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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Electronic Supplementary Information

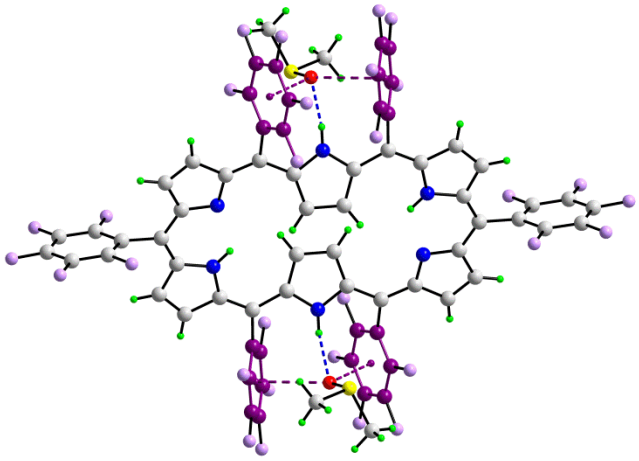
Summary of supramolecular aggregation involving DMSO-O(lone pair)...π(arene) or DMSO-S(lone pair)...π(arene) interactions. Only interacting species are included {spectator species are omitted}.

Table ESI S(1). Zero-dimensional aggregates featuring DMSO-O(lone pair)...π(arene) interactions.

1 EGIJAG: *d* = 3.24 Å; θ = 22.4º; *d* = 3.51 Å; θ = 32.0º

meso-5,10,15,20,25,30-hexakis(Pentafluorophenyl)-(28) hexaphyrin(1.1.1.1.1.1) dimethylsulfoxide solvate

J. Sankar, S. Mori, S. Saito, H. Rath, M. Suzuki, Y. Inokuma, H. Shinokubo, K. S. Kim, Z. S. Yoon, J.-Y. Shin, J. M. Lim, Y. Matsuzaki, O. Matsushita, A. Muranaka, N. Kobayashi, D. Kim and A. Osuka, *J. Am. Chem. Soc*., 2008, **130**, 13568.

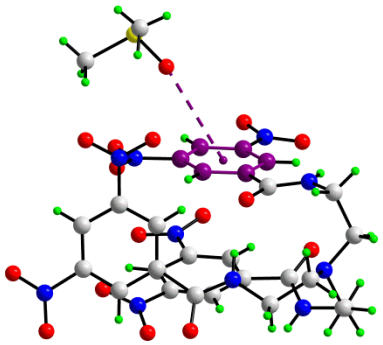


Centrosymmetric, three-molecule aggregate. There are two DMSO-O(lp)…π(arene) interactions but each DMSO molecule is held in place by an intermolecular amine-N–H…O(DMSO) hydrogen bond [H…O = 2.12 Å, N...O = 2.855(3) Å, angle at H atom = 140º].

2 EQAPUI: *d* = 3.54 Å; θ = 33.7º

N,N',N''-(Nitrilotriethane-2,1-diyl)tris(3,5-dinitrobenzamide) dimethylsulfoxide solvate

S. K. Dey and G. Das, *Chem. Commun.*, 2011, **47**, 4983

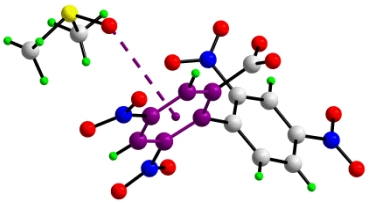


Two-molecule aggregate sustained by a DMSO-O(lp)…π(arene) interaction.

3 DELGEG: *d* = 3.64 Å; θ = 37.3º

2',4,4',6-Tetranitro-2-carboxy-biphenyl dimethylsulfoxide

E. G. Popova, L. A. Chetkina, V. K. Bel'skii, A. M. Andrievskii, A. N. Poplavskii and K. M. Dyumaev, *Zh. Strukt. Khim.*, 1985, **26**, 139.

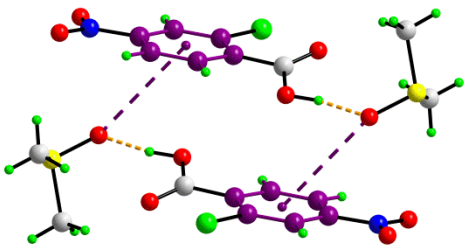


Two-molecule aggregate sustained by a DMSO-O(lp)…π(arene) interaction.

4 IKEYAZ: *d* = 3.77 Å; θ = 35.4º

2-Chloro-4-nitrobenzoic acid dimethylsulfoxide solvate

S. Aitipamula, P. S. Chow and R. B. H.Tan, *CrystEngComm*, 2011, **13**, 1037.

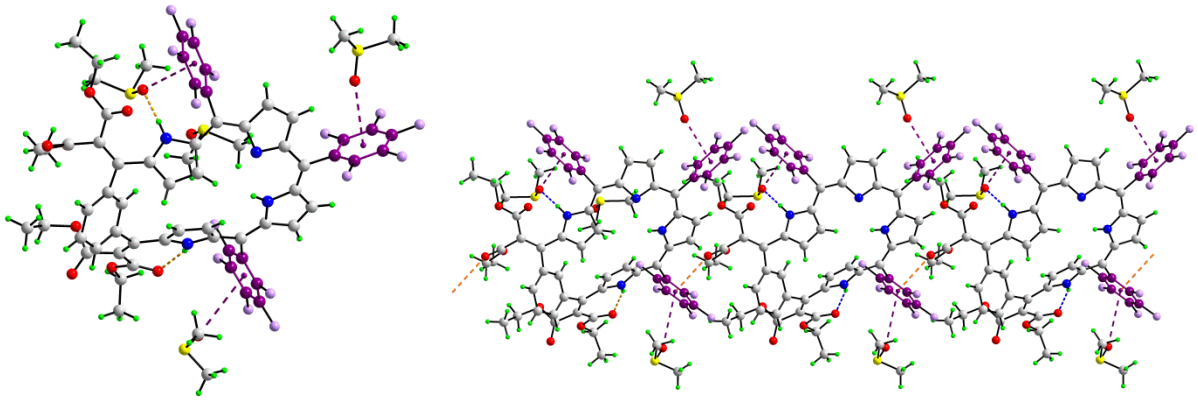


Two-molecule aggregates are stabilised by an hydroxyl-O–H…O(DMSO) hydrogen bond [H…O = 1.65 Å, N...O = 2.569(3) Å, angle at H atom = 163º]. These are connected into a centrosymmetric four-molecule aggregate by a pair of DMSO-O(lp)…π(arene) interactions.

5 MAFJOU: *d* = 3.04 Å; θ = 16.8º; *d* = 3.20 Å; θ = 18.3º; *d* = 3.54 Å; θ = 35.8º

6,26-bis(Diethoxycarbonylmethylidene)-11,16,21-tris(pentafluorophenyl)-27-(μ-benzi)-pentaphyrin dimethylsulfoxide solvate

S.-D. Jeong, A. Nowak-Krol, Y. Kim, S.-J. Kim, D. T. Gryko and C.-H. Lee, *Chem. Commun.*, 2010, **46**, 8737.

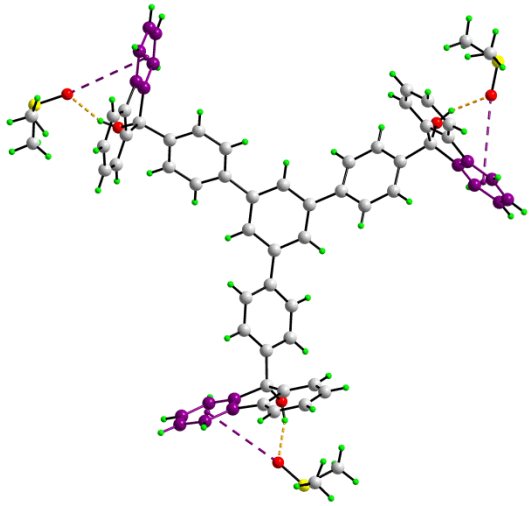


Four-molecule aggregate. One DMSO-O(lp) interaction [*d* = 3.20 Å] is stabilised by an amine-N–H…O(DMSO) hydrogen bond [H…O = 1.95 Å, N...O = 2.806(6) Å, angle at H atom = 165º] with the other two DMSO-O(lp)…π(arene) interactions being stand alone. The aggregates are connected into a supramolecular chain *via* carbonyl-O…π(arene) interactions [*d* = 3.06 Å].

6 VAWWAT: *d* = 3.90 Å; θ = 34.6º

1,3,5-tris(4-(9-Hydroxy-9-fluorenyl)phenyl)benzene dimethylsulfoxide solvate

A. Holzel, W. Seichter and E. Weber, *J. Inclusion Phenom. Macrocyclic Chem.*, 2011, **71**, 113.



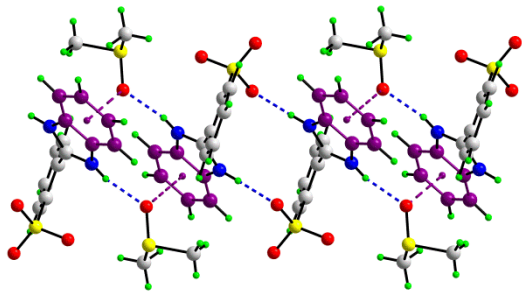
The organic molecule has crystallographic three-fold symmetry. Each hydroxyl forms an hydroxyl-O–H...O hydrogen bond to O(DMSO) [H…O = 1.88 Å, N...O = 2.696(3) Å, angle at H atom = 162º]. The four-molecule aggregate feature intramolecular DMSO-O(lp)…π(arene) interactions.

Table ESI S(2). One-dimensional aggregates featuring DMSO-O(lone pair)...π(arene) interactions.

