Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Intermolecular C—H···O and C—H···*X* interactions in substituted spiroacenaphthylene structures

J. Suresh,[a]* R. Vishnupriya,[a] S. Sivakumar,[b] R. Ranjith Kumar[b] and S. Athimoolam[c]

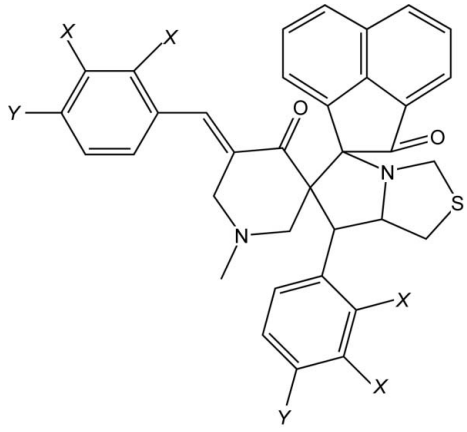
[a]Department of Physics, Madura College, Madurai 625 011, India, [b]Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India, and [c]Department of Physics, University College of Engineering Nagercoil, Anna University of Technology Tirunelveli, Nagercoil 629 004, India
Correspondence e-mail: ambujasureshj@yahoo.com

Received 4 March 2012
Accepted 29 May 2012
Online 13 June 2012

In the three spiroacenaphthylene structures 5″-[(*E*)-2,3-dichlorobenzylidene]-7′-(2,3-dichlorophenyl)-1″-methyldispiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*][1,3]thiazole-6′,3″-piperidine]-2,4″-dione, $C_{35}H_{26}Cl_4N_2O_2S$, (I), 5″-[(*E*)-4-fluorobenzylidene]-7′-(4-fluorophenyl)-1″-methyldispiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*][1,3]thiazole-6′,3″-piperidine]-2,4″-dione, $C_{35}H_{28}F_2N_2O_2S$, (II), and 5″-[(*E*)-4-bromobenzylidene]-7′-(4-bromophenyl)-1″-methyldispiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*][1,3]thiazole-6′,3″-piperidine]-2,4″-dione, $C_{35}H_{28}Br_2N_2O_2S$, (III), the substituted aryl groups are 2,3-dichloro-, 4-fluoro- and 4-bromophenyl, respectively. The six-membered piperidine ring in all three structures adopts a half-chair conformation, the thiazolidine ring adopts a slightly twisted envelope and the pyrrolidine ring an envelope conformation; in each case, the C atom linking the rings is the flap atom. In all three structures, weak intramolecular C—H···O interactions are present. The crystal packing is stabilized through a number of intermolecular C—H···O and C—H···*X* interactions, where *X* = Cl in (I) and F or S in (II), and C—H···O interactions are observed predominantly in (III). In all three structures, molecules are linked through centrosymmetric ring motifs, further tailored through a relay of C—H···*X* [Cl in (I), Br in (II) and O in (III)] interactions.

Comment

The piperidine ring is a distinct structural feature in a variety of alkaloid natural products and drug candidates. During the past decade, thousands of piperidine compounds have been reported in clinical and preclinical studies (Watson *et al.*, 2000). Piperidinones, though less prominent, are also precursors to a host of biologically active compounds and natural alkaloids, prior to their conversion to piperidines. Spiro systems are also of interest as they exhibit a wide range of biological activities (Kobayashi *et al.*, 1991; James *et al.*, 1991). Spiropyrrolidines have attracted much attention as potential antileukaemic and anticonvulsant agents (Abou Gharbia *et al.*, 1979), with antiviral (Lundahl *et al.*, 1972) and local anaesthetic (Kornett & Thio, 1976) activities. Our interest in preparing pharmacologically active piperidones led us to the title 5″-arylmethyl-7′-aryl-1″-methyldispiro[acenaphthylene-1,5′-pyrrolo[1,2-*c*][1,3]thiazole-6′,3″-piperidine]-2,4″-dione compounds, where aryl is 2,3-dichlorophenyl in (I), 4-fluorophenyl in (II) and 4-bromophenyl in (III), and especially the study of their conformational features. There are few structures in the Cambridge Structral Database (CSD, Version 5.26; Allen, 2002) containing pyrrolothiazine ring systems and this is the first report with the attached five-membered ring. Hence, these structures are presumed to be interesting and contain rarely studied moieties.



