Hydrogen bond patterns in aromatic and aliphatic dioximes

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Despite their established hydrogen bonding capability, oxime functional groups (–C(R′)=NOH) have received far less attention in supramolecular chemistry than their carboxyl and amide counterparts. Here we report a series of dioximes (R′=H, CH_3, NH_2) for which hydrogen bonding patterns have been examined in the solid state to establish the reliability of hydrogen-bonded synthons available for use in supramolecular syntheses using oximes. In all cases, network structures were formed, most frequently propagated through oxime–oxime O–H···N hydrogen-bonded dimer formation [$R_2^2(6)$ graph set] and less often using C(3) chain or $R_4^4(12)$ ring arrangements. Even in the systems where R′ = NH_2, robust and dominant oxime–oxime hydrogen bonding prevails, with amino groups playing a supporting role in network construction primarily *via* weaker N–H···O hydrogen bonds. The compounds studied are aromatic dioximes 1,3-C_6H_4(C(R′)=NOH)$_2$ **1**–**3** and 1,4-C_6H_4(C(R′)=NOH)$_2$ **4**–**6** (R′ = H, CH_3, NH_2), and aliphatic dioximes fumaramide dioxime **7** (R′ = NH_2) and succinamide dioxime **8** (R′ = NH_2).

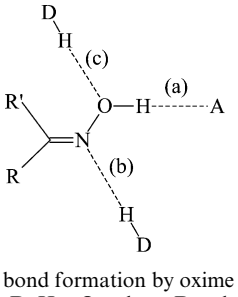
Introduction

In supramolecular chemistry a major aim is to control the aggregation of molecules *via* intermolecular interactions.[1] This is most readily achieved when such interactions are strong and directional. For this reason hydrogen bonds are often employed. More specifically, molecular building blocks can be designed to carry particular functional groups that are capable of recognition of other groups or of self-recognition through the formation of one or more hydrogen bonds. By such a synthetic approach even quite complex molecular aggregates (supermolecules) can be prepared in a deliberate manner.[2] Where infinite assemblies are formed, the opportunity arises to construct crystalline solids in which one-, two- or three-dimensional networks are propagated by hydrogen bonds.[3]

Despite studies establishing its capability to form hydrogen bonds,[4,5] the oxime functional group has received far less attention in supramolecular chemistry and crystal engineering[6–8] than have other groups such as carboxyl,[9] amide[10] and alcohol.[11] In an early study, Bertolasi *et al.* established that oximes are able to form three types of hydrogen bond (Scheme 1).[4] All other cases are rare by comparison. Formation of only an O–H···A hydrogen bond is typical of the situation in which another strong hydrogen bond acceptor group is present, as is illustrated by the structures of oxime derivatives of pyridine.[8b,c] The situation in which both O–H···A and D–H···N hydrogen bonds form is typified by the absence of other hydrogen bonding functional groups, or at least ones strong enough to compete with the oxime. Thus, O–H···N hydrogen bonds form between oxime groups, most often as either an $R_2^2(6)$[13] dimeric arrangement (**I**)[5a,6] or a C(3) catemer (**II**)[5f,g] resembling the $R_2^2(8)$ (**III**) and C(4) arrangements (**IV**, **V**) that are well established for carboxyl groups (Scheme 2).

One potential advantage to the use of oximes is the possibility of greater tunability by facile variation of the substituent R′ (Scheme 1), which is not present in carboxylic acids or primary amides. Choice of this substituent also permits the solubility of the oxime building block to be modified, facilitating supramolecular synthesis in a wider range of solvent systems. Oximes can also exhibit geometric isomerism about the C=N bond, though the *E*-isomer is thermodynamically preferred to the *Z*-isomer in most cases and interconversion in solution is insignificant at ambient temperatures.[6a,14] The orientation of the O–H group can, in principle, give rise to *synplanar* (C=N–O–H torsion angle close to 0°) or *antiperiplanar* (C=N–O–H torsion angle close to 180°) conformations, though overwhelmingly the latter is preferred.[4b]

In the present work we explore the efficacy of hydrogen-bonding arrangements **I** and **II** as supramolecular synthons[15]



Scheme 1 Hydrogen bond formation by oxime groups. (a) O–H···A, (b) D–H···N, and (c) D–H···O, where D = hydrogen bond donor, A = hydrogen bond acceptor.

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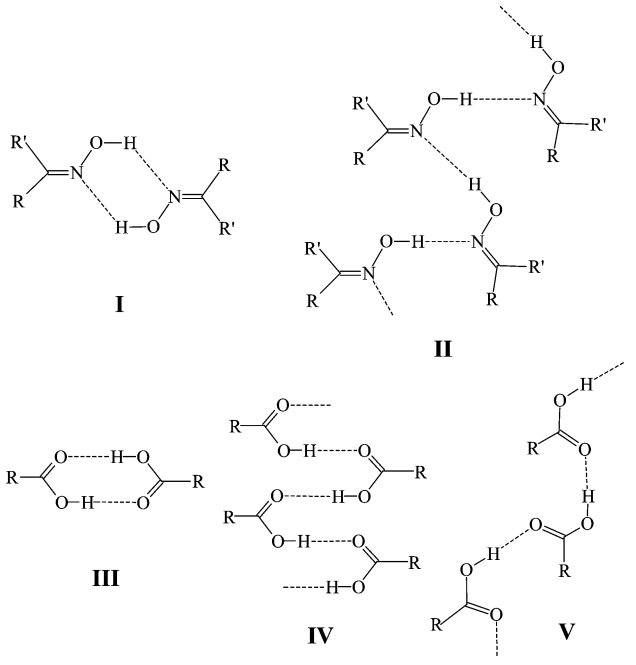


Scheme 2 Common hydrogen bonding arrangements for oxime (**I**, **II**) and carboxyl (**III**–**V**) groups. Oxime $R_2^2(6)$ dimer **I** (134 observations in the CSD[12b]); oxime C(3) catemer **II** (32 observations in the CSD); carboxyl $R_2^2(8)$ dimer **III**; carboxyl C(4) catemer **IV**; carboxyl C(4) catemer **V**.

in crystal syntheses using a series of dioxime molecules as building blocks. Dioximes linked by aromatic and aliphatic spacer groups are examined. The robustness of the oxime synthons is examined through modification of the hydrogen bonding capability of the substituent R′ (*viz.* R′ = H, CH_3 or NH_2).

Experimental

General procedures

All aldehydes, ketones and nitriles were purchased from Acros Organics or Avocado Research Chemicals Ltd. and used as received. NMR data were recorded on a Varian Unity Plus-300, Bruker Avance-300 or Varian-400 spectrometer. Chemical shifts are referenced to the residual proton signal of the deuterated solvents. Melting points are uncorrected. Elemental analyses were conducted by Atlantic Microanalytical Laboratories, Inc., Norcross, GA, USA or at the Applied Technology Division, BWTX Pantex, LLC.