7 GABPEG: *d* = 3.60 Å; θ = 32.0º

2-(1H-Benzimidazol-3-ium-2-yl)benzenesulfonate dimethylsulfoxide solvate

A. Esparza-Ruiz, G. Gonzalez-Gomez, E. Mijangos, A. Pena-Hueso, H. Lopez-Sandoval, A. Flores-Parra, R. Contreras and N. Barba-Behrens, *Dalton Trans*., 2010, **39**, 6302.

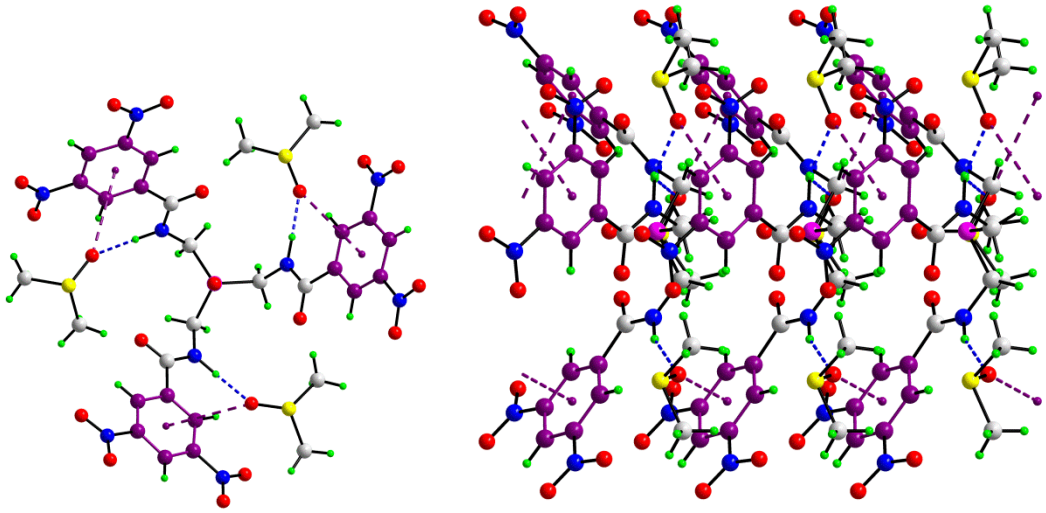


Two-component crystal. The organic molecules associate into a dimeric aggregate *via* N–H…O(sulphonate) hydrogen bonds [H…O = 1.84 Å, N...O = 2.717(3) Å, angle at H atom = 176º]. These are bridged into a linear supramolecular chain by N–H…O(DMSO) hydrogen bonds [H…O = 1.92 Å, N...O = 2.696(4) Å, angle at H atom = 160º] and DMSO-O(lone pair)…π(arene) interactions.

8 UVETOF: *d* = 3.60 Å; θ = 32.7º

N,N',N''-(Phosphoryltris(methylene))tris(3,5-dinitrobenzamide) dimethylsulfoxide solvate

J. V. Gavette, J. Lara, O. B. Berryman, L. N. Zakharov, M. M. Haley and D. W. Johnson, *Chem. Commun*., 2011, **47**, 7653.

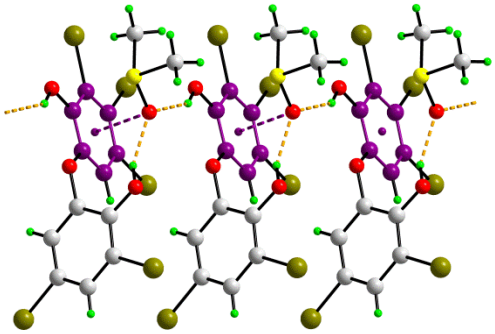


The organic molecule has crystallographic three fold symmetry. Each amine-N–H forms a hydrogen bond to O-DMSO [H…O = 1.86 Å, N...O = 2.844(6) Å, angle at H atom = 159º]. The four-molecule aggregates are connected into a linear supramolecular chain *via* DMSO-O(lp)…π(arene) interactions. The left-view is a projection down the axis of propagation.

9 YUNXAH: *d* = 3.67 Å; θ = 31.9º

2,3,4-Tribromo-6-(3,5-dibromo-2-hydroxyphenoxy)phenol dimethylsulfoxide solvate

L. Calcul, R. Chow, A. G. Oliver, K. Tenney, K. N. White, A. W. Wood, C. Fiorilla and P. Crews, *J. Nat. Prod*., 2009, **72**, 443.

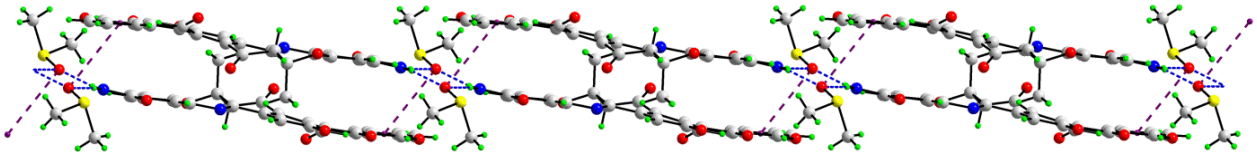


The DMSO-O atom is bifurcated, forming two hydroxyl-O–H...O hydrogen bonds [H…O = 1.95 Å, N...O = 2.696(8) Å, angle at H atom = 147º; 1.88 Å, 2.646(7) Å, 151º]. The two-molecule aggregates are connected into a linear supramolecular chain *via* DMSO-O(lp)…π(arene) interactions.

10 YOKHIP: *d* = 3.76 Å; θ = 34.7º

3-Amido-7,9-dihydroxy-18-methyl-5-azo-16-oxo-dibenzo(b,k)chrysene-8,13,14-trione dimethylsulfoxide solvate

A. M. Hassan, M. C. Cone, C. R. Melville and S. J. Gould, *Bioorg. Med. Chem. Lett*., 1995, **5**, 191.

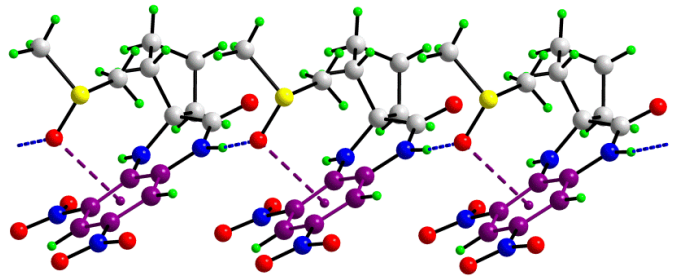


Centrosymmetrically related organic molecules are connected *via* two DMSO molecules whereby each DMSO-O atom is bifurcated, forming two N–H...O hydrogen bonds [H…O = 2.01 Å, N...O = 2.904(6) Å, angle at H atom = 155º; 2.07 Å, 3.021(7) Å, 172º]. The four-molecule aggregates are connected into a supramolecular double chain *via* DMSO-O(lp)…π(arene) interactions.

11 TACXAW: *d* = 3.82 Å; θ = 32.1º

1',2',3',4'-Tetrahydro-5',7'-dinitrospiro(cyclopentane-1,3'-quinazoline)-2'-one dimethylsulfoxide solvate

J. M. Villalgordo, B. R. Vincent and H. Heimgartner, *Helv. Chim. Acta*, 1990, **73**, 959.

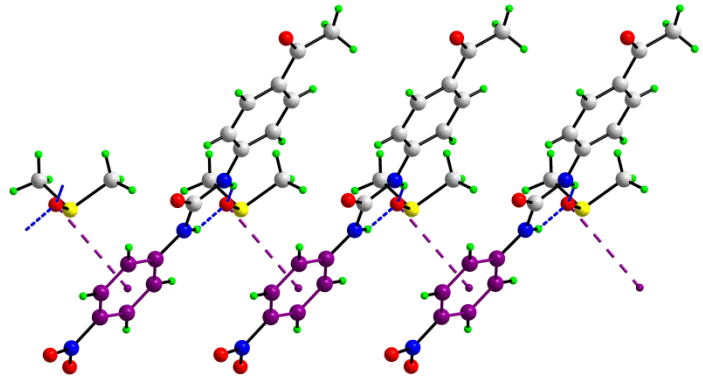


The components are linked into a two molecule aggregate *via* a N-H...O(DMSO) hydrogen bond [H…O = 1.90 Å, N...O = 2.813(3) Å, angle at H atom = 169º]. These are connected into a linear supramolecular chain by DMSO-O(lp)…π(arene) interactions.

12 TIVPEU: *d* = 3.85 Å; θ = 18.2º

N-(4-Acetylphenyl)-N'-(4-nitrophenyl)urea dimethylsulfoxide solvate

L. S. Reddy, S. K. Chandran, S. George, N. J. Babu and A. Nangia, *Cryst. Growth Des*., 2007, **7**, 2675.

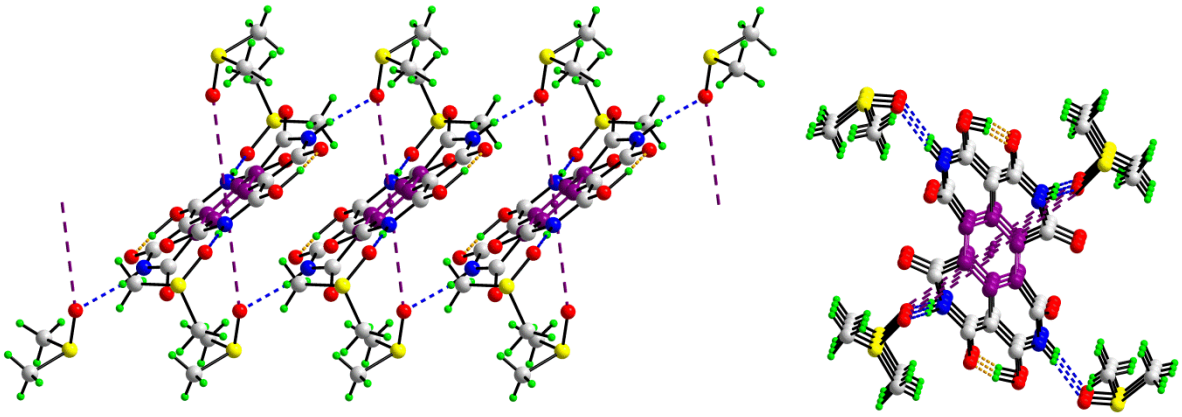


Pairs of molecules are connected by two urea-N–H...O(DMSO) hydrogen bonds [H…O = 2.12 Å, N...O = 2.877(3) Å, angle at H atom = 151º; 2.08 Å, 2.796(3) Å, 158º]. These are connected into a linear supramolecular chain *via* DMSO-O(lp)…π(arene) interactions.