(I) *X* = Cl, *Y* = H
(II) *X* = H, *Y* = F
(III) *X* = H, *Y* = Br

The six-membered piperidine rings in all three compounds (Figs. 1–3) adopt the half-chair conformation, with deviations of atoms N1 and C5 from the least-squares plane defined by atoms C2/C3/C4/C6 of 0.613 (3) and 0.509 (3) Å in (I),

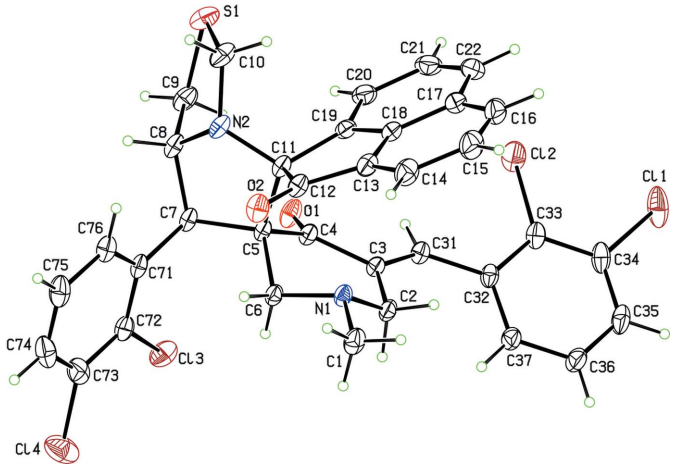


Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

 doi:10.1107/S0108270112024584

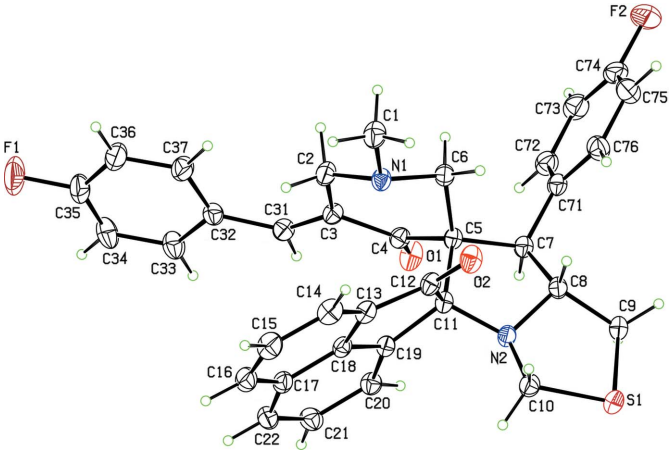


Figure 2
The molecular structure of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

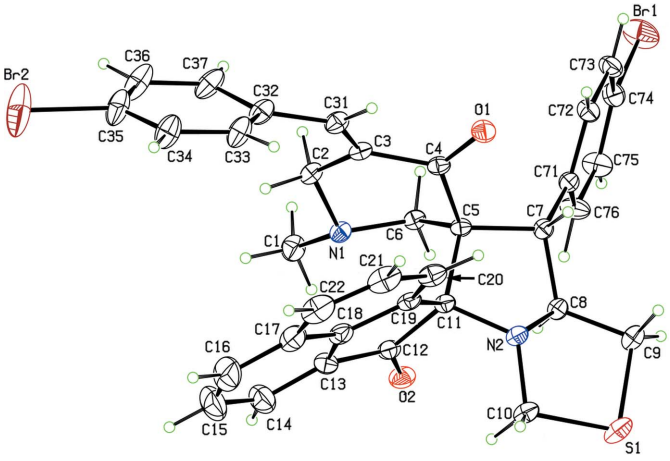


Figure 3
The molecular structure of (III), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

