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On the role of DMSO-O(lone pair)... π (arene), DMSO-S(lone pair)... π (arene) and S=O... π (arene) interactions in the crystal structures of dimethylsulphoxide (DMSO) solvates[†]

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[†] Full details of all surveyed structures are given in electronic format see DOI:

Abstract

Dimethylsulphoxide (DMSO) molecules in their all-organic solvates are shown to interact with arene rings of organic molecules *via* DMSO-O(lone pair)... π (arene) or DMSO-S(lone pair)... π (arene) interactions in approximately 5-6% of their crystal structures, often in

conjunction with conventional hydrogen bonding involving the O(DMSO) atom, to give rise to zero-, one- and two-dimensional supramolecular architectures. Zero-, one- and two-dimensional supramolecular architectures were also found to be sustained by parallel S=O... π (arene) interactions operating in combination with hydrogen bonding.

Introduction

A key concern in crystal engineering is the recognition of common modes of supramolecular association of specific functional groups with the goal to utilise this information for subsequent rational design of specific architectures. The Cambridge Structural Database (CSD)¹ offers an unrivalled resource which allows investigation of propensities of designated functional groups to engage in specific supramolecular synthons. In this context, it is perhaps surprising given their relatively large representation, that there have not been more systematic studies into aggregation patterns adopted by solvent molecules from which general principles of packing can be deduced. The notable exceptions to this observation are studies detailing intermolecular interactions of hydrates,² methanol solvates,³ chloroform and dichloromethane solvates,⁴ and, directly relevant to the present study, dimethylsulphoxide (DMSO) solvates.⁵ The latter study of a sub-set of DMSO-containing structures, showed two different hydrogen bonding environments, *i.e.* the DMSO-O atom was more often a double (60%) rather than a single hydrogen bond acceptor. The question then arises: how is DMSO incorporated into a crystal structure when the DMSO molecule does not participate in hydrogen bonds.

Bibliographic reviews have shown that element(lone pair)... π (aromatic ring) interactions are important in guiding supramolecular arrangements in a variety of heavy-element systems, *i.e.* tin,^{6,7} lead,⁸ arsenic-triad,^{9,10} selenium^{11,12} and tellurium;^{7,12} here “aromatic ring” incorporates arene, pyridyl, thienyl rings, *etc.* Lighter elements are also capable of forming analogous interactions, as first recognised in biological systems,^{13,14} specifically O(lone pair)... π (aromatic ring), imparting stability estimated to be less than 10 kJ mol⁻¹.¹⁵ Element(lone pair)... π (aromatic ring) interactions are also known in light-atom molecular structures,¹⁶ but with the exception of surveys of metal-carbonyls,¹⁷ [M]-C \equiv O, which feature O(lone pair)... π (arene) interactions

leading to specific supramolecular architectures, the role of light-element(lone pair)... π (aromatic ring) interactions remains largely unexplored, certainly in a systematic fashion. Herein, using the CSD¹ as a resource, DMSO solvates of all-organic systems are analysed for the presence of DMSO-O(lone pair)... π (arene) and DMSO-S(lone pair)... π (arene) interactions during which S=O... π (arene) interactions have also be revealed.

Search protocols

The protocols employed for the current survey were similar to those utilised in earlier bibliographic investigations of element(lp)... π (arene) interactions,⁶⁻¹² lp = lone pair. The Cambridge Structural Database (CSD: Version 5.34 + 2 updates)¹ was searched using CONQUEST (Version 1.15)¹⁸ with the structural protocols outlined in Fig. 1, for O(lp)... π (arene) interactions. The only key geometric restriction that was applied is that d , the maximum distance between the O or S atom and the centroid (Cg) of the arene ring, was set at 4.0 Å so as to capture all reasonable contacts, following recent literature precedents.¹⁹ This distance precludes putative ring-C-H...O or S interactions as under these circumstances the Cg...O or S separations would be well beyond 4.0 Å. The angle, θ , defined as the angle between the normal to the plane through the arene ring (V_1) and the vector passing through Cg to the heteroatom (V_2) gives a sense of the relative location of the O or S above the plane. It is noted that the maximum angles for the hits involving O and S were 37 and 26°, respectively.

Results

The search of all-organic, non-disordered single crystal structures with no errors yielded 474 DMSO solvates, of which 38 were identified to have DMSO... π (arene) contacts that fell within the geometric search criteria. These were manually evaluated and the results are discussed below with full details given in the ESI, including geometric parameters characterising hydrogen bonding interactions, when present. Geometric data characterising DMSO... π (arene) contacts are collected in Table 1. The 38 structures have been categorised into seven classes depending on the nature of the DMSO... π (arene) interaction and within each category, structures are arranged in terms of increasing aggregation patterns, zero- before one-dimensional, *etc.*, and within these, increasing DMSO...ring centroid(arene) separation.

Compounds **1-13**, Fig. 2, feature O(lp)... π (arene) interactions with **1-6** participating in zero-dimensional aggregation patterns. In two examples, **2**²¹ and **3**,²² Fig. 3a, the O(lp)... π (arene) interaction operates in isolation of other intermolecular association; these are accorded motif **I**. In **4**,²³ a two-molecule aggregate is sustained by a O–H...O(DMSO) hydrogen bond and a pair of these associate into a centrosymmetric four-molecule aggregate *via* O(lp)... π (arene) interactions, Fig. 3b, motif **II**. In each of **1**²⁰ and **6**,²⁵ hydrogen bonds are similarly formed as are O(lp)... π (arene) interactions but these are intramolecular, motif **III**, and do not contribute to additional supramolecular association. Such cooperative hydrogen bond/O(lp)... π (arene) interactions are illustrated for **5**²⁴ in Fig. 3c, where both cooperative (motif **III**) and stand-alone O(lp)... π (arene) (motif **I**) interactions are observed, there being three independent DMSO molecules in the structure.