13 CIDNEJ: *d* = 3.87 Å; θ = 37.4º

meso-4,10-Dihydroxy-5,11-dihydro-2,5,8,11-tetra-azaperylene-1,3,6,7,9,12-hexaone dimethylsulfoxide solvate

Y. Zhang, B. Illarionov, A. Bacher, M. Fischer, G. I. Georg, Q.-Z. Ye, D. V. Velde, P. E. Fanwick, Y. Song and M. Cushman, *J. Org. Chem*., 2007, **72**, 2769.



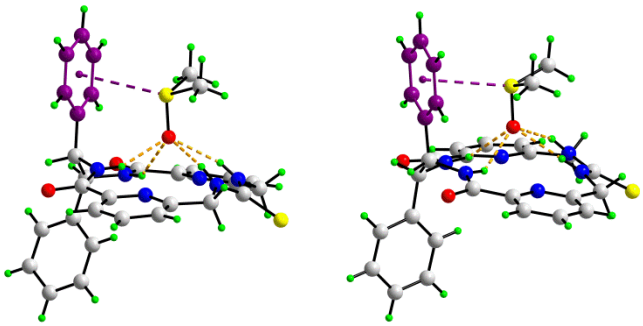
The centrosymmetric organic molecule features strong intramolecular hydroxyl-O–H…O(carbonyl) hydrogen bonds [H…O = 1.31 Å, O...O = 2.485(2) Å, angle at H atom = 162º]. Each amide-N–H forms a hydrogen bond to O-DMSO [terminal: H…O = 1.96 Å, N...O = 2.817(3) Å, angle at H atom = 173º; bridging: 1.83 Å, N...O = 2.722(2) Å, angle at H atom = 171º]. One of the DMSO-O molecules is bridging, forming a DMSO-O(lp)…π(arene) interaction with the central ring, which, owing to be centrosymmetric, forms two such interactions.

Table ESI S(3). Zero-dimensional aggregates featuring DMSO-S(lone pair)...π(arene) interactions.

14 NENSEF: *d* = 3.38 Å; θ = 11.0º; *d* = 3.43 Å; θ = 10.7º

4,5-Diphenyl-2,7-dioxo-15-thio-3,6,14,16,22,23-hexaaza[16.3.1.18,12]tricosa-1(22),8(23),9,11, 18,20-hexaene dimethylsulfoxide solvate

A. Ragusa, J. M. Hayes, M. E. Light and J. D. Kilburn, *Eur. J. Org. Chem*., 2006, 3545.

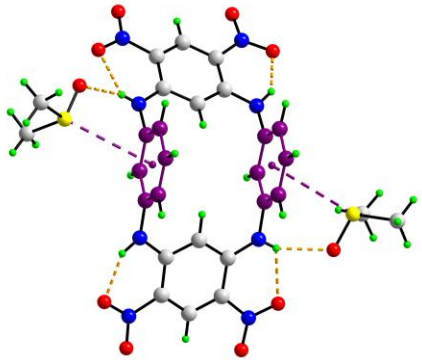


Two independent pairs of molecules comprise the asymmetric unit and each forms a DMSO-S(lp)…π(arene) interaction. The DMSO molecule is held in place by four intramolecular amine-N–H…O(DMSO) hydrogen bonds [Molecule 1: H…O = 2.12 Å, N...O = 2.927(5) Å, angle at H atom = 152º; 2.12 Å, 2.947(6) Å, 157º; 2.12 Å, 2.947(6) Å, 157º; 139º; 2.15 Å, 2.979(6) Å, 157º. Molecule 2: H…O = 2.12 Å, N...O = 2.927(5) Å, 153º; 2.13 Å, 2.944(5) Å, 154º; 139º; 2.37 Å, 3.097(5) Å, 140º; 139º; 2.03 Å, 2.841(7) Å, 153º]

15 YOPFOZ: *d* = 3.56 Å; θ = 24.0º

2,4,6,8-tetraaza-14,16,54,56-tetranitro-1,3,5,7(1,3)-tetrabenzenacyclooctaphane dimethylsulfoxide solvate

H. Konishi, S. Hashimoto, T. Sakakibara, S. Matsubara, Y. Yasukawa, O. Morikawa and K. Kobayashi, *Tetrahedron Lett.*, 2009, **50**, 620.

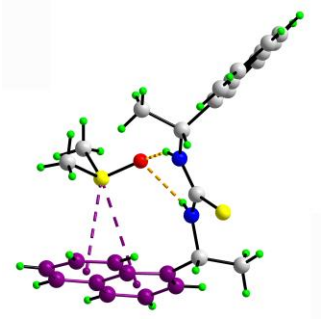


The organic molecule has two-fold symmetry and forms a N–H-O(DMSO) hydrogen bond [H…O = 2.05 Å, N...O = 2.696(5) Å, angle at H atom = 151º]. The DMSO molecule also forms a DMSO-S(lp)…π(arene) interaction.

16 QUCRAI: *d* = 3.58 Å; θ = 15.1º; *d* = 3.77 Å; θ = 23.9º

1,3-bis((R)-1-(1-Naphthyl)ethyl)thiourea dimethylsulfoxide solvate

H. D. P. Ali, S. J. Quinn, T. McCabe, P. E. Kruger and T. Gunnlaugsson, *New J. Chem.*, 2009, **33**, 793.

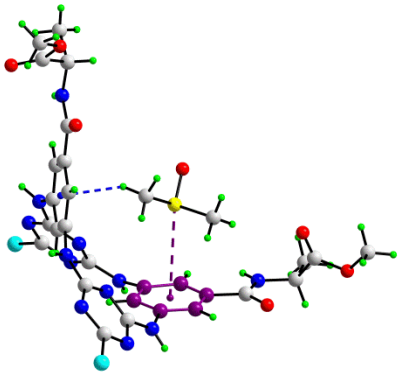


The organic and DMSO molecules forms a pair of DMSO-S(lp)…π(arene) interactions. The DMSO molecule is held in place by a pair of intramolecular amine-N–H…O(DMSO) hydrogen bonds [H…O = 2.18 Å, N...O = 2.979(4) Å, angle at H atom = 155º; 2.17 Å, 2.944(4) Å, 149º]

17 NAQDEQ: *d* = 3.62 Å; θ = 7.2º

Dimethyl 2,2'-((5,17-dichloro-2,4,6,8,14,16,18,20,26,28-decaazapentacyclo[19.3.1.13,7.19, 13.115,19]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene-11,23-diyl)-bis(carbonylimino)) dipropanoate dimethylsulfoxide solvate dihydrate

A. I. Vicente, J. M. Caio, J. Sardinha, C. Moiteiro, R. Delgado and V. Felix, *Tetrahedron*, 2012, **68**, 670.



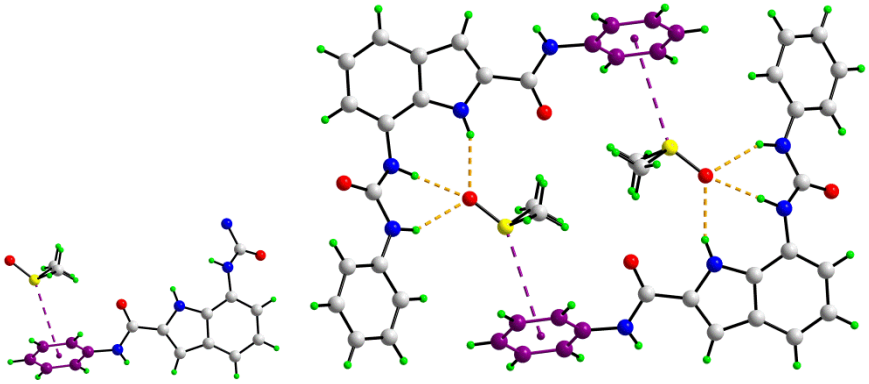
There are two independent organic molecules and nine DMSO molecules, one of which forms a DMSO-S(lp)…π(arene) interaction leading to a zero-dimensional architecture. While the

DMSO-O atom does not form an interaction, a methyl-H forms a C–H…π(arene) interaction [H…Cg = 2.46 Å; C…Cg = 3.209(12) Å and angle at H = 133º]

18 DISVAD: *d* = 3.82 Å; θ = 21.4º

7-((Phenylcarbamoyl)amino)-N-phenyl-1H-indole-2-carboxamide dimethylsulfoxide solvate

G. W. Bates, Triyanti, M. E. Light, M. Albrecht and P. A. Gale, *J. Org. Chem.*, 2007, **72**, 8921.

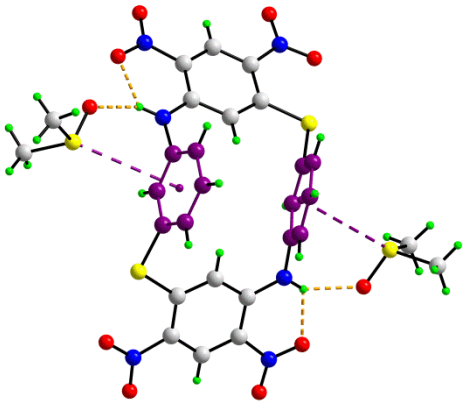


Centrosymmetric four-molecule aggregate sustained by DMSO-S(lp)…π(arene) and N–H…O(DMSO) [H…O = 1.98 Å; N…O = 2.8300(19) Å and angle at H = 154º; 2.12 Å, 2.811(2) Å,158º; 2.21 Å, 3.0123(19) Å, 148º] interactions. The exocyclic N–H and carbonyl-O atoms also form N–H...O hydrogen bonds leading to a supramolecular layer in the *ab*-plane.