0.553 (3) and 0.562 (3) Å in (II), and 0.545 (3) and 0.565 (3) Å in (III), respectively. The differences in the deviations are due to steric hindrance of the different substituents at the C3 and C5 positions of the piperidine ring. The olefinic double bond in all three structures has an *E* conformation and the pyrrolidine ring is in an envelope conformation. The thiazolidine ring is in a twisted envelope conformation with atom C8 at the flap, with a pseudo-twofold axis passing through atom S1 and the C8—N2 bond. The puckering parameters (Cremer & Pople, 1975) and the smallest displacement asymmetry parameters (Nardelli, 1983) are q_2 = 0.356 (2) Å, φ = −78.0 (4)° and Δs(C8) = 0.035 (1) Å for the thiazolidine ring, and q_2 = 0.263 (2) Å, φ = −178.2 (4)° and Δs(C8) = 0.010 (1) Å for the pyrrolidine ring of (I); q_2 = 0.419 (2) Å, φ = −93.3 (3)° and Δs(S1) = 0.016 (1) Å for the thiazolidine ring, and q_2 = 0.456 (2) Å, φ = −0.4 (3)° and Δs(C8) = 0.001 (1) Å for the pyrrolidine ring of (II); and q_2 = 0.440 (3) Å, φ = −75.0 (4)° and Δs(C8) = 0.029 (1) Å for the thiazolidine ring, and q_2 = 0.460 (3) Å, φ = 144.6 (4)° and Δs(C8) = 0.011 (1) Å for the pyrrolidine ring of (III).

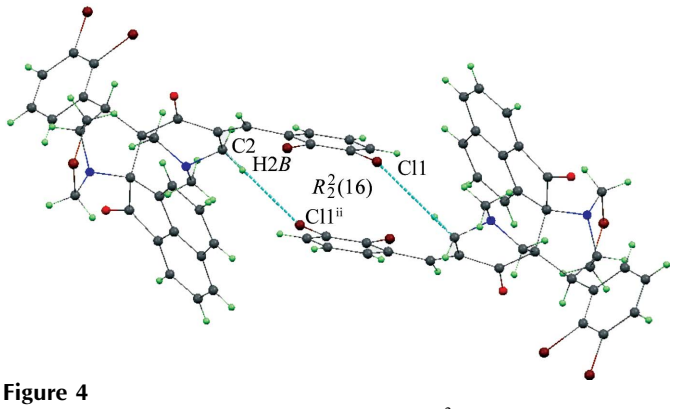


Figure 4
A partial packing view for (I), showing the $R_2^2(16)$ ring. Dashed lines indicate hydrogen bonds. [Symmetry code: (ii) $-x+1, -y+1, -z$.]

The aryl rings in all three structures are not coplanar with the mean plane of the piperidone ring; the torsion angle C3—C31—C32—C37 is 32.4 (3)° in (I), 9.6 (4)° in (II) and −44.0 (5)° in (III). This lack of coplanarity is caused by nonbonded interactions between one of the *ortho* H atoms in the aryl ring and the equatorial H atoms at the 2-position of the piperidone ring (H37/H2*A* or H2*B*). Steric repulsions are reduced by the expansion of the C3—C31—C32 angle [129.57 (19)° in (I), 132.7 (2)° in (II) and 127.1 (3)° in (III)]. The dihedral angle between the dichlorophenyl rings is 58.4 (1)° in (I), that between the fluorophenyl rings is 87.2 (1)° in (II) and that between the bromophenyl rings is 86.1 (1)° in (III), and these rings make angles of 56.5 (1) and 65.2 (1)° in (I), 45.4 (1) and 43.1 (1)° in (II), and 48.7 (1) and 48.4 (1)° in (III) with their respective acenaphthylene group.

The C—C bond lengths and C—C—C angles in the acenaphthylene groups of (I)–(III) compare with those of related structures (Hazell, 1976; Hazell & Hazell, 1977; Hazell & Weigelt, 1976; Jones *et al.*, 1992; Sundar *et al.*, 2002). The C8—N2 bond length is 1.451 (3) Å in (I), 1.448 (3) Å in (II) and 1.455 (3) Å in (III), and these values are comparable with the Csp^2—Nsp^2 distances found in similar structures (Sussman & Wodak, 1973; Wodak, 1975). All three title structures feature a weak intramolecular C—H···O interaction linking pyrrolidine and piperidine rings.

