a methanol of solvation, which was refined with 50 % occupancy. No hydrogen atoms were included in the refinement for the methanol. In addition, the structure showed disorder for the C13 methyl group that was refined as disordered over two split positions with equal occupancy. CCDC 258893–258991 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Table 3. Continued.

Compound	5	6	7	8
chemical formula	C ₂₇ H ₄₀ N ₂ O ₄	C ₃₁ H ₃₆ N ₂ O ₄	C ₂₉ H ₃₈ N ₂ O ₆ •½CH ₃ OH	C ₂₀ H ₂₅ ClN ₂ O ₄
mol. wt.	456.61	500.62	526.64	392.87
color	colorless	colorless	colorless	colorless
habit	cube	parallelepiped	block	plate
crystal size (mm)	0.15×0.15×0.15	0.55×0.1×0.09	0.4×0.3×0.2	0.4×0.3×0.1
lattice type	triclinic	triclinic	triclinic	triclinic
space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
<i>a</i> (Å)	11.946(5)	10.301(2)	9.853(4)	9.369(3)
<i>B</i> (Å)	14.596(5)	10.437(2)	10.941(3)	10.702(4)
<i>C</i> (Å)	17.247(7)	13.292(3)	15.230(4)	11.613(4)
α (°)	107.65(3)	98.85(3)	70.51(2)	104.69(3)
β (°)	101.60(3)	103.18(3)	87.36(3)	103.11(3)
γ (°)	108.54(3)	102.66(3)	69.68(2)	106.89(3)
<i>V</i> (Å ³)	2566(2)	1326.0(6)	1446.9(9)	1019.4(7)
<i>Z</i>	4	2	2	2
<i>d</i> _{calc} (Mg m ⁻³)	1.182	1.254	1.211	1.280
radiation	Cu K α	Cu K α	Mo K α	Cu K α
λ (Å)	1.54178	1.54178	0.71073	1.54178
μ (mm ⁻¹)	0.626	0.660	0.085	1.887
<i>T</i> (K)	130	130	130	130
θ_{max} (°)	56.46	54.30	27.50	56.18
collec. reflections	7179	3412	7042	2811
indep. reflections	6785	3193	6646	2666
reflections	4817	2762	4102	2394
<i>F</i> > 4.0 σ (<i>F</i>)				
<i>R</i> _{int}	0.0508	0.0317	0.0391	0.0413
Parameters	607	340	350	250
$\Delta\rho_{max}$ (e Å ⁻³)	0.000	0.000	0.000	0.000
<i>S</i>	1.007	1.017	1.020	1.039
<i>R</i> 1 [<i>F</i> >4.0 σ (<i>F</i>)]	0.0604	0.0607	0.0747	0.0574
w <i>R</i> 2 (all data)	0.1710	0.1726	0.2156	0.1413

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