In the remaining structures in this category, **7-13**, the O(lp)... π (arene) interactions are found in one-dimensional architectures, each of which also features conventional hydrogen bonding

interactions. In analogous interactions leading to motif **II**, in **11**³⁰ and **12**,³¹ Fig. 4a, hydrogen bonding interactions involving the DMSO-O atoms are found but, simultaneously, O(lp)... π (arene) interactions form with neighbouring molecules leading to a linear supramolecular chain, motif **IV**. In **9**,²⁸ a similar arrangement is found but the DMSO-O atom forms two hydrogen bonds. In motif **V**, found for **7**,²⁶ Fig. 4b, **10**²⁹ (the DMSO-O atom forms two hydrogen bonds) and **13**,³² two O(lp)... π (arene) bridges by two separate DMSO molecules provide links between successive organic residues, and three bridges are found in motif **VI**, adopted by **8**.²⁷

Fourteen, **14-27**, DMSO solvates feature DMSO-S(lp)... π (arene) interactions, Fig. 5, *i.e.* about equal to the number of structures featuring DMSO-O(lp)... π (arene) interactions. Six compounds, **14-19**, are incorporated within zero-dimensional aggregates. Five of the structures adopt motif **III**, where the DMSO-O is held in place by one (**17**³⁶), two (**15**³⁴, **16**³⁵ and **19**³⁸) and four (**14**³³) hydrogen bonds, and where the DMSO-S(lp)... π (arene) interaction is considered intramolecular. Structure **16**³⁵ is particularly notable as the DMSO-S(lp)... π (arene) interaction appears to be bifurcated, Fig. 6a. Similar bifurcated interactions are rarely observed but have been noted in some antimony(III) and bismuth(III)¹⁰ as well as in tellurium(IV) structures.¹² There is a sole example, **18**,³⁷ where the DMSO-S(lp)... π (arene) interaction (motif **II**) leads to the formation of centrosymmetric four-molecule aggregate, Fig. 6b. Here, the DMSO-O atom is associated with the organic molecule *via* three N-H...O hydrogen bonds, and the DMSO-S(lp)... π (arene) interaction is formed with a phenyl ring of a centrosymmetrically related organic molecule.

Five compounds feature bridging DMSO molecules whereby the O atom forms one (**22**⁴¹ and **23**⁴²) or two (**20**,³⁹ **21**,⁴⁰ Fig. 7, and **24**⁴³) hydrogen bonds, and the DMSO-S atom forms DMSO-

S(lp)... π (arene) interactions to neighbouring molecules/aggregates to form supramolecular chains, motif **IV**. Unlike structures with DMSO-O(lp)... π (arene) interactions, there are three examples of two-dimensional aggregation patterns sustained by a combination of DMSO-O hydrogen bonding and DMSO-S(lp)... π (arene) interactions, akin to motif **IV**. In motif **VII**, adopted by **25**,⁴⁴ Fig. 8, and **27**,⁴⁶ the DMSO-O forms O–H...O hydrogen bond with donors from different molecules and the DMSO-S(lp)... π (arene) interaction consolidates the two-dimensional array. A variation occurs in **26**⁴⁵ where the organic molecules are connected by a O–H...O bond and these are bridged by DMSO-O...H–O hydrogen bonds and DMSO-S(lp)... π (arene) interactions, motif **VIII**.

The remaining structures to be described, **28–38**, Fig. 9, are truly remarkable in that both DMSO-O(lp)... π (arene) and DMSO-S(lp)... π (arene) interactions are indicated based on the search protocols. In reality the S=O moiety lies over an arene ring suggesting a π ... π -type interaction best indicated as S=O... π (arene) in all but one example (**38**). The S=O... π (arene) interactions occur concurrently with conventional hydrogen bonds, and contribute to the stability of zero-, one- and two-dimensional aggregation patterns. The simplest examples are found in **29**,⁴⁸ Fig. 10a and **30**,⁴⁹ where the DMSO-O atom is held in place by a single hydrogen bond and S=O interacts with an adjacent ring (motif **IX**) to form two molecule aggregates. A simple variation occurs in **31**,⁵⁰ Fig. 10b, and **33**,⁵² where three-molecule aggregates result. Motif **X** sees the DMSO-O atom held in place by two hydrogen bonds as found in salt **32**,⁵¹ Fig. 10c, and **36**.⁵⁵ Structures **28**,⁴⁷ with two DMSO-O...H–N hydrogen bonds, Fig. 10d, and **35**,⁵⁴ with one DMSO-O...H–O hydrogen bond, Fig. 10e, are also zero-dimensional and worthy of special mention as the DMSO molecules bridge two rings. In **28**,⁴⁷ one bridge is provided by a DMSO-O(lp)... π (arene) interaction and the other by a S=O... π (arene) interaction (motif **XI**); each of the

two independent molecules comprising the asymmetric unit have similar association. In **35**,⁵⁴ one bridge is provided by a DMSO-S(lp)... π (arene) interaction and the other by a S=O... π (arene) interaction (motif **XII**). The remaining structures to be discussed are of higher dimensionality.

In **37**,⁵⁶ centrosymmetric three-molecule aggregates akin to motif **X** are formed with the connection between the molecules being two pairs of DMSO-O...H-N hydrogen bonds. The DMSO molecules simultaneously bridge neighbouring aggregates *via* S=O... π (arene) interactions to form a linear supramolecular chain (motif **XIII**), Fig. 11a. Two-dimensional arrays are found in each of co-crystal **34**⁵³ and **38**.⁵⁷ In the former (motif **XIV**), if the S=O... π (arene) interactions were ignored, the supramolecular architecture persists owing to an extensive network of hydrogen bonds. However, the supramolecular association is still of interest as two S=O moieties are bridged by a phenyl ring.

The supramolecular structure of **38**⁵⁷ appears to be the sole example where DMSO provides a bridging role by forming a DMSO-O(lp)... π (arene) as well as a DMSO-S(lp)... π (arene) interaction (motif **XV**). As illustrated in Fig. 11b, the DMSO-O atom forms a hydrogen bond with a hydroxyl group and simultaneously forms a DMSO-O(lp)... π (arene) interaction with a nearby phenyl ring. At the same time, the DMSO-S atom forms a DMSO-S(lp)... π (arene) interaction with the same ring, but symmetry related. In this way, a two-dimensional array is generated.