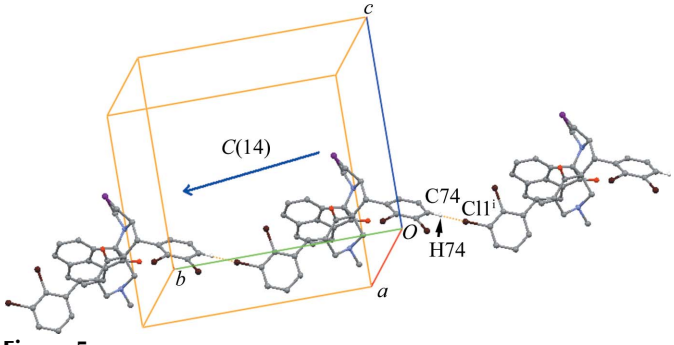


Figure 5
A partial packing view for (I), showing the *C*(14) chain extending along the *b* axis of the unit cell. Dashed lines indicate hydrogen bonds. Some H atoms have been omitted for clarity. [Symmetry code: (i) $x, y-1, z$.]

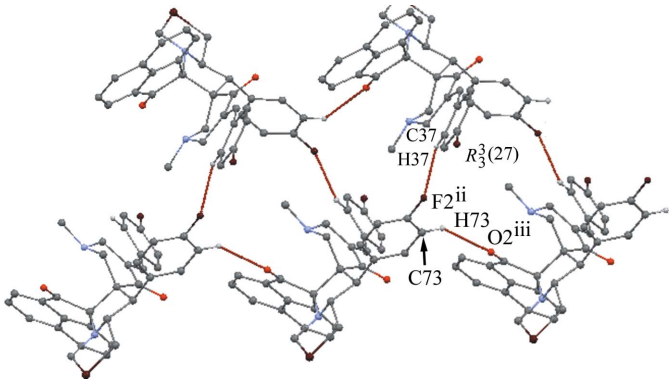


Figure 6
A partial packing view for (II), showing the unusual $R_3^3(27)$ ring. Dashed lines indicate hydrogen bonds. Some H atoms have been omitted for clarity. [Symmetry codes: (ii) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x, y-1, z$.]

In all three structures, due to the lack of suitable donor and acceptor atoms for classical hydrogen bonding, the crystal structures are stabilized through intermolecular C—H···X interactions [X = Cl in (I), F in (II) and O in (III)]. These C—H···X interactions lead to primary ring motifs around inversion centres, which are further connected through chain motifs (Bernstein *et al.*, 1995).

In (I), the molecules are connected through a C2—H2B···Cl1^{ii} interaction, leading to an $R_2^2(16)$ ring around the inversion centres of the unit cell (Fig. 4), and this ring, translated by a unit cell along the b axis connected by an intermolecular C74—H74···Cl1^{i} interaction (see Table 1 for symmetry codes), leads to a $C(14)$ chain extending along the b axis (Fig. 5). These chains or rings do not have linking C—H···O or C—H···π interactions.

In (II), one C73—H73···O2^{iii} and two C37—H37···F2^{ii} interactions lead to an unusual $R_3^3(27)$ ring (Fig. 6), which is connected through a secondary $C_2^2(14)$ chain extending along the ab diagonal of the unit cell (Fig. 7), formed through C37—H37···F2^{ii} and C33—H33···S1^{i} interactions (see Table 2 for symmetry codes).

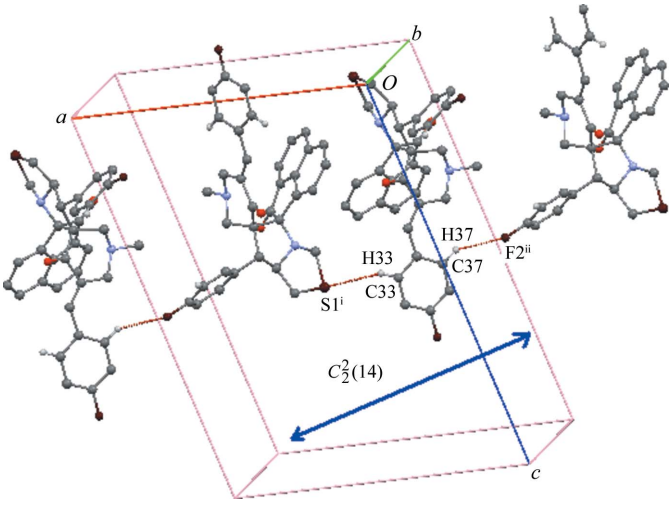


Figure 7
A partial packing view for (II), showing the $C_2^2(14)$ chain extending along the ab diagonal of the unit cell. Dashed lines indicate hydrogen bonds. Some H atoms have been omitted for clarity. [Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.]