19 SAKMEY: *d* = 3.85 Å; θ = 25.3º

4,6,16,18-tetranitro-2,14-dithia-8,20-diazapentacyclo[19.3.1.13,7.19,13.115,19]octacosa-1(25),3(28),4,6,9(27),10,12,15(26),16,18,21,23-dodecaene dimethyl sulfoxide solvate

J.-M. Raimundo, Z. Chen and O. Siri, *Chem. Commun.*, 2011, **47**, 10410.



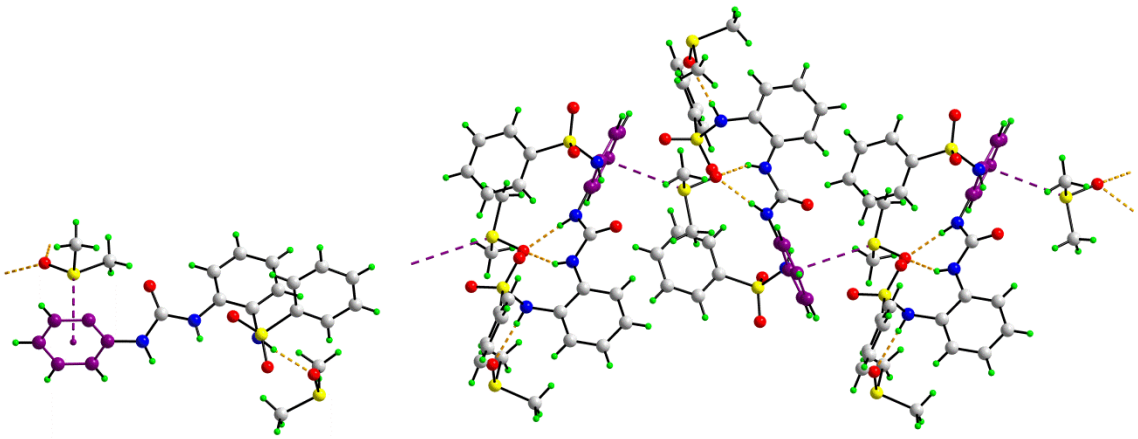
The cyclic molecule has crystallographic two-fold symmetry and the phenyl ring forms a DMSO-S(lp)…π(arene) interaction. The DMSO molecule is held in place by an intramolecular amine-N–H…O(DMSO) hydrogen bond [H…O = 2.01 Å, N...O = 2.739(5) Å, angle at H atom = 142º]

Table ESI S(4). One-dimensional aggregates featuring DMSO-S(lone pair)...π(arene) interactions.

20 HITFOG: *d* = 3.56 Å; θ = 8.3º

N,N'-(2,2'-Carbonylbis(azanediyl)bis(2,1-phenylene))dibenzenesulfonamide dimethylsulfoxide solvate

C. Caltagirone, G. W. Bates, P. A. Gale, M. E. Light, *Chem.Commun.*, 2008, 61.

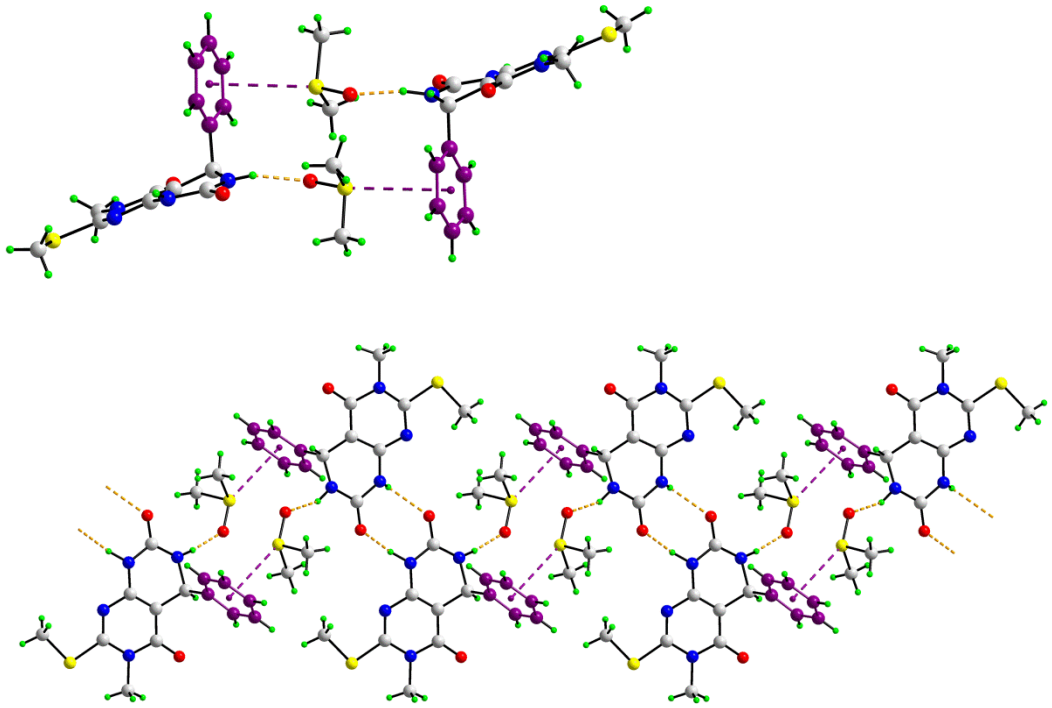


There are two independent DMSO molecules in the structure and one of these forms a DMSO-S(lp)…π(arene) interaction. This oxygen atom of this molecule is bifurcated, forming two amine-N–H…O(DMSO) hydrogen bonds [H…O = 1.88 Å; N…O = 2.733(3) Å and angle at H = 157º; 2.30 Å, 2.991(3) Å, 147º] to a symmetry related molecule, with the result that helical supramolecular chain is formed. The second DMSO molecule forms a hydrogen bond with another amine-N-H atom H…O = 2.00 Å; N…O = 2.833(3) Å and angle at H = 173º].

21 YIZGEU: *d* = 3.65 Å; θ = 13.1º; *d* = 3.68 Å; θ = 13.5º

3,4-Dihydro-6-methyl-7-(methylthio)-4-phenylpyrimido(4,5-d)pyrimidine-2,5(1H,6H)-dione dimethylsulfoxide solvate

M. Dabiri, H. Arvin-Nezhad, H. R. Khavasi and A. Bazgir, *J. Heterocycl. Chem*., 2007, **44**, 1009.



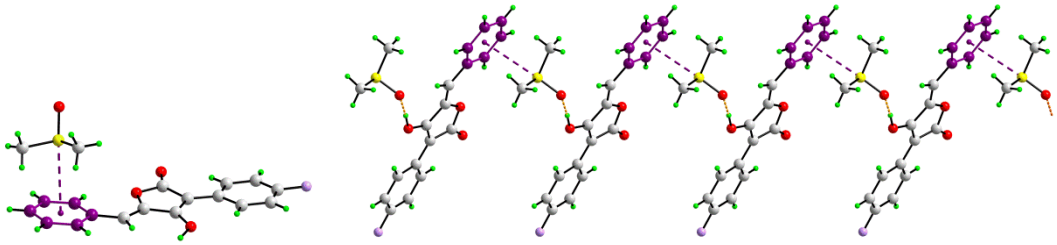
Two independent pairs of molecules and each forms a single DMSO-S(lp)…π(arene) interaction involving the phenyl ring. These are connected into a four-molecule aggregate by amide-N-H…O(DMSO) hydrogen bonds [H…O = 2.04 Å; N…O = 2.811(14) Å and angle at H = 145º; 1.81 Å, 2.788(14) Å, 166º]. The four-molecule aggregates are connected into a supramolecular

tape by eight-membered {…HNCO}$_2$ amide synthons [H…O = 2.29 Å; N…O = 2.890(12) Å and angle at H = 150º; 1.90 Å, 22.870(12) Å, 159º]

22 AQABUQ: *d* = 3.66 Å; θ = 7.6º

5-Benzylidene-3-(4-fluorophenyl)-4-hydroxyfuran-2(5H)-one dimethylsulfoxide solvate

B. Nadal, J. Rouleau, H. Besnard, P. Thuery and T. Le Gall, *Tetrahedron*, 2011, **67**, 2605.

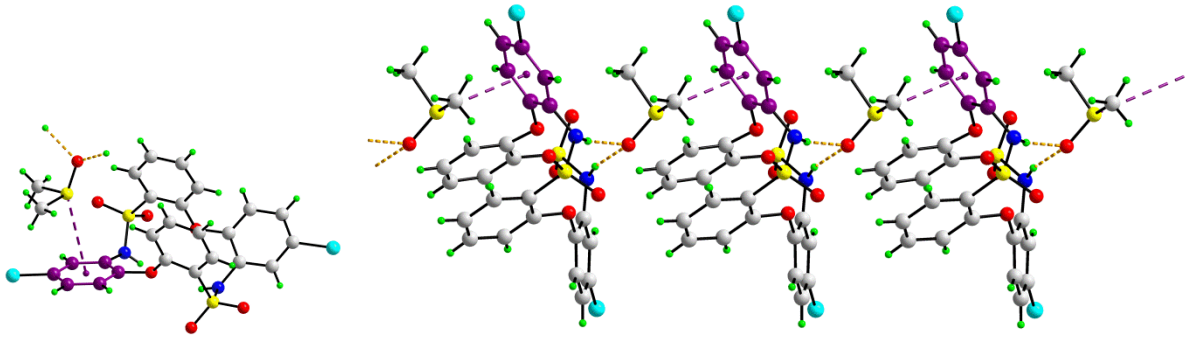


Linear supramolecular chains sustained by DMSO-S(lp)…π(arene) and O–H…O(DMSO)] interactions.