Discussion

A survey of the crystallographic literature reporting DMSO solvates in all-organic molecules provides evidence that the DMSO can form both DMSO-O(lp)... π (arene) and DMSO-

S(lp)... π (arene) interactions in their crystal structures. In a minority of cases, these operate in isolation of other intermolecular interactions to give rise to specific supramolecular architectures. More often than not, these interactions work in a complementary manner with conventional hydrogen bonding involving the O(DMSO) atom as the acceptor.⁵ More intriguing was the observation of parallel S=O... π (arene) interactions. In all, 15 different structural motifs were identified leading to zero-, one, and two-dimensional architectures based on these synthons. In terms of prevalence, the identification of DMSO-O(lp)... π (arene) and DMSO-S(lp)... π (arene) interactions in 27 out of 474 possible structures, suggest these occur in 5-6% of their crystal structures, which is an intermediate frequency when compared to a low 2-3% for tin(II)⁷ and lead(II)⁸ and a high 9% for bismuth(III) structures.¹⁰ The S=O... π (arene) interactions have a prevalence of 2-3%.

The investigation of supramolecular interactions involving π -systems is gaining prominence in the *Crystal Engineering* community.⁵⁸ Interactions between π -systems of aromatic rings are well-established⁵⁹ with studies on comparable C=O...C=O⁶⁰ and C \equiv N...C \equiv N⁶¹ interactions documented. While investigations of π ... π interactions involving disparate π -systems have not attracted the same systematic investigation, parallel interactions between C=O and an arene ring have been shown to be important in mediating solid-state transformations,⁶² persist in solution,⁶³ and contribute to the stability of crystal structures;^{64,65} interestingly, analogous C=O... π (arene) interactions were discussed prior to these studies.^{66,67} Analogous, S=O... π (arene) interactions are comparatively rare it seems, at least not disclosed in the original crystal structure analysis, with the work of Mak *et al.* being the notable exception.⁶⁸ The nature of element(lp)... π (arene) interactions are not yet fully understood yet have attracted the interest of theoreticians for several years.⁶⁹ Models appear to range from the lone-pair inducing significant polarisation and

interacting largely with the carbon atoms of the ring⁹ to interactions akin to those established for halogen bonding,⁷⁰ *i.e.* the lone pair has a positive hole, in other words more as a Lewis acid/base-type of interaction.⁷¹ Whatever the nature of the element(lp)... π (arene) interaction, the energy of stabilisation it contributes to a crystal structure is low, being less than 10 kJ/mol,¹⁵ *i.e.* comparable to a C–H... π (arene) interaction.⁷²

Conclusions

The systematic evaluation of crystal structures of DMSO solvates of all-organic molecules show that O(lp)... π (arene) and S(lp)... π (arene) interactions contribute to supramolecular cohesion independently of or, in the majority of cases, in conjunction with conventional hydrogen bonding involving the O-DMSO atom. Relatively unusual parallel S=O... π (arene) interactions have also been identified. The foregoing analysis suggests that O(lp)... π (arene), S(lp)... π (arene) and parallel S=O... π (arene) interactions should be included in any thorough analysis of crystal structures containing sulphonyl residues. That being stated, given their inherently weak nature their utilisation as a design element in crystal engineering is problematic.

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Table 1 Geometric parameters characterising DMSO... π (arene) interactions in **1-38**

Compound	CSD Ref. Code	d (Å)	θ (°)	Motif	Ref.
<i>Zero-dimensional aggregates featuring DMSO-O(lone pair)...π(arene) interactions</i>					
1	EGIJAG	3.24	22.4	III	20
		3.51	32.0		
2	EQAPUI	3.54	33.7	I	21
3	DELGEG	3.64	37.3	I	22
4	IKEYAZ	3.77	35.4	II	23
5	MAFJOU	3.04	16.8	I & III	24
		3.20	18.3		
		3.54	35.8		
6	VAWWAT	3.90	34.6	III	25
<i>One-dimensional aggregates featuring DMSO-O(lone pair)...π(arene) interactions</i>					
7	GABPEG	3.60	32.0	V	26
8	UVETOF	3.60	32.7	VI	27
9	YUNXAH	3.67	31.9	IV	28
10	YOKHIP	3.76	34.7	V	29
11	TACXAW	3.82	32.1	IV	30
12	TIVPEU	3.85	18.2	IV	31
13	CIDNEJ	3.87	37.4	V	32
<i>Zero-dimensional aggregates featuring DMSO-S(lone pair)...π(arene) interactions</i>					
14	NENSEF	3.38	11.0	III	33
		3.43	10.7		
15	YOPFOZ	3.56	24.0	III	34
16	QUCRAI	3.58	15.1	III	35
		3.77	23.9		
17	NAQDEQ	3.62	7.2	III	36
18	DISVAD	3.82	21.4	II	37
19	SAKMEY	3.85	25.3	III	38

One-dimensional aggregates featuring DMSO-S(lone pair)... π (arene) interactions

20	HITFOG	3.56	8.3	IV	39
21	YIZGEU	3.65	13.1	IV	40
		3.68	13.5		
22	AQABUQ	3.66	7.6	IV	41
23	MUGCEX	3.80	9.5	IV	42
24	COXWES	3.87	14.5	IV	43

Two-dimensional aggregates featuring DMSO-S(lone pair)... π (arene) interactions

25	WUJDOU	3.46	8.0	VII	44
		3.49	8.1		
26	EJIWAV	3.81	16.2	VIII	45
27	EPAVUN	3.88	25.9	VII	46

Aggregates featuring S=O... π (arene) interactions

28	FAFSOW	3.14	12.5 (O) &	XI	47
		3.39	19.8 (O)		
		3.64	7.9 (S)		
		3.18	17.4 (O) &		
		3.37	19.6 (O)		
		3.72	6.3 (S)		
29	NAWQOS	3.43	12.3 (O)	IX	48
		3.90	10.9 (S)		
30	IRUZOL	3.60	14.8 (O)	IX	49
		3.87	11.9 (S)		
31	VAJYEL	3.75	25.6 (O)	IX	50
		3.78	11.0 (S)		
32	QOVQAU	3.80	20.1 (O)	X	51
		3.62	15.3 (S)		
33	TAJGIW	3.80	24.0 (O)	IX	52
		3.53	5.0 (S)		
34	WOMGIP	3.87	25.9 (O)	XIV	53
		3.82	19.3 (S)		

35	JEZRIP	3.85	18.1 (O)	XII	54
		3.72	8.2 (S)		
		3.88	20.7 (S)		
36	TIVNOC	3.87	2.4 (O)	X	55
		3.67	20.3 (S)		
37	GUTBAZ	3.63	8.8 (O)	XIII	56
		3.76	15.8 (S)		

Two-dimensional aggregate featuring both DMSO-O(lone pair)... π (arene) and DMSO-S(lone pair)... π (arene) interactions

38	KUMHOP	3.81	33.7 (O)	XV	57
		3.77	2.3 (S)		

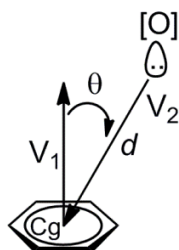


Fig. 1 An illustration of the search protocols and geometric parameters for establishing/characterising O(lone pair)... π (arene) interactions in DMSO solvates.