Synthesis

Isophthalaldoxime, 1. To a solution of isophthalaldehyde (0.299 g, 2.23 mmol) in absolute ethanol–distilled water (*ca.* 20 mL : 5 mL) was added $NH_2OH{\cdot}HCl$ (0.510 g, 7.35 mmol) and Na_2CO_3 (0.391 g, 4.65 mmol). The reaction was stirred under reflux overnight. The solvent was removed and the product taken up in diethyl ether and washed with water. Yield 0.262 g (72%); mp 181–184 °C. ^{1}H NMR: δ_H (300 MHz; DMSO-d_6) 11.30 (2H, s), 8.16 (2H, s), 7.80 (1H, s), 7.60 (2H, dd), 7.42 (1H, t); ^{13}C NMR: δ_C (75 MHz; acetone-d_6) 149.07, 134.83, 129.94, 128.34, 125.57. Calc.: C, 58.53; H, 4.91; N, 17.06. Found: C, 58.73; H, 5.05; N, 16.78%. Colourless rectangular plates suitable for X-ray diffraction were grown by slow evaporation from acetone solution.

1,3-Diacetylbenzene dioxime, 2[16]. To a stirred solution of 1,3-diacetylbenzene (0.643 g; 3.96 mmol) in ethanol (*ca.* 20 mL) was added $NH_2OH{\cdot}HCl$ (0.616 g; 8.86 mmol), K_2CO_3 (0.677 g; 4.90 mmol) and distilled water (*ca.* 10 mL). The reaction was refluxed and monitored by TLC until no starting material was present. The solvent was removed and the product taken up in diethyl ether and washed with water. Yield: 0.710 g (93%); mp 206–208 °C; ^{1}H NMR: δ_H (300 MHz; acetone-d_6) 2.24 (6H, s), 7.37 (1H, t), 7.66 (1H, d), 7.68 (1H, d), 8.02 (1H, s), 10.31 (2H, s). ^{13}C NMR: δ_C (75 MHz; acetone-d_6) 11.63, 124.04, 126.92, 129.16, 138.35, 154.32. Calc.: C, 62.47; H, 6.30; N, 14.58. Found: C, 62.88; H, 6.48; N, 14.45%. Colourless rectangular plates suitable for X-ray diffraction were grown by slow evaporation from acetone solution.

1,3-Benzenediamide dioxime, 3[17]. 1,3-Dicyanobenzene (1.063 g, 8.294 mmol) was dissolved in ethanol (*ca.* 40 mL) together with $NH_2OH{\cdot}HCl$ (1.450 g, 20.86 mmol). To the ethanolic solution was added a solution of K_2CO_3 (1.458 g, 10.55 mmol) in distilled water (*ca.* 25 mL). The solution was refluxed overnight and monitored by TLC until no starting material remained. The solvent was removed and the white solid was washed with water. Yield: 0.650 g (43%); mp 180–181 °C. ^{1}H NMR: δ_H (300 MHz; acetone-d_6) 5.53 (4H, s), 7.37 (1H, t), 7.72 and 7.74 (2H, dd), 8.04 (1H, t), and 8.98 (2H, s); ^{13}C NMR: δ_C (75 MHz; acetone-d_6) 123.7, 127.1, 128.9, 134.6, 152.1. Calc: C, 49.48; H, 5.19; N, 28.85. Found: C, 49.42; H, 5.20; N, 28.56%. Colorless rectangular plates suitable for X-ray diffraction were grown by slow evaporation from nitromethane solution.

Terephthalaldoxime, 4. To a solution of terephthalaldehyde (0.500 g, 3.73 mmol) in absolute ethanol (*ca.* 20 mL) was added $NH_2OH{\cdot}HCl$ (0.524 g, 7.54 mmol) and Na_2CO_3 (0.315 g, 3.75 mmol). The reaction was stirred overnight at room temperature. The solvent was removed and the product taken up in diethyl ether and washed with water. Yield 0.489 g (80%); mp 219–220 °C. Calc.: C, 58.53; H, 4.91; N, 17.06. Found: C, 58.65; H, 4.96; N, 16.82%. ^{1}H NMR: δ_H (300 MHz; DMSO-d_6) 11.32 (s), 8.31 (s), 7.60 (s); ^{13}C NMR: δ_C (75 MHz; DMSO-d_6) 147.38, 133.43, and 126.32. Colourless needles suitable for X-ray diffraction were grown by slow evaporation from methanol solution.

1,4-Diacetylbenzene dioxime, 5[16]. 1,4-Diacetylbenzene (2.00 g; 12.3 mmol) was dissolved in ethanol (40 ml) with stirring and gentle heating. $NH_2OH{\cdot}HCl$ (1.71 g; 24.7 mmol) in 15 ml distilled water and Na_2CO_3 (1.31 g; 12.3 mmol) in 25 ml distilled water were added to the ethanolic 1,4-diacetylbenzene solution. The mixture was heated under reflux for 49 h, resulting in the formation of a white precipitate. After cooling the reaction mixture in an ice bath, the white precipitate was collected *via* vacuum filtration, washed with cold water, and dried with an aspirator. Yield: 2.15 g (91%); mp 170 °C (dec.); Calc: C, 62.47; H, 6.30; N, 14.58. Found: C, 62.14; H, 6.41; N, 14.57%. ^{1}H NMR: δ_H (400 MHz; acetone-d_6) 2.23 (6H, s), 7.70 (4H, s), and 10.33 (2H, s). Colourless rods suitable for X-ray diffraction were obtained by sublimation.

1,4-Benzenediamide dioxime, 6[17]. 1,4-Dicyanobenzene (1.009 g, 7.87 mmol) was dissolved in ethanol (*ca.* 40 mL) together with $NH_2OH{\cdot}HCl$ (1.380 g, 19.86 mmol). To the ethanolic solution was added a solution of K_2CO_3 (1.441 g, 10.21 mmol) in water (*ca.* 30 mL). The solution was refluxed overnight and monitored by TLC until no starting material remained. The solvent was removed and the white solid was washed with water. Yield: 1.07 g (70%); mp 210 °C (dec). Calc: C, 49.48; H, 5.19; N, 28.85. Found: C, 49.63; H, 5.27; N, 28.55%. ^{1}H NMR: δ_H (300 MHz; DMSO-d_6) 5.82 (2H, s), 7.66 (2H, s), 9.69 (1H, s); ^{13}C NMR: δ_C (75 MHz; DMSO-d_6) 125.1, 133.7, 150.5. Colourless rectangular plates suitable for X-ray