23 MUGCEX: *d* = 3.80 Å; θ = 9.5º

2,13-dichloro-11H,22H-tetrabenzo[b,f,i,m][1,8,4,11,5,12]dioxadithiadiazacyclotetradecine 10,10,21,21-tetraoxide dimethylsulfoxide solvate

M. Altamura, V. Fedi, D. Giannotti, P. Paoli and P. Rossi, *New J. Chem.*, 2009, **33**, 2219.

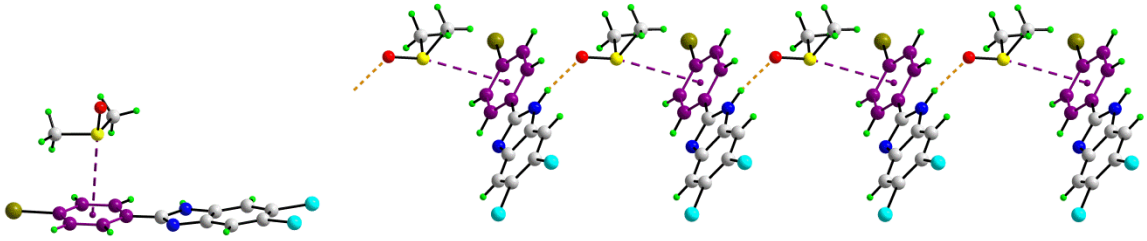


One of the chlorophenyl rings forms a DMSO-S(lp)…π(arene) interaction and the bifurcated DMSO-O atom forms two hydrogen bonds with two amine-H atoms [H…O = 1.97 Å; N…O = 2.808(5) Å and angle at H = 172º; 2.03 Å, 2.815(6) Å, 165º]. The result is a supramolecular linear chain.

24 COXWES: *d* = 3.87 Å; θ = 14.5º

2-(4'-Bromophenyl)-5,6-dichloro-1H-benzimidazole dimethylsulfoxide solvate

C. Mukhopadhyay, P. K. Tapaswi and R. J. Butcher, *Aust. J. Chem.*, 2009, **62**, 140.



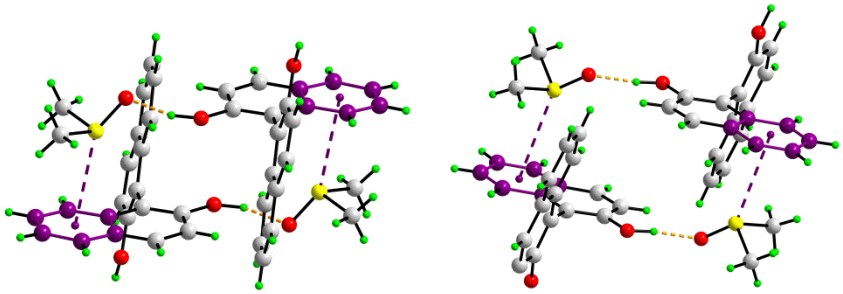
Linear supramolecular chains sustained by DMSO-S(lp)…π(arene) and N–H…O(DMSO) [H…O = 1.94 Å; N…O = 2.811(2) Å and angle at H = 168º] interactions.

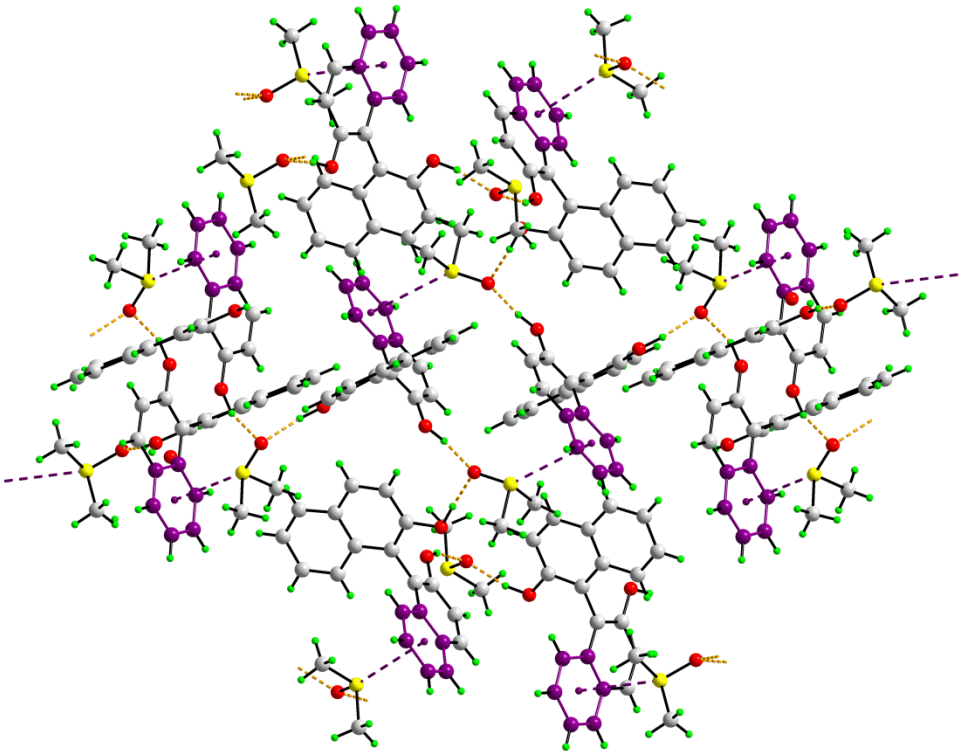
Table ESI S(5). Two-dimensional aggregates featuring DMSO-S(lone pair)...π(arene) interactions.

25 WUJDOU: *d* = 3.46 Å; θ = 8.0º; *d* = 3.49 Å; θ = 8.1º

2,2'-Dihydroxy-1,1'-binaphthyl dimethylsulfoxide clathrate

L. R. Nassimbeni and H. Su, *New J. Chem.*, 2002, **26**, 989.



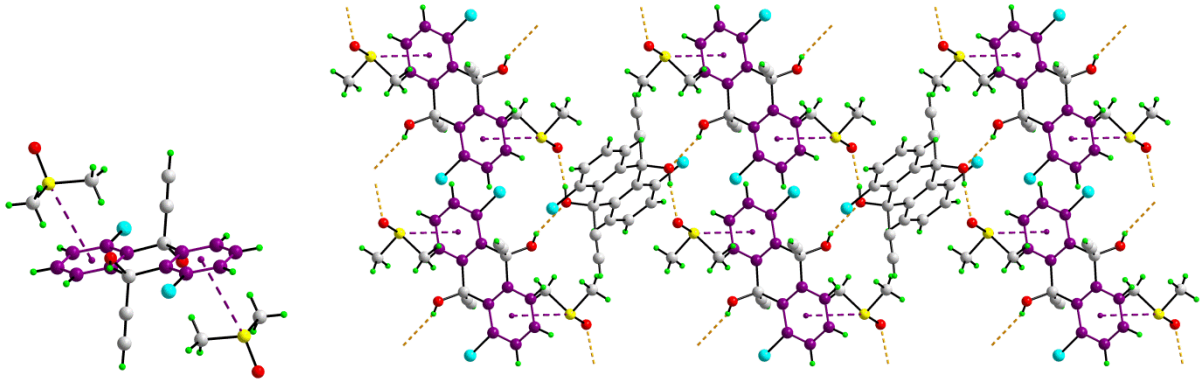


There are two independent pairs of molecules. The organic molecule forms a single DMSO-S(lp)…π(arene) interaction involving one of the outer phenyl rings. Concurrently, the DMSO-O atom forms a O–H…O hydrogen bond with the hydroxyl group [H…O = 1.78 Å; O…O = 2.720(9) Å and angle at H = 157º; 1.72 Å, 2.698(9) Å, 172º] to form a centrosymmetric four-molecule aggregate. These four-molecule aggregates are connected into a flat two-dimensional array by additional hydroxyl-O-H…O(DMSO) hydrogen bonds [H…O = 1.77 Å; O…O = 2.727(9) Å and angle at H = 169º; 1.65 Å, 2.661(9) Å, 175º]

26 EJIWAV: *d* = 3.81 Å; θ = 16.2º

trans-1,5-Dichloro-9,10-diethynyl-9,10-dihydroxy-9,10-dihydroanthracene dimethylsulfoxide clathrate

R. Banerjee, G. R. Desiraju, R. Mondal, A. S. Batsanov, C. K. Broder and J. A. K. Howard, *Helv. Chim. Acta*, 2003, **86**, 1339.