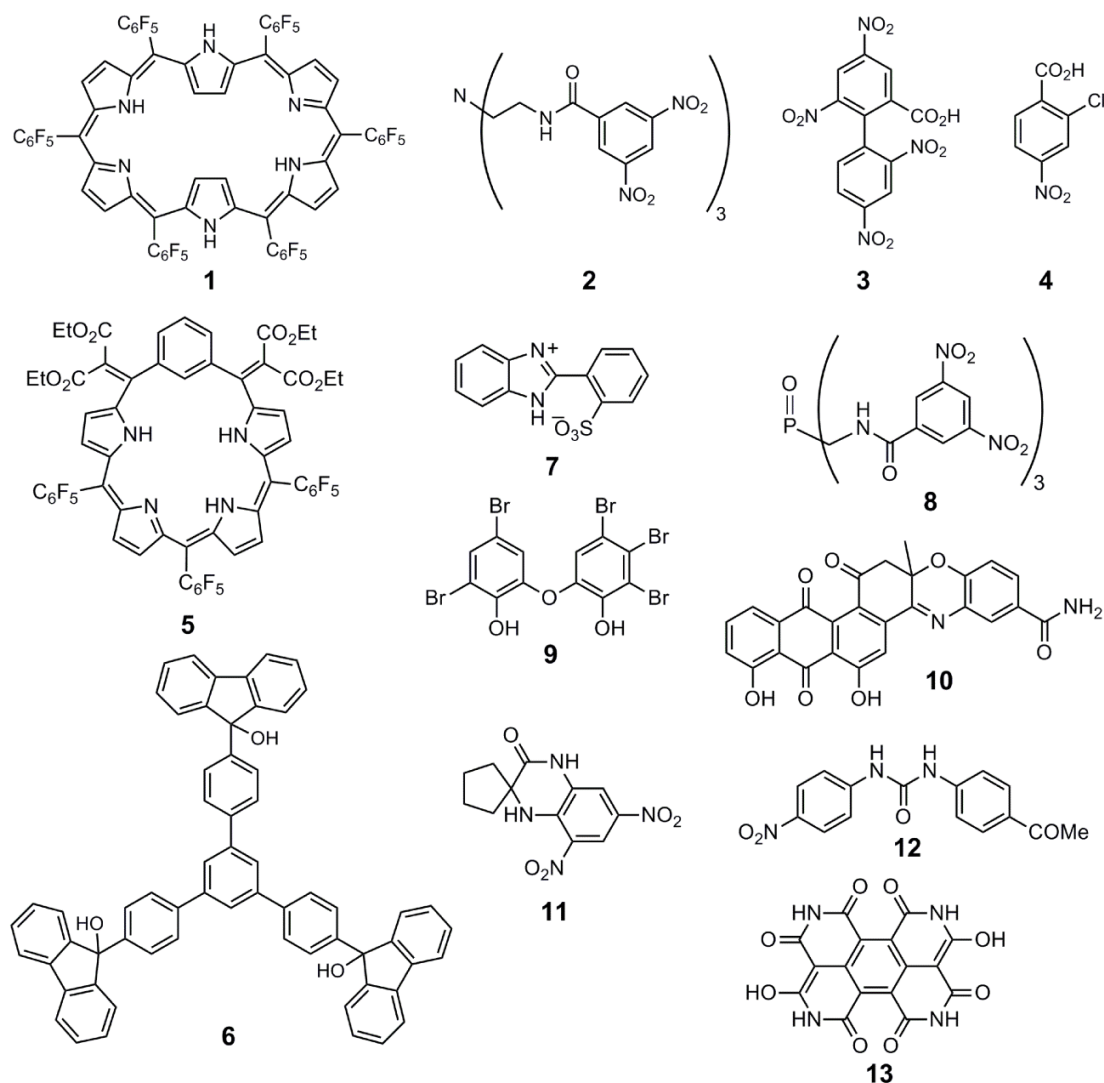


Fig. 2 Chemical structures for DMSO-containing compounds, **1-13**, which form zero- or one-dimensional aggregation patterns based on DMSO-O(lp)... π (arene) interactions. In this and subsequent figures, only species participating in these interactions (but not DMSO) are shown with innocent species, typically, other solvent, omitted.