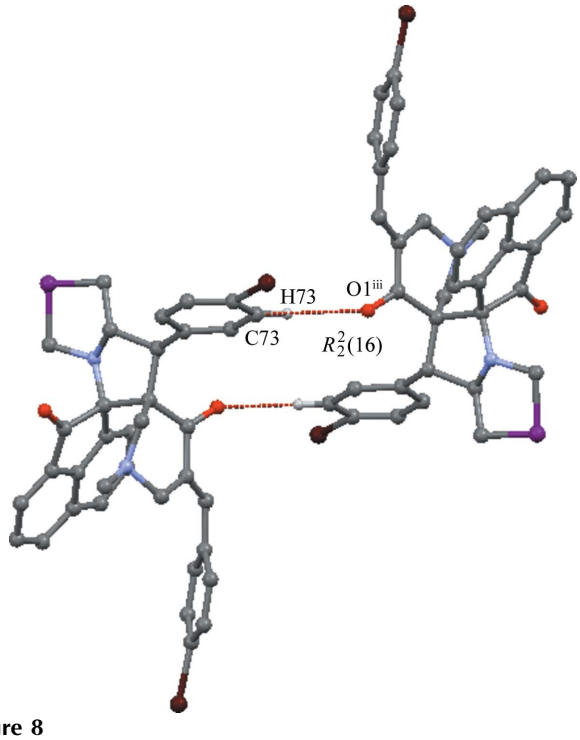


Figure 8
A partial packing view for (III), showing the $R_2^2(16)$ ring. Dashed lines indicate hydrogen bonds. Some H atoms have been omitted for clarity. [Symmetry code: (iii) $-x+1, -y+1, -z+1$.]

In (III), all the intermolecular interactions are of the C—H···O type (Table 3). The crystal packing features two dimeric $R_2^2(16)$ and $R_2^2(14)R_2^2(16)$ ring motifs formed through C73—H73···O1^{iii} and C76—H76···O2^{ii}/C9—H9B···O2^{ii} hydrogen bonds (Figs. 8 and 9). These C—H···O hydrogen-bonded dimers are arranged in tandem and form a zigzag $C(8)$ chain extending along the b axis through a C34—H34···O1^{i} interaction (Fig. 10) (see Table 3 for symmetry codes).

Thus, all three title spiroacenaphthylene crystal structures are stabilized through nonclassical C—H···X interactions with primary ring and secondary chain motifs.

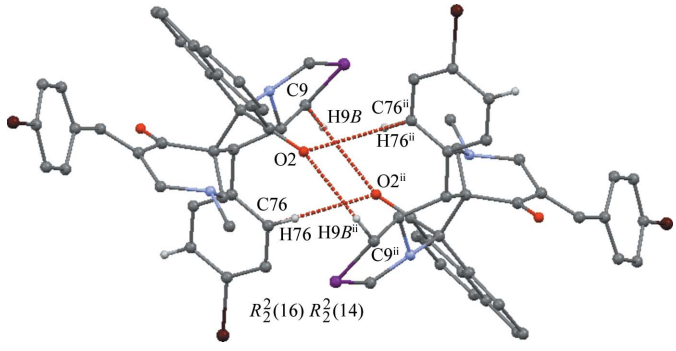


Figure 9
A partial packing view for (III), showing the $R_2^2(14)R_2^2(16)$ ring. Dashed lines indicate hydrogen bonds. Some H atoms have been omitted for clarity. [Symmetry code: (ii) $-x, -y+1, -z+1$.]