Table 1 Data collection and structure refinement details for **1**–**8**

	1	2	3	4	5	6	7	8
Formula	$C_8H_8N_2O_2$	$C_{10}H_{12}N_2O_2$	$C_8H_{10}N_4O_2$	$C_8H_8N_2O_2$	$C_{10}H_{12}N_2O_2$	$C_8H_{10}N_4O_2$	$C_4H_6N_4O_2$	$C_4H_8N_4O_2$
M	164.16	192.22	194.19	164.16	192.22	194.19	142.12	146.16
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space Group, Z	$C2/c$, 4	$P2_1/n$, 4	C2/c, 8	$C2/c$, 4	$P2_1/c$, 4	$P2_1/c$, 2	$Pca2_1$, 4	$P2_1/n$, 2
a/Å	10.1860(4)	3.897(2)	13.1956(15)	13.6142(8)	8.1553(14)	8.401(6)	16.6296(17)	4.8552(5)
b/Å	11.0510(3)	14.757(9)	12.1099(17)	4.5032(3)	14.208(3)	4.985(5)	3.6679(3)	5.1714(2)
c/Å	7.6536(3)	16.305(9)	11.8156(17)	13.1697(8)	8.5134(14)	10.714(10)	10.0529(10)	13.2126(8)
α/°	90	90	90	90	90	90	90	90
β/°	119.445(2)	91.668(14)	101.412(8)	107.263(4)	108.525(4)	107.41(7)	90	100.205(6)
γ/°	90	90	90	90	90	90	90	90
V/Å^3	750.25(5)	937.2(9)	1850.8(4)	771.03(8)	935.3(3)	428.2(7)	613.18(10)	326.50(4)
T/K	133(5)	148(5)	123(5)	173(5)	173(2)	133(5)	173(2)	173(2)
D_c/Mg m^{-3}	1.453	1.362	1.394	1.414	1.365	1.506	1.561	1.487
θ Range/°	2.94–28.27	1.86–28.34	2.30–28.29	3.13–28.28	2.63–28.31	2.54–28.27	2.45–27.49	3.13–22.49
Measured reflections	5209	8752	7314	5413	6388	5153	741	488
Indep. reflecns.	930	2237	2145	945	2152	1052	741	429
No. of parameters	72	175	167	71	57	84	91	46
$R_1(F)$ [$I > 2\sigma(I)$]	0.0423	0.0614	0.0475	0.0443	0.1139	0.0425	0.0368	0.0512
$wR_2(F^2)$ (all data)	0.0512	0.0902	0.1092	0.0807	0.3456	0.0779	0.0423	0.0520
$S(F^2)$ (all data)	1.065	1.039	0.974	1.028	0.782	1.017	1.071	1.224

diffraction were grown by slow evaporation from acetone solution.

Fumaramide dioxime, 7[18]**.** Fumaronitrile (2.50 g; 32.0 mmol) was dissolved in ethanol (20 ml) with stirring and gentle heating. $NH_2OH{\cdot}HCl$ (4.45 g; 64.0 mmol) in 20 ml distilled water and Na_2CO_3 (3.39 g; 32.0 mmol) in 30 ml distilled water were added to the ethanolic fumaronitrile solution. The mixture was stirred at room temperature for 48 h, during which an off-white precipitate formed. The vessel was cooled in an ice bath, and the solid was collected *via* vacuum filtration. The precipitate was dried with an aspirator and recrystallized from a 1:1 EtOH–H_2O mixture to yield white, flaky crystals. Yield: 3.18 g (69%); mp 213 °C (dec.). Calc: C, 33.33; H, 5.59; N, 38.87. Found: C, 32.99; H, 5.41; N, 41.90%. ^{1}H NMR: δ_H (400 MHz; DMSO-d_6) 5.53 (4H, s), 6.28 (2H, s), and 9.73 (2H, s). Colourless prisms suitable for X-ray diffraction were grown by slow evaporation from a saturated solution of **7** in absolute ethanol.

Succinamide dioxime, 8[19]**.** Succinonitrile (2.74 g; 34.2 mmol) was dissolved in ethanol (10 ml) with stirring. $NH_2OH{\cdot}HCl$ (4.76 g; 68.4 mmol) in 16 ml distilled water and Na_2CO_3 (3.63 g; 34.2 mmol) in 40 ml distilled water were added to the ethanolic succinonitrile solution. The mixture was stirred at room temperature for 72 hours. The resulting solution was concentrated under reduced pressure, producing a pale green precipitate. The precipitate was collected *via* vacuum filtration, dried with an aspirator, and recrystallized from a 1:1 EtOH–H_2O mixture to yield white, flaky crystals. Yield: 3.55 g (71%); mp 173–176 °C. Calc: C, 32.87; H, 6.90; N, 38.34. Found: C, 32.94; H, 6.70; N, 40.81%. ^{1}H NMR: δ_H (400 MHz; DMSO-d_6) 2.18 (4H, s), 5.35 (4H, s), 8.78 (2H, s). Colorless, hexagonal prisms suitable for X-ray diffraction were grown by slow evaporation from saturated solution of **8** in 1:1 EtOH–H_2O.

Crystallography†

Crystals of **1**–**8** were mounted on glass fibres and placed directly into the cold nitrogen stream of the diffractometer. Intensity data were collected using either a Bruker SMART diffractometer (**1**–**4**, **6**), a Bruker SMART 1000 diffractometer (**5**) or a Bruker P4 diffractometer (**7**, **8**) and corrected for absorption (**1**–**6**) by empirical means using the program SADABS[20] based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. Crystal structures were solved by direct methods and refined to convergence against all F^2 data using the SHELXTL suite of programs.[21] Non-hydrogen atoms were refined anisotropically without constraints for **1**–**4**, **6**–**8** and isotropically for **5**. For **1**–**4** and **6**–**8** all hydrogen atoms were located from Fourier difference maps. For **5** the oxime hydrogen atoms were located from difference maps; other hydrogen atoms were placed in calculated positions. The hydrogen atoms of **1**–**4** and **6** were refined isotropically without constraints. Those of **5**, **7** and **8** were refined using a riding model with fixed isotropic displacement parameters. Crystallographic details can be found in Table 1. Figures illustrating hydrogen bonding patterns were prepared using the program Mercury, version 1.1, produced by the Cambridge Crystallographic Data Centre.[12c] Searches of the Cambridge Structural Database (CSD)[12b] were conducted using version 5.23 (April, 2002 release).

† CCDC reference numbers 203661–203668. See http://www.rsc.org/suppdata/nj/b3/b301045g/ for crystallographic data in .cif or other electronic format.

Results

Two series of related benzene dioxime compounds, 1,3-C_6H_4(C(R′)=NOH)$_2$ **1**–**3** and 1,4-C_6H_4(C(R′)=NOH)$_2$ **4**–**6** (R′ = H, CH_3, NH_2; Fig. 1), have been synthesized and their crystal structures are examined here in order to explore the efficacy of oxime–oxime hydrogen bonding in the non-covalent synthesis of crystalline solids. The related aliphatic dioximes fumaramidoxime **7** (R′ = NH_2) and succinamidoxime **8** (R′ = NH_2; Fig. 1), have also been prepared and are compared with their aromatic counterparts.