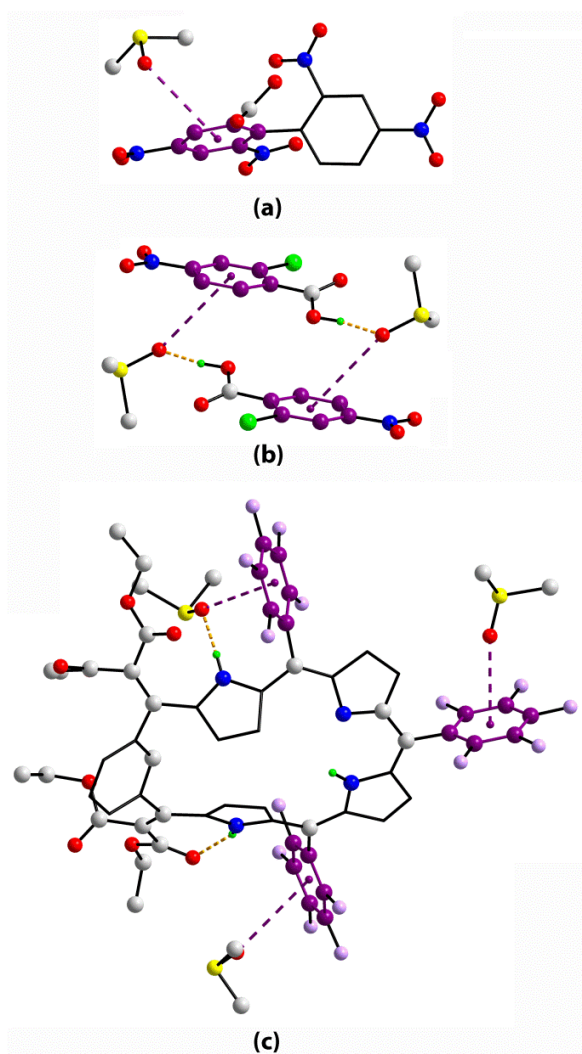


Fig. 3 Examples of structures featuring DMSO-O(lp)... π (arene) interactions leading to zero-dimensional aggregates: (a) operating in isolation in **3**,²² (b) forming a O–H...O(DMSO) hydrogen bond and simultaneously bridging in **4**,²³ and (c) operating in isolation coupled with being held in place by a N–H...O(DMSO) hydrogen bond in **5**.²⁴ In these and subsequent structural diagrams, the DMSO... π (arene) interaction is shown as a purple dashed line and the interacting ring is highlighted in purple. Hydrogen bonds, when present, are shown as orange dashed lines.

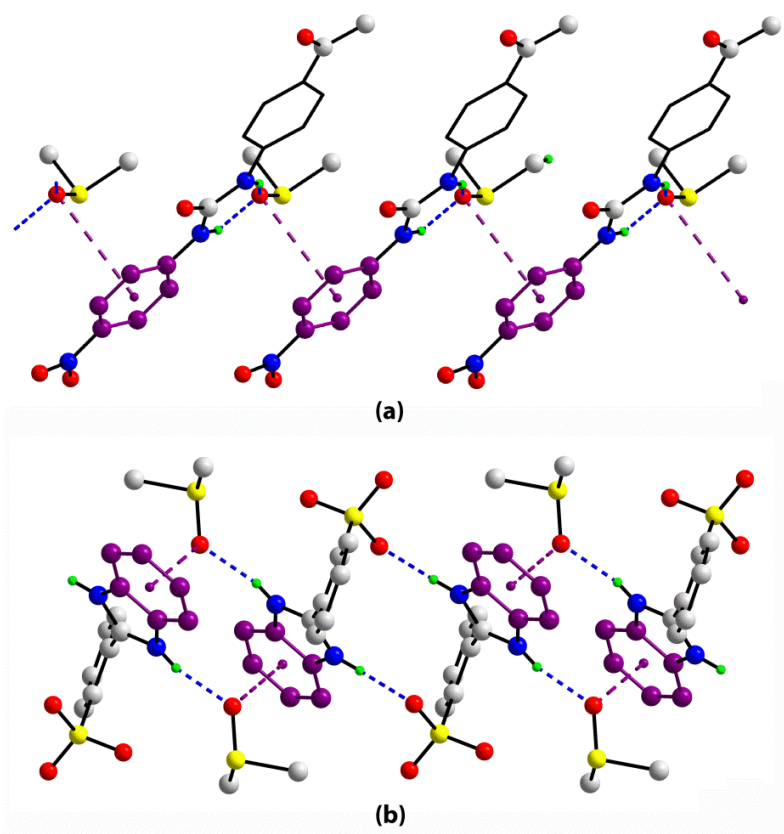


Fig. 4 Example of a one-dimensional supramolecular chain in (a) 12^{31} sustained by a single DMSO-O(lp)... π (arene) interactions between neighbouring organic molecules, and (b) 7^{26} sustained by a two DMSO-O(lp)... π (arene) interactions between neighbouring organic aggregates.

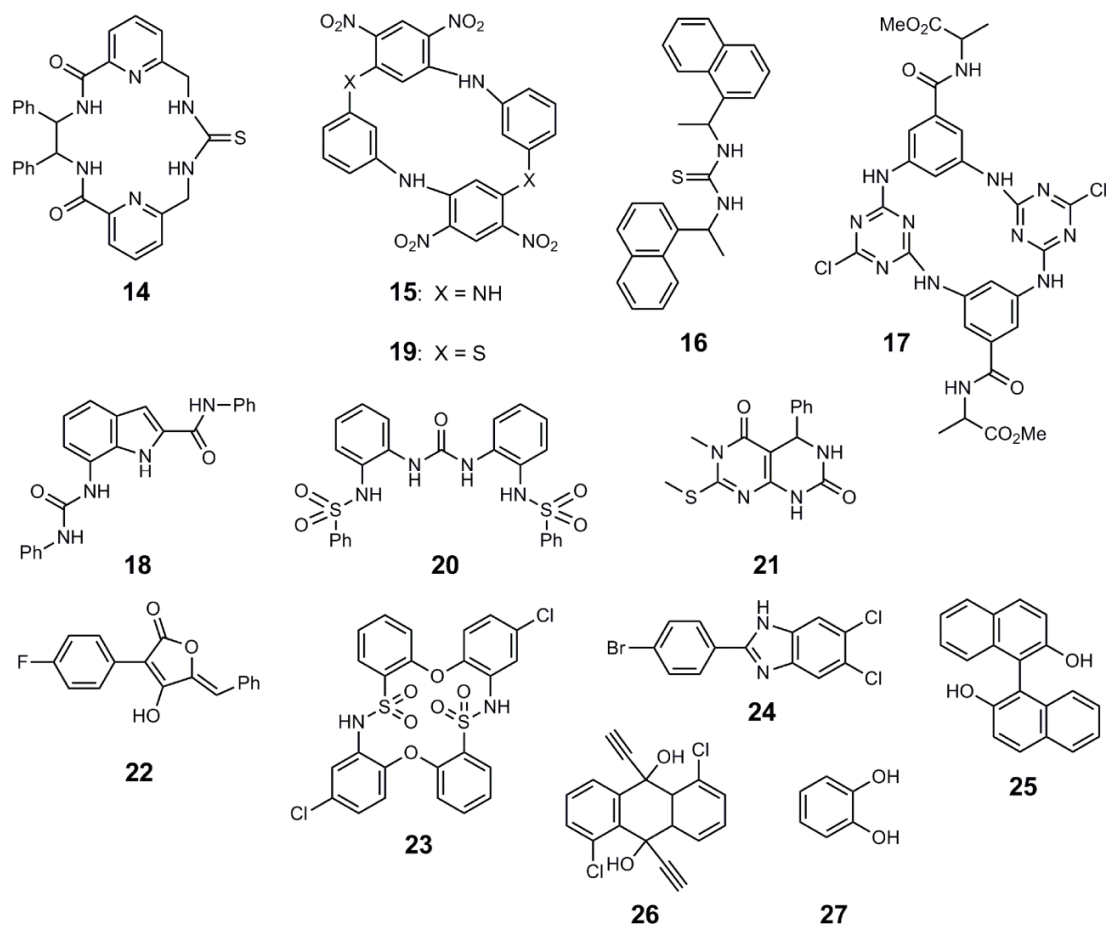


Fig. 5 Chemical structures for DMSO-containing compounds, **14-27**, which form zero-, one- or two-dimensional aggregation patterns based on DMSO-S(lp)... π (arene) interactions.