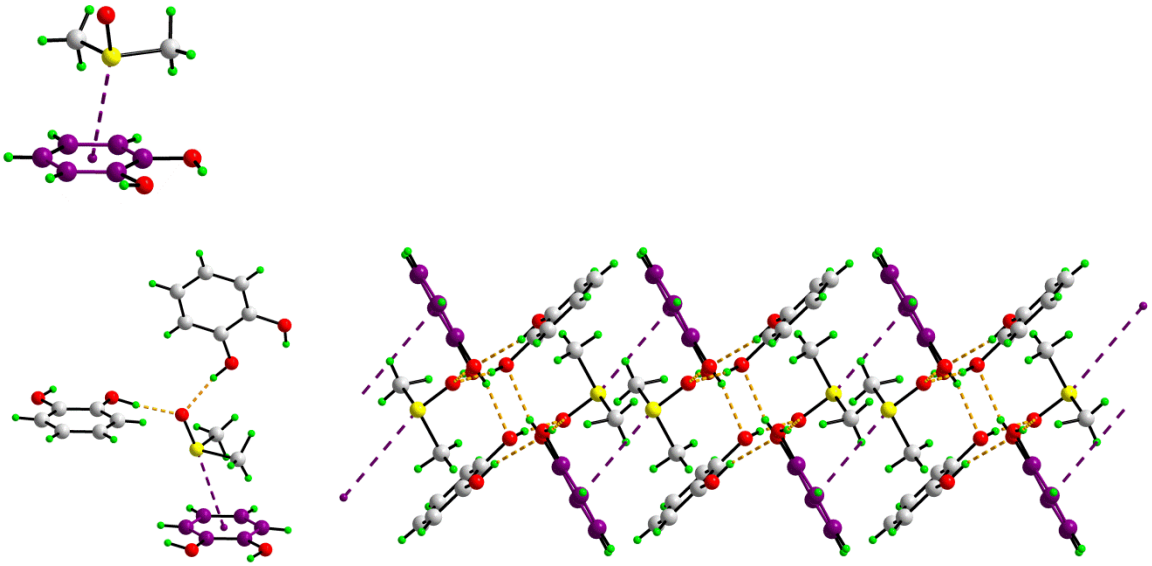


Two independent and centrosymmetric anthracene derivatives one of which forms DMSO-S(lp)…π(arene) interactions. The DMSO provides a bridge between the independent molecules by forming an O–H…O(DMSO) [H…O = 1.95 Å; N…O = 2.7327(18) Å and angle at H = 171º] hydrogen bond. An additional link between the independent molecules is a hydroxyl-O-H…O(hydroxyl) hydrogen bond [H…O = 2.18 Å; N…O = 2.8529(18) Å and angle at H = 155º].

27 EPAVUN: *d* = 3.88 Å; θ = 25.9º

1,2-Dihydroxybenzene dimethylsulfoxide solvate

T. M. Polyanskaya, K. A. Khaldoyanidi and A. I. Smolentsev, *Zh. Strukt. Khim.*, 2010, **51**, 342.



Two independent 1,2-dihydroxybenzene molecules one of which participates in a DMSO-S(lp)…π(arene) interactions. The DMSO provides a bridge between the independent molecules

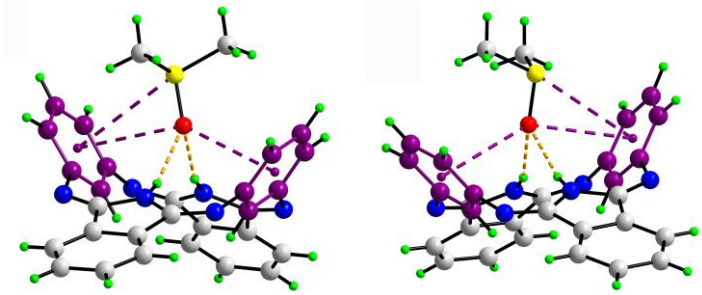
by forming two O–H…O(DMSO) [H…O = 1.79 Å; N…O = 2.639(3) Å and angle at H = 168º; 1.75 Å, 2.657(3) Å, 170º] hydrogen bonds. Additional links between the independent molecules are of the type hydroxyl-O–H…O(hydroxyl) [H…O = 2.15 Å; N…O = 2.884(3) Å and angle at H = 146º; 2.02 Å, 2.829(3) Å, 152º]; intramolecular hydroxyl-O-H…O(hydroxyl) hydrogen bonds are noted. The result is a supramolecular layer whereby the organic molecules define channels in which reside the DMSO molecules.

Table ESI S(6). Aggregates featuring S=O...π(arene) interactions.

28 FAFSOW: Molecule 1: *d* = 3.14 Å; θ = 12.5º (O) & *d* = 3.39 Å; θ = 19.8º (O); *d* = 3.64 Å; θ = 7.9º (S) Molecule 2: *d* = 3.18 Å; θ = 17.4º (O) & *d* = 3.37 Å; θ = 19.6º (O); *d* = 3.72 Å; θ = 6.3º (S)

2,8,17,23,31,33-hexaazaheptacyclo[22.6.1.13,7.19,16.118,22.010,15.025,30]tetratriaconta-1,3(34),4,6,8,10,12,14,16,18(32),19,21,23,25,27,29-hexadecaene dimethylsulfoxide methanol solvate

S. Sripothongnak, N. V. Barone, A. Cetin, R. Wu, W. S. Durfee and C. J. Ziegler, *J. Porphyrins Phthalocyanines*, 2010, **14**, 170.



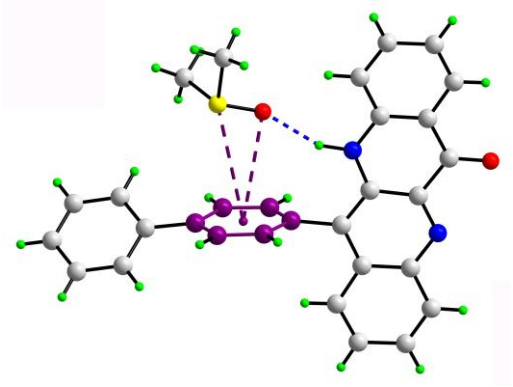
Two independent organic, two DMSO and two methanol molecules comprise the asymmetric unit. Two DMSO molecules associate with two N-bound phenyl rings of each molecule but the primary connection between them are a pair of N–H…O(DMSO) hydrogen bond [Molecule 1: H…O = 2.03 Å, N...O = 2.864(3) Å, angle at H atom = 158º; 2.09 Å, 2.907(3) Å, 154º. Molecule 2: H…O = 2.00 Å, N...O = 2.833(3) Å, 156º; 2.08 Å, 2.907(3) Å, 155º]. Complimenting these are two S(lp)…π(arene) interactions, indicating that each DMSO molecule

forms two lp interactions. The placement of the molecules is such that each ring forming the S(lp)…π(arene) is close to the oxygen atom as well.

29 NAWQOS: *d* = 3.43 Å; θ = 12.3º (O); *d* = 3.90 Å; θ = 10.9º (S)

12-(4-Biphenylyl)dibenzo(b,g)-1,5-naphthyridin-6(11H)-one dimethylsulfoxide solvate

W. Thuer, R. Gompper and K. Polborn (2005) Private Communication to the CSD.

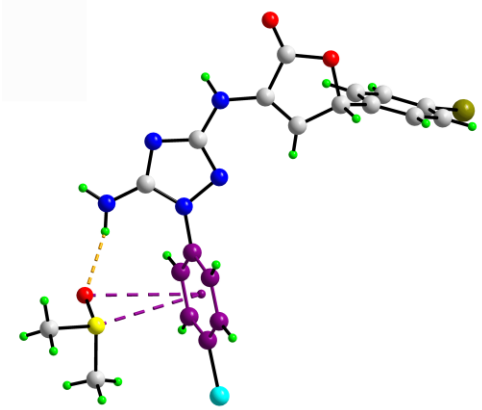


Two-molecule aggregate is stabilised by an amine-N–H…O(DMSO) hydrogen bond [H…O = 1.92 Å, N...O = 2.864(4) Å, angle at H atom = 158º] and further connected by a DMSO-O(lp)…π(arene) interaction. It is noted that the sulphur atom is in close proximity to the ring as well so that the DMSO molecule might be considered interacting side-on.

30 IRUZOL: *d* = 3.60 Å; θ = 14.8º (O); *d* = 3.87 Å; θ = 11.9º (S)

3-((5-Amino-1-(4-chlorophenyl)-1H-1,2,4-triazol-3-yl)amino)-5-(4-bromophenyl)furan-2(5H)-one dimethylsulfoxide solvate

Y. I. Sakhno, S. M. Desenko, S. V. Shishkina, O. V. Shishkin, V. I. Musatov and V. A. Chebanov, *Synthesis*, 2011, 1120.

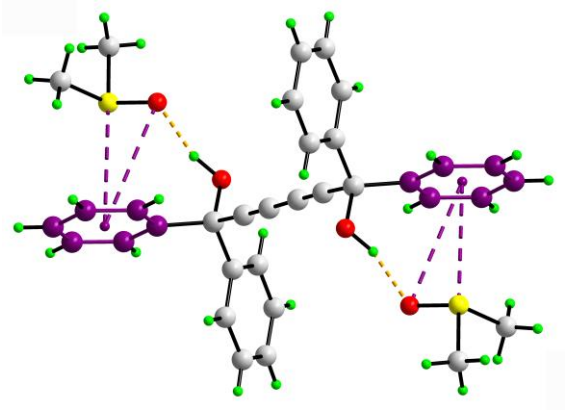


Two-molecule aggregate is stabilised by an amine-N–H…O(DMSO) hydrogen bond [H…O = 2.15 Å, N...O = 2.918(6) Å, angle at H atom = 147º] and further connected by DMSO-O(lp)…π(arene) and DMSO-S(lp)…π(arene) interactions as the DMSO molecule is interacting side-on.