1,3-Benzene dioximes (R′ = H, CH_3, NH_2). Each of the three benzene-1,3-dioxime compounds (**1**–**3**) adopts a structure in which the molecular units are linked *via* oxime-oxime hydrogen bonds. The aldoxime (R′ = H) **1** and ketoxime (R′ = CH_3) **2** form 1D tapes propagated *via* $R_2^2(6)$ synthon **I** (Scheme 2). The molecular conformations of **1** and **2** differ in the relative orientations of the oxime groups (Fig. 1) leading to generation of a linear tape for **1** and a zigzag tape for **2**

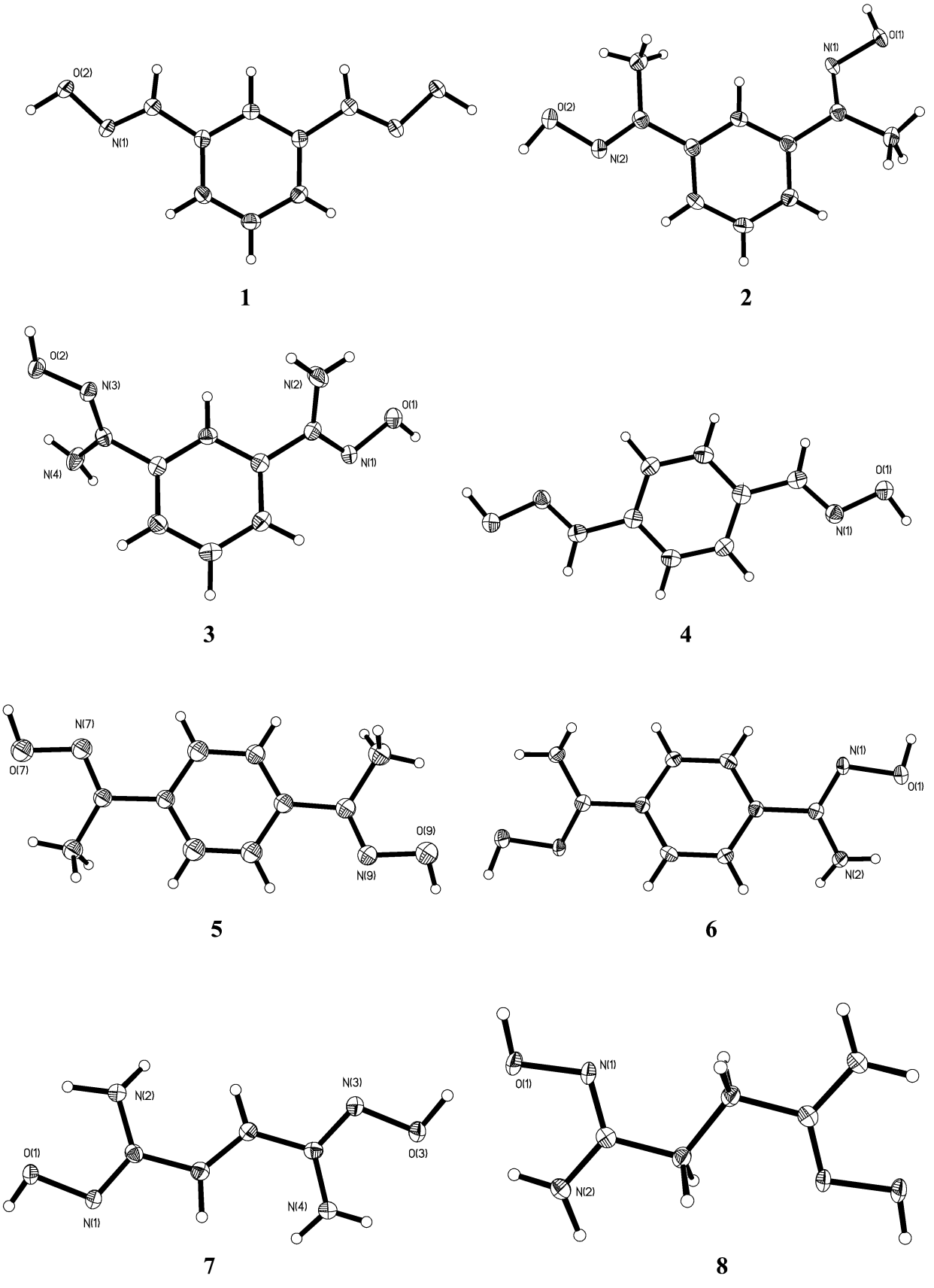


Fig. 1 Molecular structures of isophthalaldoxime (**1**), 1,3-diacetylbenzene dioxime (**2**), 1,3-benzenediamide dioxime (**3**), terephthalaldoxime (**4**), 1,4-diacetylbenzene dioxime (**5**), 1,4-benzenediamide dioxime (**6**), fumaramide dioxime (**7**) and succinamide dioxime (**8**). All are shown with non-hydrogen atoms represented as 50% probability ellipsoids.

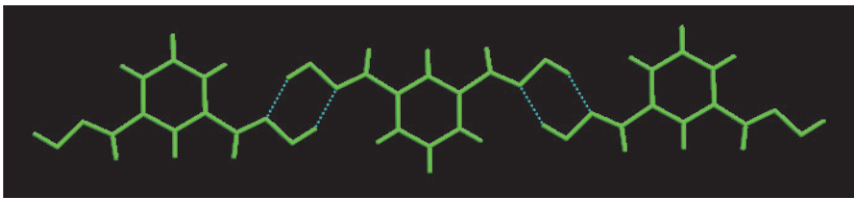


Fig. 2 Crystal structure of **1** showing linear hydrogen-bonded tape propagated *via* $R_2^2(6)$ O–H···N hydrogen-bonded rings. (O)H···N 1.878 Å, O–H···N 151.0°.