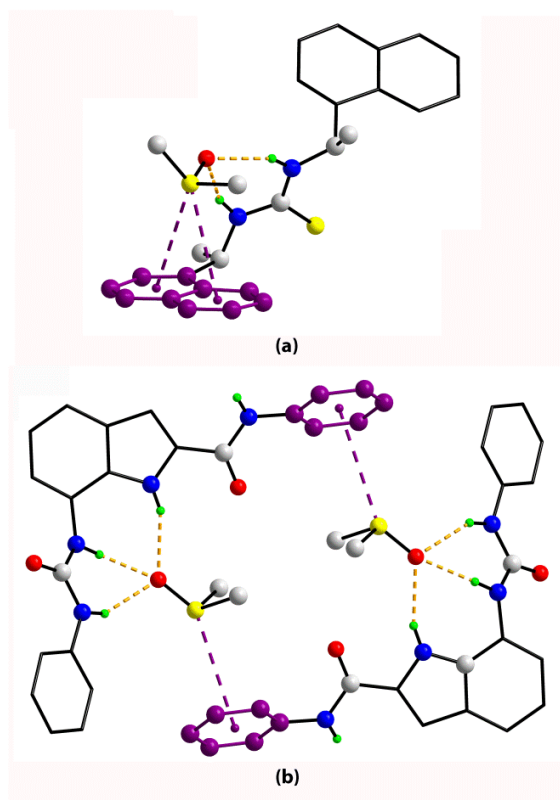


Fig. 6 Examples of zero-dimensional aggregates sustained by DMSO-S(lp)... π (arene) interactions: (a) a rare example of a bifurcated interaction in **16**,³⁵ and (b) a four-molecule aggregate sustained by two DMSO-S(lp)... π (arene) interactions in **18**.³⁷

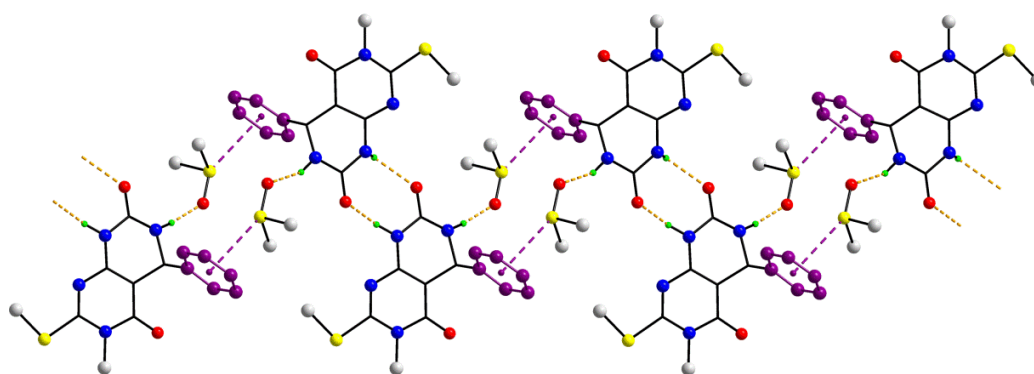


Fig. 7 Example of a one-dimensional supramolecular chain sustained by DMSO-O...H-N and DMSO-S(lp)... π (arene) interactions in **21**.⁴⁰ Here, centrosymmetrically related pyrimidine molecules associate *via* eight-membered {...HNCO}₂ synthons and these form N-H...O(DMSO) hydrogen bonds on either side to form four-molecule aggregates which are linked into a supramolecular chain by bridging DMSO-S(lp)... π (arene) interactions.

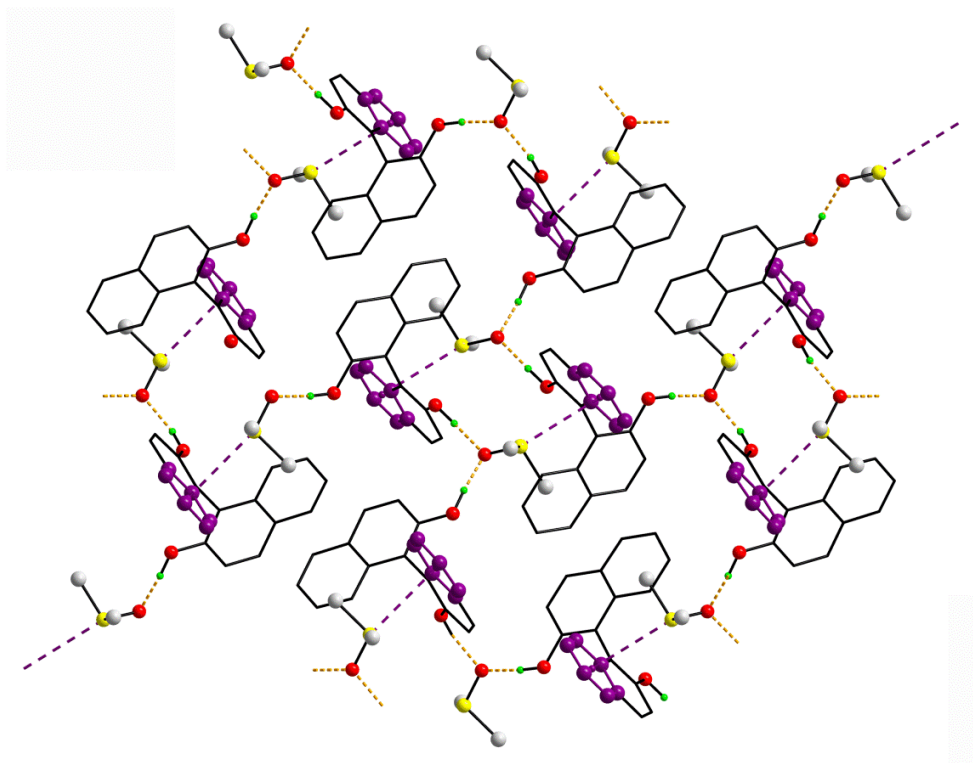


Fig. 8 Example of a two-dimensional supramolecular layer in **25**,⁴⁴ sustained by DMSO-O...H-O and DMSO-S(lp)... π (arene) interactions. Here, the two independent organic molecules are connected by O...H-O hydrogen bonds and these are linked by bridging DMSO molecules which form DMSO-O...H-O and DMSO-S(lp)... π (arene) interactions.