31 VAJYEL: *d* = 3.75 Å; θ = 25.6º (O); *d* = 3.78 Å; θ = 11.0º (S)

1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol bis(dimethylsulfoxide) clathrate

M. R. Caira, A. Jacobs, L. R. Nassimbeni and F. Toda, *CrystEngComm*, 2003, **5**, 150.

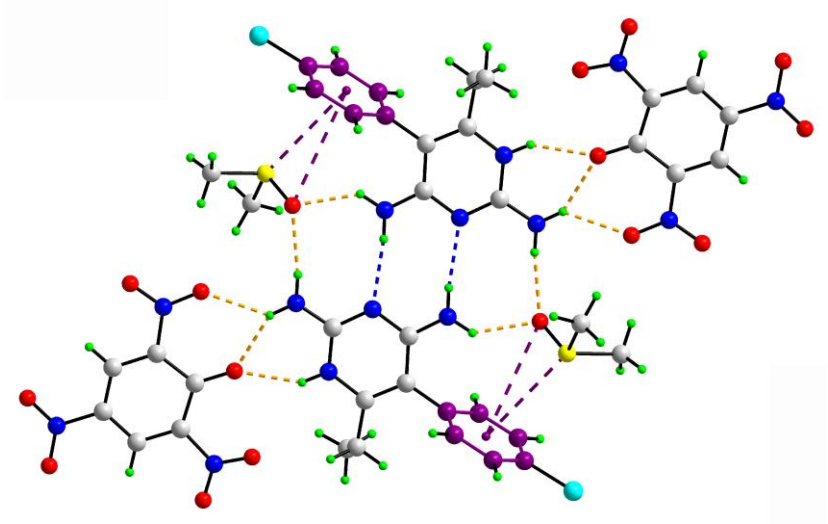


The molecule is disposed about a centre of inversion and one of the terminal phenyl rings forms both DMSO-O(lp)…π(arene) and DMSO-S(lp)…π(arene) interactions, as the DMSO associates side-on. The DMSO molecule is held in place by an intramolecular hydroxyl-O–H…O(DMSO) hydrogen bond [H…O = 1.73 Å, O...O = 2.676(4) Å, angle at H atom = 161º]

32 QOVQAU: *d* = 3.80 Å; θ = 20.1º (O); *d* = 3.62 Å; θ = 15.3º (S)

2,4-Diamino-5-(4-chlorophenyl)-6-ethylpyrimidin-1-ium picrate dimethylsulfoxide solvate

K. Thanigaimani, A. Subashini, P. T. Muthiah, D. E. Lynch and R. J. Butcher, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*., 2009, **65**, o42.

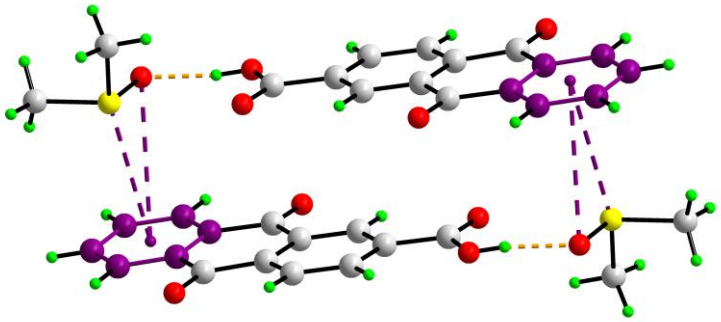


Three-component crystal. The chlorophenyl ring forms both DMSO-O(lp)…π(arene) and DMSO-S(lp)…π(arene) interactions, as the S=O bond approaches the ring side-on. The DMSO molecule is held in place by an intramolecular amine-N–H…O(DMSO) hydrogen bonds with the cation [H…O = 2.05 Å, N...O = 2.765(2) Å, angle at H atom = 137º] and also forms an intermolecular amine-N–H…O(DMSO) hydrogen bonds [H…O = 2.08 Å, N...O = 2.953(3) Å, angle at H atom = 169º] with a centrosymmetrically related cation connected by an eight-membered $\{...HNCN\}_2$ synthon [H…N = 2.12 Å, N...N = 2.996(2) Å, angle at H atom = 170º]. Connections between the ions are of the type N–H...O [amine-H…O = 2.05 Å, N...O = 2.827(2) Å, angle at H atom = 147º, and primary amine-H…O = 2.04 Å, N...O = 2.827(2) Å, angle at H atom = 148º; 2.18 Å, N...O = 2.862(2) Å, 134º]

33 TAJGIW: *d* = 3.80 Å; θ = 24.0º (O); *d* = 3.53 Å; θ = 5.0º (S)

9,10-Dioxo-9,10-dihydroanthracene-2-carboxylic acid dimethylsulfoxide solvate

T. Gruber, S. F. Helas, W. Seichter and E. Weber, *Struct. Chem.*, 2010, **21**, 1079.

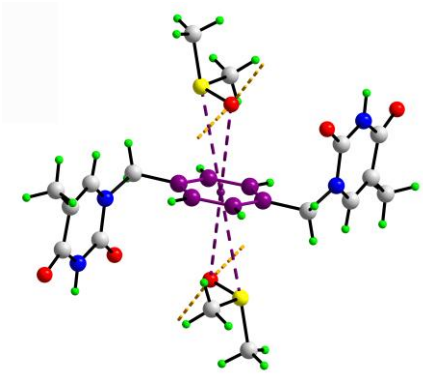


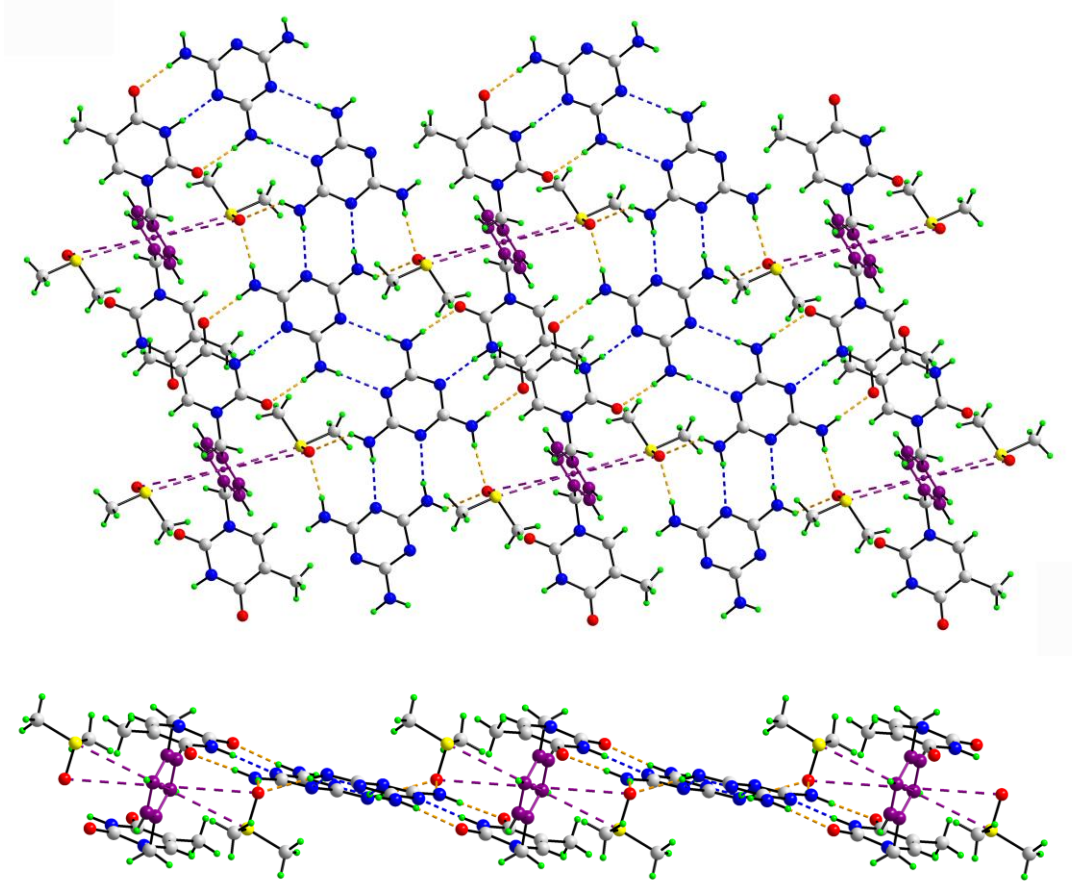
The terminal arene ring participates in DMSO-O(lp)…π(arene) and DMSO-S(lp)…π(arene) interactions while the DMSO-O atom forms a O–H…O hydrogen bond with the carboxylic acid residue [H…O = 1.74 Å; O…O = 2.5747(15) Å and angle at H = 172º] leading to a centrosymmetric four-molecule aggregate.