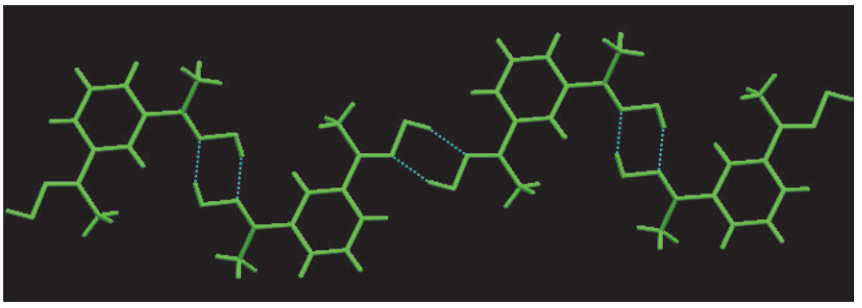
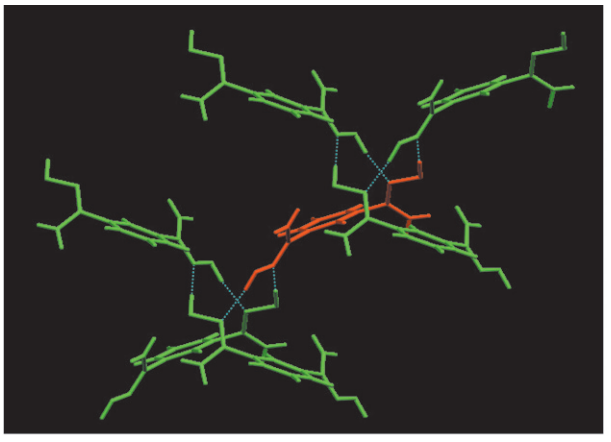
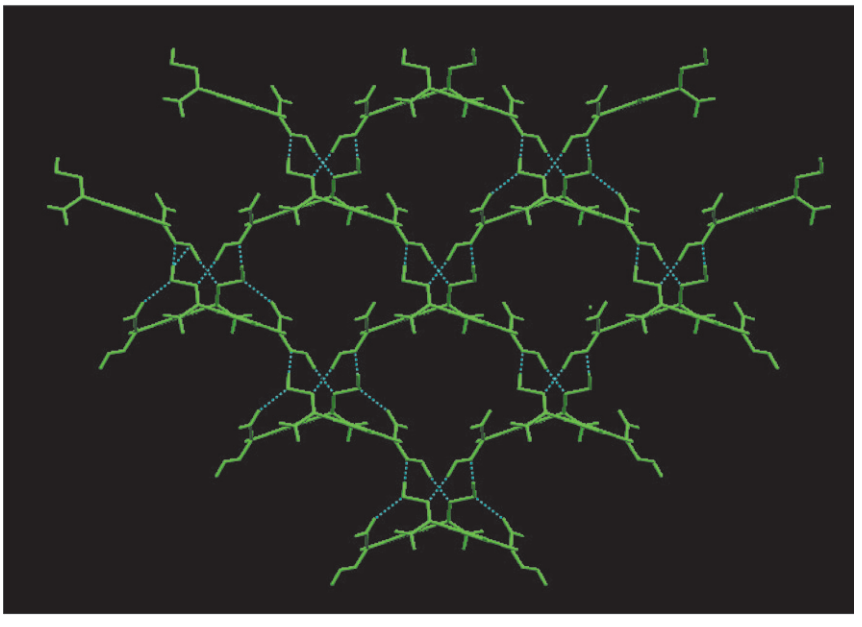


Fig. 3 Crystal structure of **2** showing zigzag hydrogen-bonded tape propagated *via* $R_2^2(6)$ O–H···N hydrogen-bonded rings. (O)H···N 1.858 Å, O–H···N 156.2°; (O)H···N 1.854 Å; O–H···N 159.9°.



(a)



(b)

Fig. 4 Crystal structure of **3** showing: (a) two $R_4^4(12)$ hydrogen-bonded rings linked by one molecule of **3** (in red); (b) one hydrogen-bonded layer. (O)H···N 1.873 Å, O–H···N 158.1°; intralayer (N)H···O 2.201 Å, N–H···N 147.3° (shown); interlayer (N)H···O 2.234 Å, N–H···O 133.8° (not shown).

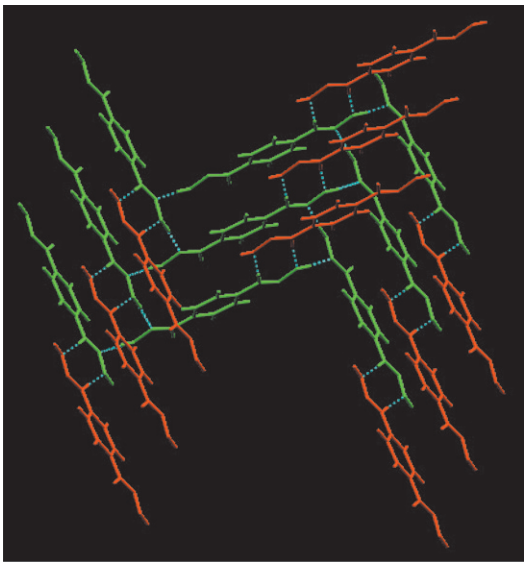


Fig. 5 Structure of **4** showing C(3) O–H···N hydrogen-bonded chains linking molecules shown in green within one layer and $R_2^2(8)$ C–H···O hydrogen-bonded rings linking molecules shown in green with those shown in red from a neighbouring layer. (O)H···N 1.797 Å, O–H···N 174.8°; (C)H···O 2.370 Å, C–H···O 175.3°.

(Figs. 2 and 3, respectively). The oxime functions in **1** are coplanar with the aromatic ring, whereas the ketoxime groups in **2** are rotated by 21.1° and 29.3° about the C_{ring}–C_{oxime} bond. Oxime groups in 1,3-benzenediamide dioxime **3** ($R' = NH_2$) interact *via* neither ring synthon **I** nor chain synthon **II**. Rather each oxime group participates in a hydrogen-bonded $R_4^4(12)$ tetramer consisting of four O–H···N interactions (Fig. 4). Each molecule links two such ring arrangements (Fig. 4a) giving rise to a sheet structure (Fig. 4b). The amidoxime group ($C(NH_2)$=NOH) is twisted markedly out of the plane of the aromatic ring (C–C–N–H torsion angles 44.5° and 58.3°). The amino groups form additional N–H···O hydrogen bonds both within and between layers.

1,4-Benzene dioximes ($R' = H, CH_3, NH_2$). Compounds **4**–**6** adopt molecular conformations in which the oxime groups are oriented in a mutually opposed manner (Fig. 1). The primary means of association of the terephthalaldoxime molecules in **4** ($R' = H$) is *via* O–H···N hydrogen bonds that contribute to C(3) tapes at both ends of the molecule. This leads to a hydrogen-bonded layer structure (Fig. 5). Molecules within one layer (shown in green in Fig. 5) undergo additional hydrogen bonding to adjacent layers (shown in red in Fig. 5) through use of the aldehydic C–H groups, which participate in a $R_2^2(8)$ C–H···O hydrogen-bonded rings involving the oxime oxygen atom as a hydrogen bond acceptor. Compounds **5** ($R' = CH_3$) and **6** ($R' = NH_2$) adopt remarkably similar zigzag tape structures propagated *via* $R_2^2(6)$ O–H···N hydrogen-bonded rings formed between oxime moieties of neighbouring molecules (Figs. 6 and 7a). These resemble the tapes formed by **2**, though the modulation of the zigzag is less pronounced due to the 1,4- *vs.* 1,3-substitution pattern of the aromatic ring. The hydrogen-bonded polymers in **5** associate *via* close packing of these rods without formation of additional hydrogen bonds, similar to structures **1** and **2**. However, the amino groups in **6** are active in hydrogen bonding, as noted in the structure of **3**, and provide cross-linking between layers of O–H···N_{oxime} bonded polymers *via* N_{amino}–H···O hydrogen bonds involving oxime oxygen atoms as hydrogen bond acceptor groups (Fig. 7b).