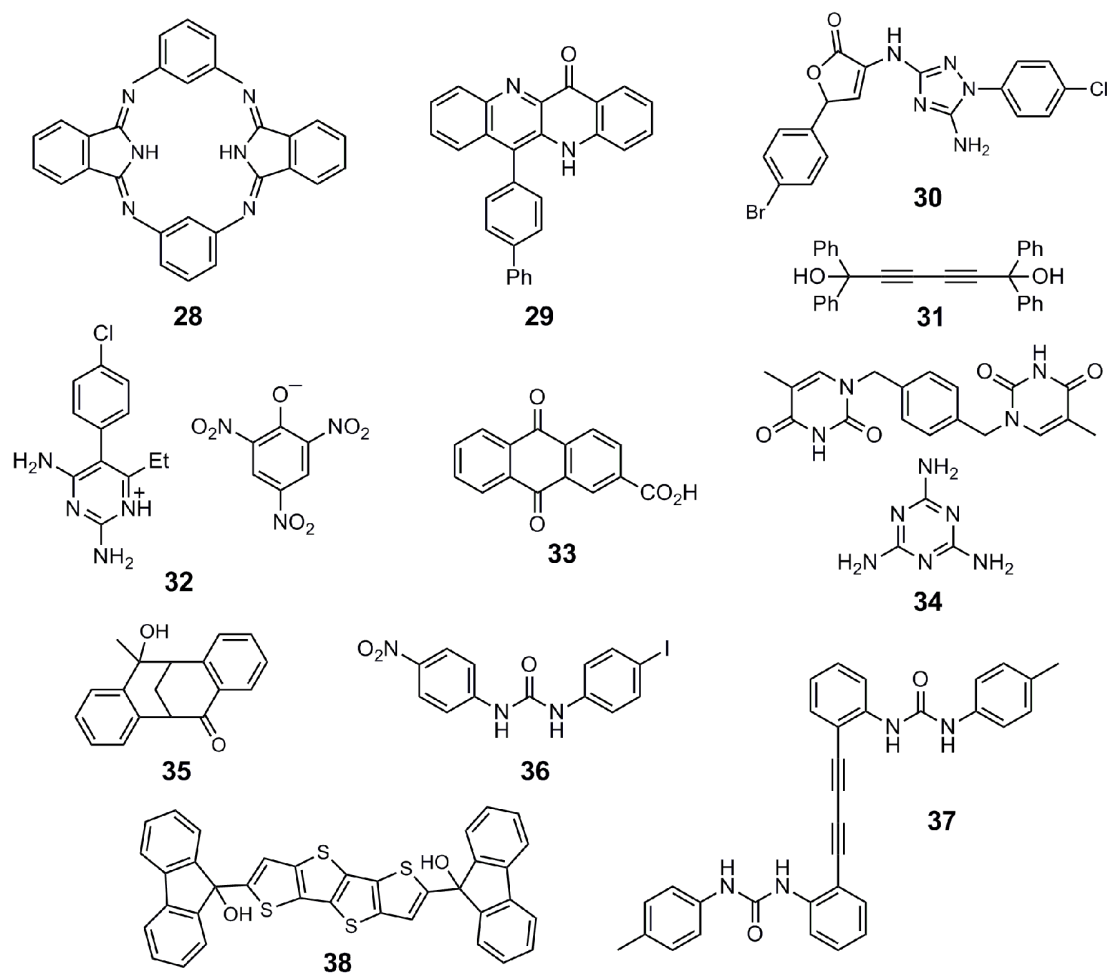


Fig. 9 Chemical structures for DMSO-containing compounds, **28-38**, featuring π ... π -type interactions with the S=O moiety lying over the ring.