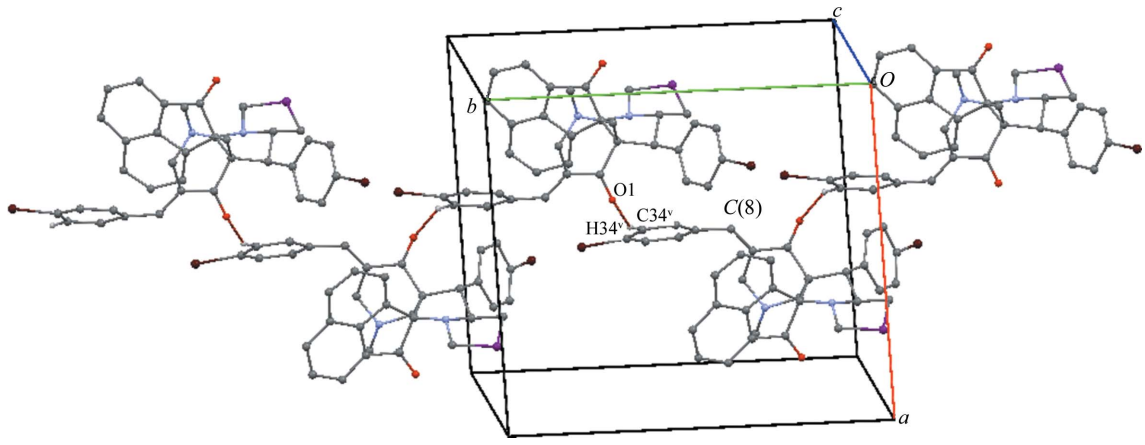


Figure 10
A partial packing view for (III), showing the $C(8)$ chain extending along the b axis of the unit cell. Dashed lines indicate hydrogen bonds. Some H atoms have been omitted for clarity. [Symmetry code: (v) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$.]

Experimental

For the preparation of (I), a mixture of 3,5-bis[(*E*)-2,3-dichlorobenzylidene]-1-methyltetrahydropyridin-4(1*H*)-one (1 mmol), acenaphthenequinone (0.182 g, 1 mmol) and 1,3-thiazolane-4-carboxylic acid (0.133 g, 1 mmol) was dissolved in methanol (10 ml) and refluxed for 30 min. After completion of the reaction, as evident from thin-layer chromatography (TLC), the mixture was poured into water (50 ml) and the precipitated solid was filtered off and washed with water (100 ml) to obtain the pure product as a pale-yellow solid. The product was recrystallized from ethyl acetate to obtain suitable crystals of (I) for X-ray analysis (yield 92%, m.p. 477 K).

For the preparation of (II), a mixture of 3,5-bis[(*E*)-4-fluorobenzylidene]-1-methyltetrahydropyridin-4(1*H*)-one (1 mmol), acenaphthenequinone (0.182 g, 1 mmol) and 1,3-thiazolane-4-carboxylic acid (0.133 g, 1 mmol) was dissolved in methanol (10 ml) and refluxed for 30 min. After completion of the reaction, as evident from TLC, the mixture was poured into water (50 ml) and the precipitated solid was filtered off and washed with water (100 ml) to obtain the pure product as a pale-yellow solid. The product was recrystallized from ethyl acetate to obtain suitable crystals of (II) for X-ray analysis (yield 91%, m.p. 483 K).

For the preparation of (III), a mixture of 3,5-bis[(*E*)-4-bromobenzylidene]-1-methyltetrahydropyridin-4(1*H*)-one (1 mmol), acenaphthenequinone (0.182 g, 1 mmol) and 1,3-thiazolane-4-carboxylic acid (0.133 g, 1 mmol) was dissolved in methanol (10 ml) and refluxed for 30 min. After completion of the reaction, as evident from TLC, the mixture was poured into water (50 ml) and the precipitated solid was filtered off and washed with water (100 ml) to obtain the pure product as a pale-yellow solid. The product was recrystallized from ethyl acetate to obtain suitable crystals of (III) for X-ray analysis (yield 91%, m.p. 485 K).

Compound (I)

Crystal data

$C_{35}H_{26}Cl_4N_2O_2S$
M_r = 680.44
Monoclinic, $P2_1/n$
a = 13.4722 (6) Å
b = 16.4269 (8) Å
c = 14.8673 (7) Å
β = 108.243 (2)°
V = 3124.9 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.48 mm^{-1}
T = 293 K
0.19 × 0.16 × 0.11 mm

Data collection

Bruker Kappa APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.912, T_{max} = 0.948
37631 measured reflections
8258 independent reflections
5375 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.134
S = 1.02
8258 reflections
397 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}

Compound (II)

Crystal data

$C_{35}H_{28}F_2N_2O_2S$
M_r = 578.65
Monoclinic, $P2_1/n$
a = 14.8802 (5) Å
b = 9.6789 (3) Å
c = 20.2209 (6) Å
β = 104.155 (2)°
V = 2823.87 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.16 mm^{-1}
T = 293 K
0.21 × 0.14 × 0.11 mm