Aliphatic dioximes ($R' = NH_2$). The crystal structures of fumaramide dioxime **7** and succinamide dioxime **8**, provide an opportunity for comparison where the rigid aromatic spacer in **6** between the two amidoxime ($C(NH_2)$=NOH) groups is replaced by either a rigid but shorter olefinic spacer (CH=CH) in **7** or a flexible alkyl spacer (CH_2CH_2) in **8**.

Fumaramide dioxime molecules form a hydrogen-bonded layer structure in which molecules within each layer are linked *via* C(3) O–H···N hydrogen bonded chains involving all oxime groups (Fig. 8a) in a manner resembling that observed in the structure of **4**. The amino groups are also active in hydrogen bonding, forming N–H···O hydrogen bonds that link together adjacent layers to give a three-dimensional hydrogen-bonded network (Fig. 8b).

Succinamide dioxime (**8**) molecules assemble *via* $R_2^2(6)$ O–H···N hydrogen-bonded rings formed between oxime groups into zigzag tapes (Fig. 9a) resembling those formed by **2**, **5** and **6**. Tapes are stacked in parallel manner into layers. Each tape is then cross-linked *via* amide–oxime N–H···O hydrogen bonds to tapes that run in an approximately orthogonal direction within adjacent layers (Fig. 9b,c).

Discussion

The clear message from the observed structures of **1**–**8** is that oxime–oxime O–H···N hydrogen bonds predominate in the association and organization of these compounds in the solid state. As such, these compounds represent a microcosm of all oxime structures. The most common manner of association is *via* $R_2^2(6)$ O–H···N hydrogen-bonded rings (synthon **I**), as observed in the structures of **1**, **2**, **5**, **6** and **8** and found to be most prevalent across all oxime structures (*vide supra*).[4a] The structures of **4** and **7** show oxime self-association *via* C(3) O–H···N hydrogen-bonded catemers (synthon **II**), while the network structure in **3** comprises nodes at which four oxime groups associate *via* a larger $R_4^4(12)$ O–H···N hydrogen-bonded ring[22] (**VI**, Scheme 3).

But what of the R′ groups? What is their role in determining the final arrangement in these structures? Perhaps most instructive is to consider the effect of changing the R′ group across the two series of aromatic dioximes. In the structures of **2** and **5** ($R' = CH_3$) the methyl group does not have a structure directing role to a first approximation in that it is not involved in any well-directed interactions between the

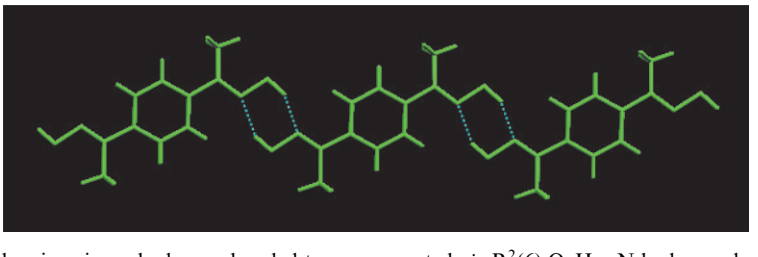
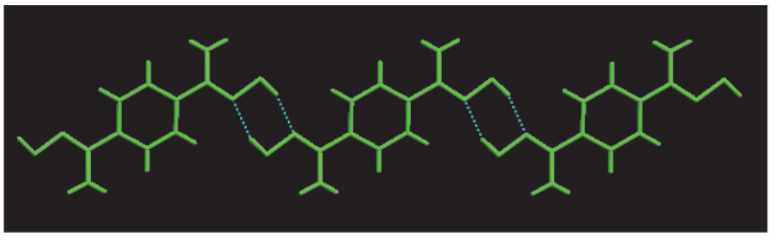


Fig. 6 Crystal structure of **5** showing zigzag hydrogen-bonded tape propagated *via* $R_2^2(6)$ O–H···N hydrogen-bonded rings. (O)H···N 1.925 Å, O–H···N 149.3°; (O)H···N 1.966 Å; O–H···N 144.5°.



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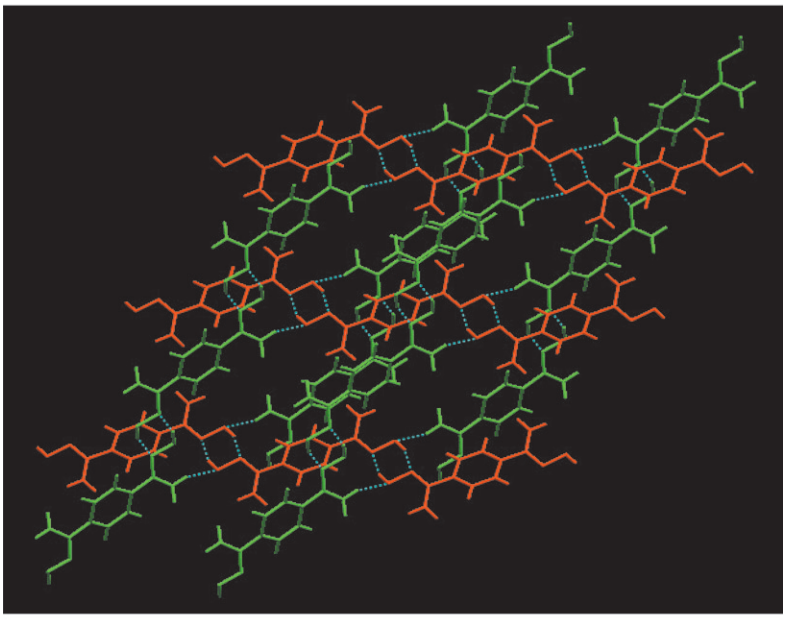