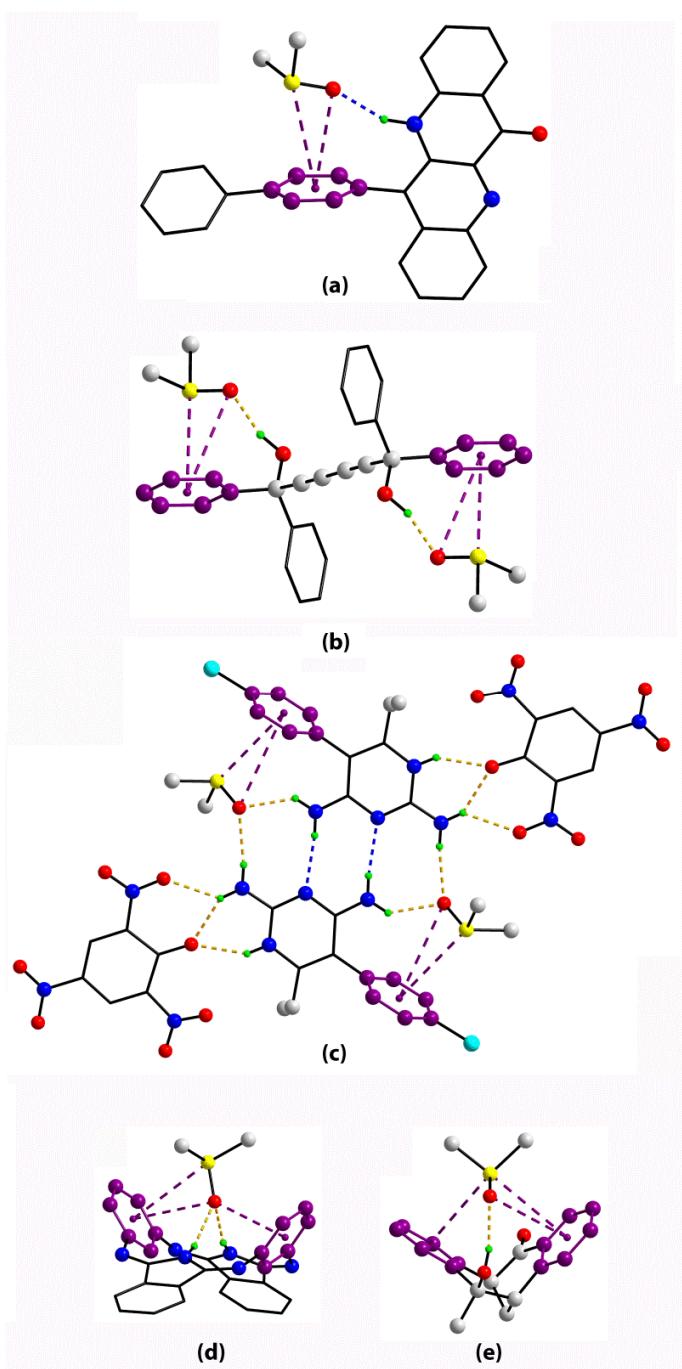


Fig. 10 Examples of zero-dimensional aggregates having S=O... π (arene) interactions: (a) a two-molecule aggregate, in **29**,⁴⁸ (b) a three-molecule aggregate featuring two S=O... π (arene) interactions, in **31**,⁵⁰ (c) a six-molecule aggregate featuring two S=O... π (arene) interactions, in **32**,⁵¹ (d) a bridging mode involving DMSO-O(lp)... π (arene) and S=O... π (arene) interactions, in

28,⁴⁷ and (e) a bridging mode involving DMSO-S(lp)... π (arene) and S=O... π (arene) interactions, in **35**.⁵⁴

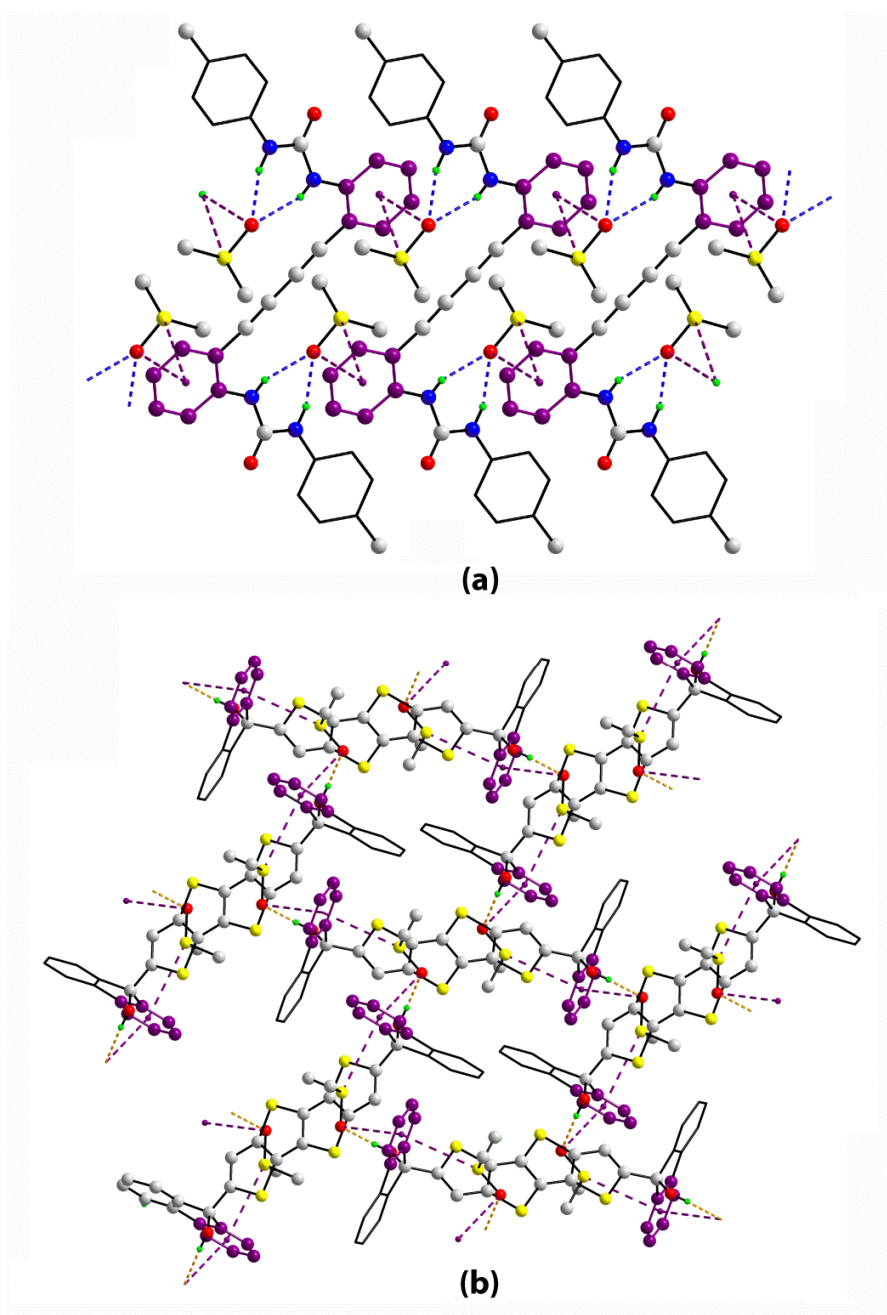


Fig. 11 (a) Supramolecular chain in **37**⁵⁶ with links between successive three-molecule aggregates being of the type $S=O \dots \pi(\text{arene})$, and (b) two-dimensional array in **38**,⁵⁷ where each DMSO molecule forms a $DMSO-O(lp) \dots \pi(\text{arene})$ as well as a $DMSO-S(lp) \dots \pi(\text{arene})$ interaction.

Graphical Abstract

DMSO-O(lone pair)... π (arene), DMSO-S(lone pair)... π (arene) and S=O... π (arene) interactions are found in DMSO solvates.