34 WOMGIP: *d* = 3.82 Å; θ = 19.3º (O); *d* = 3.82 Å; θ = 19.3º (O);

1,1'-(1,4-Phenylenebis(methylene))-bis(5-methylpyrimidine-2,4(1H,3H)-dione) bis(melamine) dimethylsulfoxide solvate

J. Hamblin, S. P. Argent, A. J. Blake, C. Wilson and N. Champness, *CrystEngComm*, 2008, **10**, 1782.



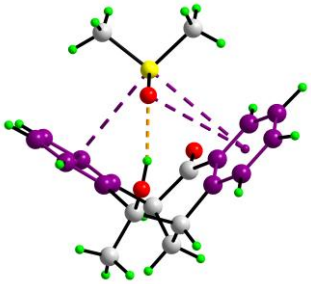


Three-component crystal. The dione molecule is disposed about a crystallographic centre of inversion and the central phenyl ring forms two DMSO-O(lp)…π(arene) interactions and two DMSO-S(lp)…π(arene) interactions, as the DMSO approaches the ring side-on. The DMSO-O atom forms two N–H…O hydrogen bonds with primary-amines of two melamine molecules [H…N = 2.17 Å; N…O = 2.842(2) Å and angle at H = 134º; 2.12 Å, 2.959(2) Å, 169º]. Connections between the dione and melamine are of the type N–H…N(melamine) [H…N = 1.97 Å; N…N = 2.908(2) Å and angle at H = 177º] and melamine-N–H…O(dione) [H…N = 2.06 Å; N…O = 3.000(2) Å and angle at H = 173º; 1.97 Å, 2.874(2) Å, 178º]. A two-dimensional array is mediated by melamine-N–H…N(melamine) interactions [H…N = 2.32 Å; N…N = 3.157(2) Å and angle at H = 175º; 2.23 Å, 3.049(2) Å, 172º]. If the DMSO-O(lp)…π(arene) and DMSO-S(lp)…π(arene) interactions were ignored a two-dimensional array would still be evident and so this interaction is classified as intramolecular.

35 JEZRIP: *d* = 3.85 Å; θ = 18.1º (O); *d* = 3.72 Å; θ = 8.2º (S); *d* = 3.88 Å; θ = 20.7º (S)

endo-8-Hydroxy-8-methyl-2,3:6,7-dibenzobicyclo(3.3.1)nona-2,6-dien-4-one dimethylsulfoxide clathrate

S. C. Hawkins, R. Bishop, D. C. Craig, S. Kim and M. L. Scudder, *Chem. Commun*., 1990, 1683.

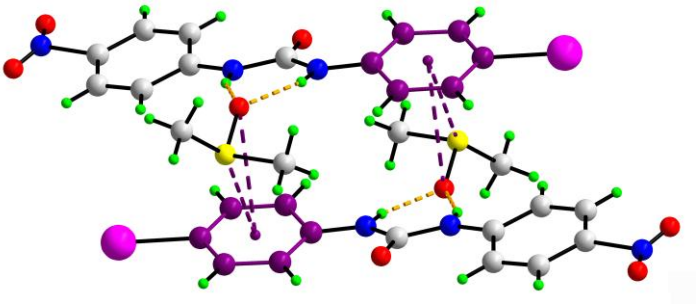


Two-molecule aggregate is stabilised by an hydroxyl-O–H…O(DMSO) hydrogen bond [H…O = 1.92 Å, O...O = 2.761(2) Å, angle at H atom = 162º] and further connected by a DMSO-O(lp)…π(arene) interaction as well as a pair of DMSO-S(lp)…π(arene) interactions. One of the DMSO molecules might be considered interacting side-on.

36 TIVNOC: *d* = 3.87 Å; θ = 2.4º (O); *d* = 3.67 Å; θ = 20.3º (S)

N-(4-Iodophenyl)-N'-(4-nitrophenyl)-urea dimethylsulfoxide solvate

L. S. Reddy, S. K. Chandran, S. George, N. J. Babu and A. Nangia, *Cryst. Growth Des.*, 2007, **7**, 2675.

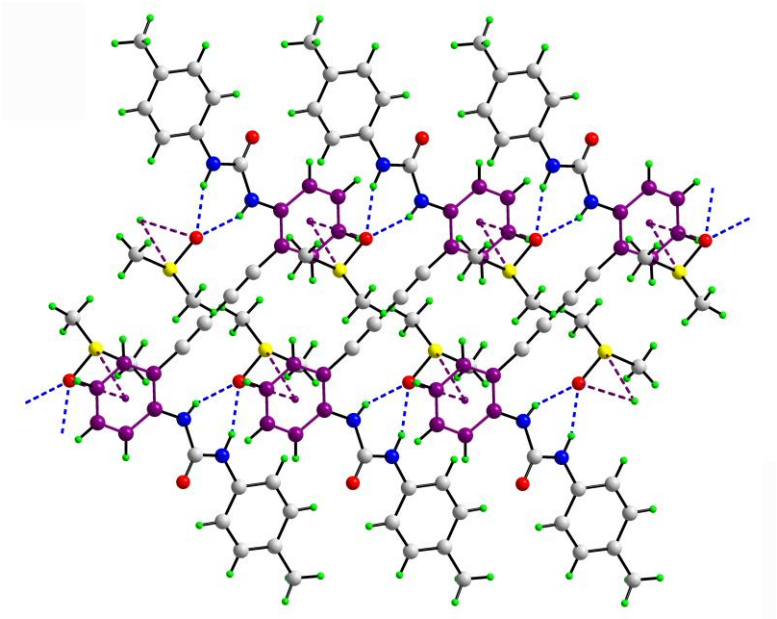


The nitrophenyl ring participates in both DMSO-O(lp)…π(arene) and DMSO-S(lp)…π(arene) interactions, as the DMSO associates side-on. At the same time the DMSO-O atom forms a pair of N–H…O hydrogen bonds with the urea residue [H…N = 2.08 Å; N…O = 2.892(10) Å and angle at H = 159º; 2.08 Å, 2.901(9) Å, 158º] leading to a centrosymmetric four-molecule aggregate.

37 GUTBAZ: *d* = 3.63 Å; θ = 8.8º (O); *d* = 3.76 Å; θ = 15.8º (S)

1,3-bis((R)-1-(1-Naphthyl)ethyl)thiourea dimethylsulfoxide solvate

A. N. Swinburne, M. J. Paterson, A. Beeby and J. W. Steed, *Chem.-Eur. J.*, 2010, **16**, 2714.



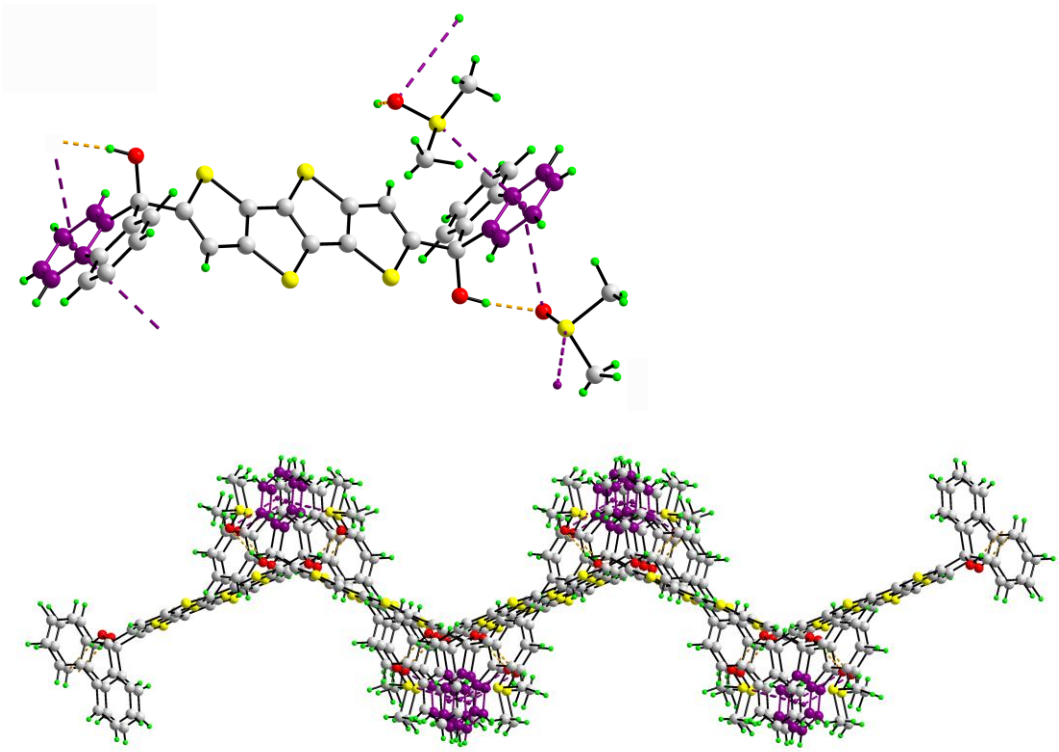
The centrosymmetric organic molecule is connected to two DMSO molecules *via* a pair of amine-N–H…O(DMSO) hydrogen bonds [H…O = 1.94 Å, N...O = 2.793(5) Å, angle at H atom = 161º; 2.24 Å, 2.941(5) Å, 152º] to form a three-molecule aggregate. These are linked into a supramolecular chain (linear topology) *via* two DMSO-O(lp)…π(arene) and two DMSO-S(lp)…π(arene) interactions per centrosymmetric molecule; the S=O bond of the DMSO lies over the ring.

Table ESI S(7). Aggregates featuring both DMSO-O(lone pair)...π(arene) and DMSO-S(lone pair)...π(arene) interactions.

38 KUMHOP: *d* = 3.77 Å; θ = 2.3º (O); *d* = 3.81 Å; θ = 33.7º (S)

2,6-bis(9-Hydroxyfluorenyl)thieno(2',3':3,2)thieno(3,2-b)thieno(2,3-d)thiophene dimethylsulfoxide clathrate

Y. Mazaki, N. Hayashi and K. Kobayashi, *Chem. Commun.*, 1992, 1381.



Centrosymmetric organic molecule forming two hydroxyl-O–H…O(DMSO) hydrogen bonds [H…O = 1.80 Å, N...O = 2.631(4) Å, angle at H atom = 172º], interactions that are further connected by a DMSO-O(lp)…π(arene) interactions. The centroid of each highlighted ring also forms a DMSO-S(lp)…π(arene) interactions with the result that a supramolecular layer is formed with a zigzag topology.