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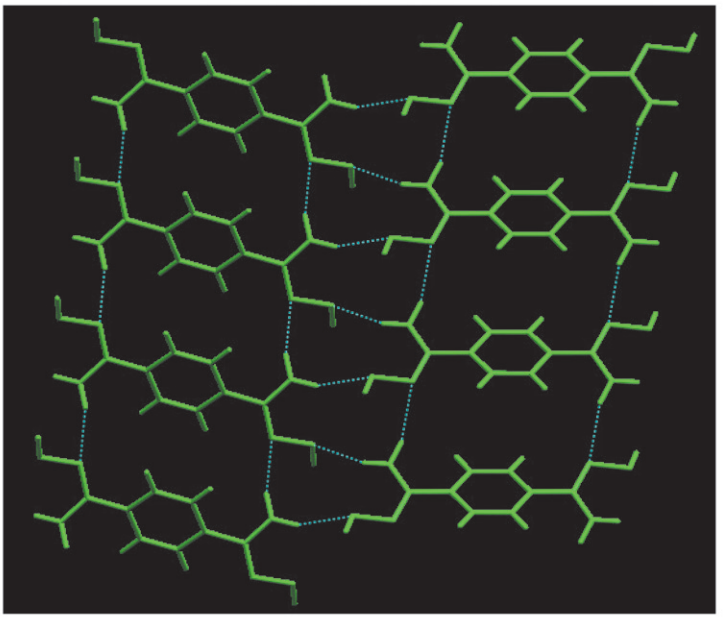


(c)

Fig. 7 Crystal structure of **6** showing: (a) zigzag hydrogen-bonded tape propagated *via* $R_2^2(6)$ O–H···N hydrogen-bonded rings [(O)H···N 1.873 Å, O–H···N 158.1°]; (b) cross-linking of tapes *via* weak N–H···O hydrogen bonds between amino and oxime groups [(N)H···O 2.199 Å, N–H···O 135.0°]; (c) hydrogen-bonded layer structure propagated *via* weak amine–oxime N–H···O and N–H···N hydrogen bonds [(N)H···N 2.278 Å, N–H···N 143.9°].

neighbouring 1D hydrogen-bonded polymers. A similar situationarises for the structure of **1** (R′ = H). However, in **4** (R′ = H) the layers propagated by oxime–oxime hydrogen bonds are further associated through the formation of hydrogen-bonded $R_2^2(8)$ C–H···O rings. Examination of the 107 aldoxime structures documented in the CSD indicates 12 occurrences of such an arrangement. However, in none of the previously published structures has this weak

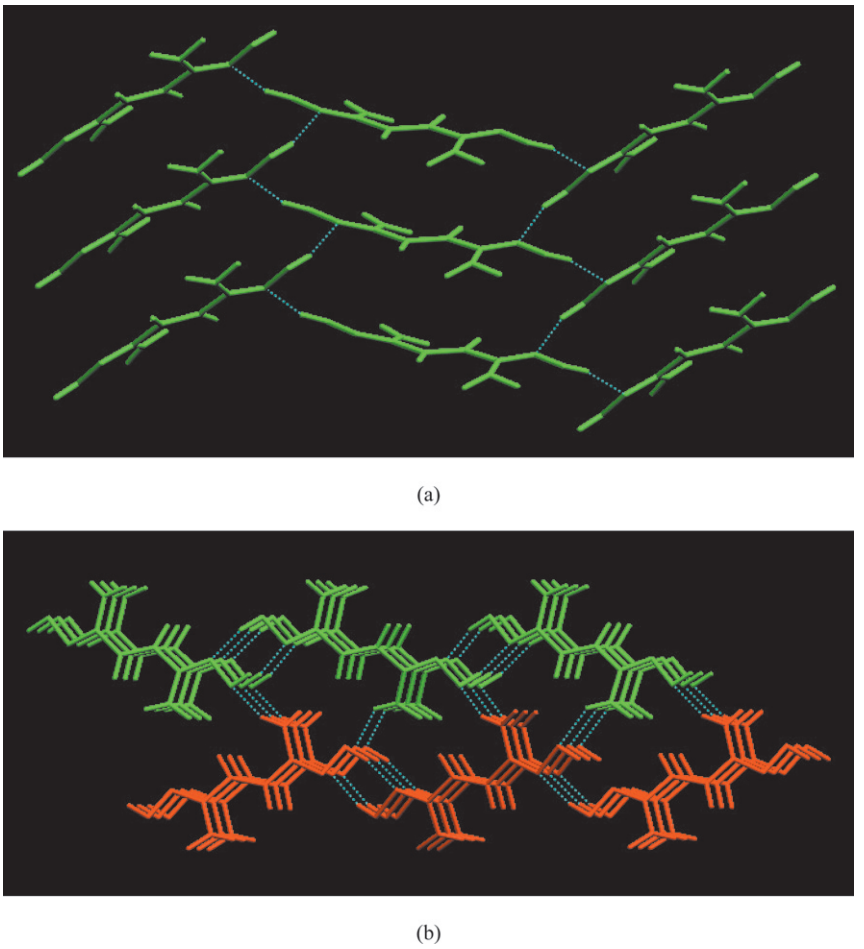


Fig. 8 Crystal structure of **7** showing: (a) a single hydrogen bonded layer formed *via* C(3) O–H···N hydrogen-bonded chains [(O)H···N 1.793 Å, O–H···N 161.3°; (O)H···N 1.897 Å, O–H···N 160.7°]; (b) two layers linked *via* N–H···O hydrogen bonds between amino and oxime groups [(N)H···O 2.302 Å, N–H···O 134.1°; (N)H···O 2.056 Å; N–H···O 149.2°].

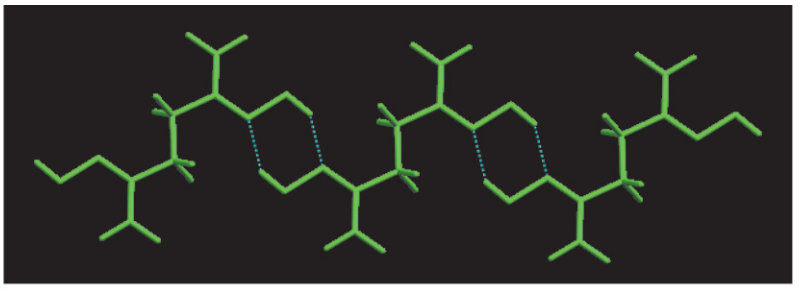
hydrogen-bonded potential synthon (**VIII**, Scheme 3) been specifically identified. In the structure of **3** and **6** (R′ = NH_2), while the shortest hydrogen bonds are of the O–H···N type involving the oxime groups, the NH_2 groups serve as hydrogen bond donors primarily forming hydrogen bonds to neighbouring molecules. These hydrogen bonds are longer and presumably weaker than those between oxime groups but serve an important role in cross linking the oxime–oxime hydrogen-bonded layers (**3**) or tapes (**6**) to generate three-dimensional hydrogen-bonded structures. In the structure of **3**, three of the four potential N–H donor groups form N–H···O hydrogen bonds. Unexpectedly, only one oxime oxygen atom accepts hydrogen bonds, necessarily forming three such interactions. Trifurcation at this acceptor group probably accounts for these (N)H···O interactions being quite long. The fourth N–H donor forms an N–H···π hydrogen bond with the aromatic ring [(N)H···π(centroid) 2.442 Å; N–H···π(centroid) 142.8°]. In the structure of **6**, each NH_2 group forms one N–H···O and one N–H···N hydrogen bond linking the molecules into a layer structure *via* hydrogen bonding arrangements that resemble the association of primary amides (Fig. 7c). The N–H···O hydrogen bonds also provide the means by which oxime–oxime hydrogen bonded tapes are cross-linked (Fig. 7b).