Data collection

Bruker Kappa APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.973, T_{max} = 0.982
26085 measured reflections
5494 independent reflections
3862 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.140
S = 1.08
5494 reflections
381 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Compound (III)

Crystal data

$C_{35}H_{28}Br_2N_2O_2S$
M_r = 700.47
Monoclinic, $P2_1/c$
a = 14.2275 (7) Å
b = 15.6753 (8) Å
c = 15.3780 (7) Å
β = 116.761 (2)°
V = 3062.3 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.75 mm^{-1}
T = 293 K
0.19 × 0.16 × 0.11 mm

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C74—H74···Cl1^{i}	0.93	2.82	3.497 (3)	130
C2—H2B···Cl1^{ii}	0.97	2.86	3.784 (2)	159
C9—H9B···O1	0.97	2.44	3.251 (3)	141

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, -y+1, -z$.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C33—H33···S1^{i}	0.93	2.87	3.716 (3)	152
C37—H37···F2^{ii}	0.93	2.48	3.302 (3)	147
C73—H73···O2^{iii}	0.93	2.68	3.454 (4)	141
C10—H10B···O2	0.97	2.59	3.202 (3)	122

Symmetry codes: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x, y-1, z$.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
C34—H34···O1^{i}	0.93	2.57	3.440 (5)	157
C76—H76···O2^{ii}	0.93	2.46	3.250 (5)	143
C73—H73···O1^{iii}	0.93	2.45	3.361 (5)	166
C9—H9B···O2^{ii}	0.97	2.62	3.298 (3)	128
C10—H10A···O2	0.97	2.54	3.176 (4)	123

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+1$.

Data collection

Bruker Kappa APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.599, T_{max} = 0.739
30894 measured reflections
6169 independent reflections
3897 reflections with $I > 2\sigma(I)$
R_{int} = 0.039

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.141
S = 1.00
6169 reflections
382 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.98 e Å^{-3}

H atoms were placed at calculated positions and allowed to ride on their carrier atoms, with C—H = 0.93 (aromatic), 0.96 (methyl), 0.97 (methylene) or 0.98 Å (methine), and with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms or 1.2U_{eq}(C) otherwise.

For all three compounds, data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

JS thanks the UGC for FIST support. JS and RV thank the management of Madura College for their encouragement and support. RRK thanks the DST, New Delhi, for funds under the Fast Track Scheme (grant No. SR/FT/CS-073/2009)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3273). Services for accessing these data are described at the back of the journal.

References

Abou Gharbia, M. A. & Doukas, P. H. (1979). *Heterocycles*, **12**, 637–640.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2004). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Hazell, A. C. (1976). *Acta Cryst.* B**32**, 2010–2013.
Hazell, A. C. & Hazell, R. G. (1977). *Acta Cryst.* B**33**, 360–365.
Hazell, A. C. & Weigelt, Å. (1976). *Acta Cryst.* B**32**, 306–308.
James, D. M., Kunze, H. B. & Faulkner, D. J. (1991). *J. Nat. Prod.* **54**, 1137–1140.
Jones, P. G., Bubenitschek, P., Sheldrick, G. M. & Dyker, G. (1992). *Acta Cryst.* C**48**, 1633–1635.
Kobayashi, J., Tsuda, M., Agemi, K., Shegemori, H., Ishibashi, M., Sasaki, T. & Mikami, Y. (1991). *Tetrahedron*, **47**, 6617–6622.
Kornett, M. J. & Thio, A. P. (1976). *J. Med. Chem.* **19**, 892–898.
Lundahl, K., Schut, J., Schlatmann, J. L. M. A., Paerels, G. B. & Peters, A. N. V. (1972). *J. Med. Chem.* **15**, 129–132.
Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Sundar, T. V., Parthasarathi, V., Álvarez-Rúa, C., García-Granda, S., Saxena, A., Pardasani, P. & Pardasani, R. T. (2002). *Acta Cryst.* E**58**, o1405–o1407.
Sussman, J. L. & Wodak, S. J. (1973). *Acta Cryst.* B**29**, 2918–2926.
Watson, P. S., Jiang, B. & Scott, B. (2000). *Org. Lett.* **2**, 3679–3681.
Wodak, S. J. (1975). *Acta Cryst.* B**31**, 569–573.