Thus, it is evident that by increasing the hydrogen bonding capability of the R′ groups a progressively more active role is imparted by these groups in defining the overall crystal structure. Nevertheless, in no case among those studied does this role prohibit the primary structural role of oxime–oxime O–H···N interactions, which form the shortest (strongest) hydrogen bonds. These conclusions are reinforced by examination of **7** and **8**, which can also be described in terms of a primary O–H···N hydrogen-bonding interaction between oxime groups that is supported by amine–oxime N–H···O interactions.

Conclusions

A series of aromatic and aliphatic dioximes has been examined with a view to their applicability hydrogen-bonded building blocks in the synthesis of crystalline solids. Oxime–oxime hydrogen bonds provide the dominant force controlling the resulting three-dimensional structures, even in the presence of competing hydrogen bond donor NH_2 groups. Since oxime groups contain an excess of hydrogen bond acceptor sites over hydrogen bond donor sites, additional hydrogen bond donor groups can be accommodated in the overall structural arrangement. Therefore, the potential usefulness of molecular building blocks containing oxime groups in the design of hydrogen-bonded network compounds seems evident. The most common hydrogen bonding arrangement in the systems studied is the $R_2^2(6)$ oxime dimer, as is the case in the larger population of structures containing oxime moieties.

There are clear parallels between the structures described of the aromatic dioximes and those of their dicarboxylic acid counterparts, isophthalic acid[23] and terephthalic acid,[24] which form zigzag and linear tape structures propagated *via* $R_2^2(8)$ O–H···O hydrogen-bonded linkages. It is further noted that amidoxime groups (C(NH_2)=NOH) can associate in a manner



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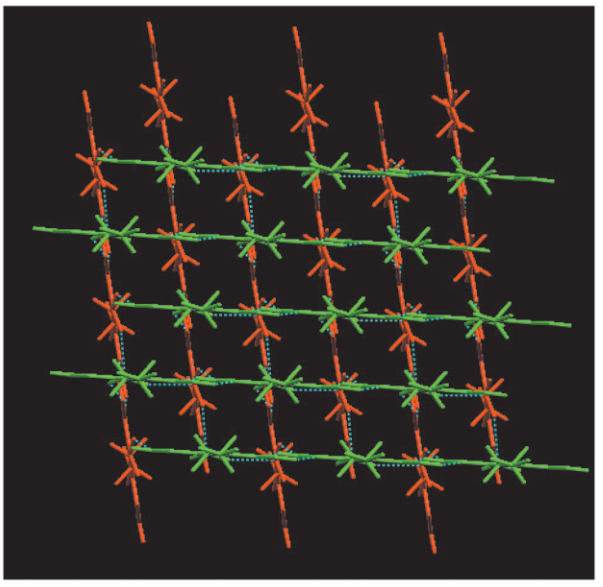

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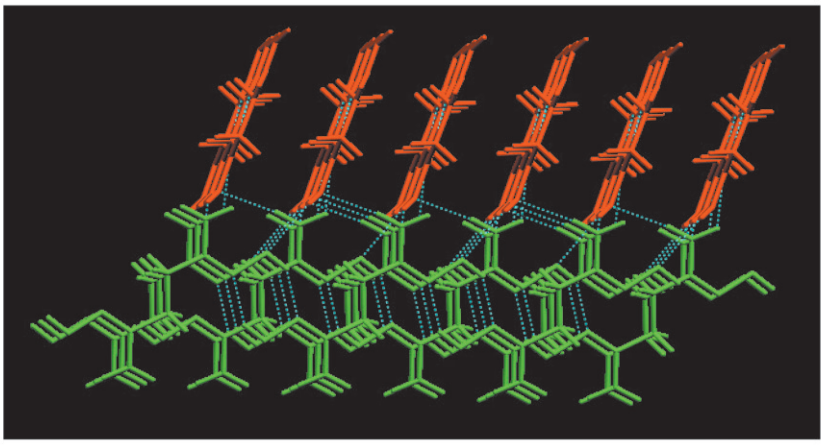

(c)

Fig. 9 Crystal structure of **8**. (a) Zigzag hydrogen-bonded tape propagated *via* $R_2^2(6)$ O–H···N hydrogen-bonded rings [(O)H···N 1.910 Å, O–H···N 141.3°]. (b) Stacking of adjacent layers (shown in green and red) of parallel tapes in "Lincoln Logs™" arrangement. (c) Alternative view showing two layers linked *via* N–H···O hydrogen bonds between amino and oxime groups [(N)H···O 2.300 Å; N–H···O 160.6°; (N)H···O 2.333 Å, N–H···O 123.5°].

that strongly resembles that of primary amides, permitting propagation of a hydrogen-bonded sheet in **6** (Fig. 7c) which closely resembles that observed in the structure of terephthalamide.[25]

The potential advantage of using oximes over carboxylic acids in designing hydrogen bonded networks is the possibility of "tuning" the characteristic of the extended network. This may be achieved through the relatively facile replacement of the R′ group by a variety of other groups that may exert a steric influence or participate in a strongly cohesive manner such as by further hydrogen bond formation. Such potential is under further investigation.

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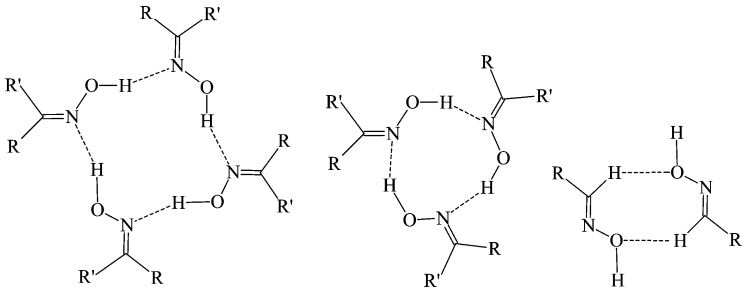

VI **VII** **VIII**

Scheme 3 Less common hydrogen bonding arrangements for oxime groups: $R_4^4(12)$ oxime tetramer **VI** (3 observations in CSD); related $R_3^3(9)$ oxime trimer **VII** (4 observations in CSD); aldoxime $R_2^2(8)$ C–H···O dimer **VIII** (12 observations in CSD).

of Missouri-St. Louis and Kansas State University is also appreciated.

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