

Molecular conformation and supramolecular aggregation in four 2,3,4,5-tetrahydro-3,4-diphenyl-benzothiazepines

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Received 12 March 2004

Accepted 13 April 2004

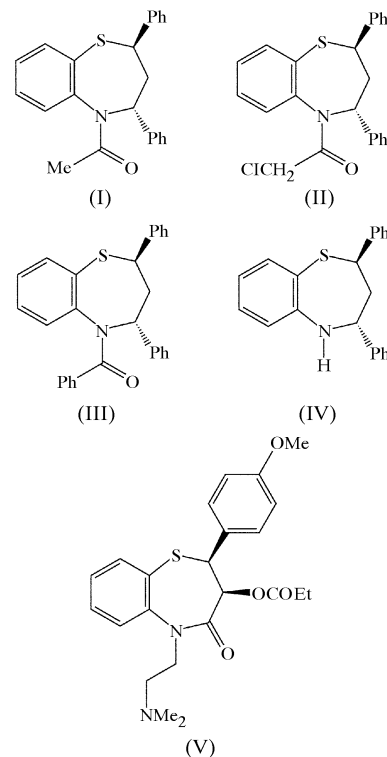
Online 22 May 2004

In (2*RS*,4*RS*)-1-acetyl-2,3,4,5-tetrahydro-2,4-diphenyl-1,5-benzothiazepine, C₂₃H₂₁NOS, (I), and (2*RS*,4*RS*)-1-chloroacetyl-2,3,4,5-tetrahydro-2,4-diphenyl-1,5-benzothiazepine, C₂₃H₂₀ClNOS, (II), the seven-membered rings have boat conformations, whereas in (2*RS*,4*RS*)-1-benzoyl-2,3,4,5-tetrahydro-2,4-diphenyl-1,5-benzothiazepine, C₂₈H₂₃NOS, (III), this ring has a conformation intermediate between the boat and twist-boat forms. The molecules of (I) are linked into isolated *R*₂²(16) dimers by two C—H...O hydrogen bonds [H...O = 2.41 and 2.47 Å, C...O = 3.268 (3) and 3.336 (3) Å, and C—H...O = 150 and 152°]. In (II), the molecules are again linked by two C—H...O hydrogen bonds [H...O = 2.42 and 2.48 Å, C...O = 3.295 (3) and 3.364 (2) Å, and C—H...O = 153 and 154°], forming chains of alternating *R*₂²(18) and *R*₂²(22) rings. Two C—H...O hydrogen bonds [H...O = 2.49 and 2.53 Å, C...O = 3.347 (2) and 3.295 (2) Å, and C—H...O = 150 and 138°] link the molecules of (III) into sheets containing alternating *R*₂²(22) and *R*₆⁴(30) rings. Re-examination of the published structure of (2*RS*,4*RS*)-2,3,4,5-tetrahydro-2,4-diphenyl-1,5-benzothiazepine shows that the molecules are linked by three C—H...π(arene) hydrogen bonds into a three-dimensional framework.

Comment

We report here the molecular and supramolecular structures of three *N*-acyl-*C*-phenylated tetrahydrobenzothiazepines, (I)–(III), and we compare these with the simpler analogue, (IV), which is unsubstituted at the *N* atom and whose structure has recently been reported (Laavanya *et al.*, 2002). These

compounds are of interest as their molecular constitutions all bear some resemblance to that of the calcium antagonist drug diltiazem [or (2*S*,3*S*)-3-acetoxy-5-(dimethylaminoethyl)-2-(4-methoxyphenyl)-2,3-dihydro-1,5-benzothiazepine-4(5*H*)-one, (V)] and its 2*R*,3*R* enantiomer (Kojić-Prodić *et al.*, 1984).



Each of (I)–(III) (Figs. 1–3) contains two stereogenic C atoms, C2 and C4, and hence the formation of diastereoisomers is possible. However, each of the crystalline samples examined contained a single pair of enantiomers, *R,R* and *S,S*, and for each compound the reference molecule was selected as having the *R,R* configuration. In this respect, the configurations of (I)–(III) are identical to that of (IV) (Laavanya *et al.*, 2002). It should, however, be noted here that the schematic view of (IV) in the original report shows the incorrect 2*S*,4*R* isomer. The interbond angles at the N atom in each of (I)–(III) sum to ~360.0°, so that no further configurational isomers are possible.

Compound (I) crystallizes with *Z'* = 2; the thiazepine rings in the two independent molecules in (I) and in the molecules of (II) and (III) all adopt similar conformations, as shown by the ring torsion angles (Table 5). Apart from the S1—C10—C11—N5 angle, there are corresponding pairs of torsion angles having similar magnitudes but opposite signs. This fact indicates conformations that, apart from the obvious differences in atom types and bond lengths, approximate in (I) and (II) to pseudo-mirror symmetry; this conformation may be best described as the boat conformation (Evans & Boeyens, 1989). The conformation of the thiazepine ring in (III) does not exhibit even approximate symmetry and it cannot be described in terms of a single primitive form (Evans & Boeyens, 1989). Instead, the conformation is intermediate between the boat and twist-boat forms. By contrast, the thia-

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zepine ring in (IV) exhibits approximate pseudo-twofold rotational symmetry, as the corresponding pairs of torsion angles have similar magnitudes with the same signs, although all four primitive forms contribute to the overall conformation of (IV).

The only significant difference between the bond lengths in (I)–(III) and those in (IV) occurs for the N5–C11 bond. In (I)–(III), where atom N5 is coplanar with the thiazepine ring, this distance lies in the range 1.427 (3)–1.439 (2) Å, whereas in (IV), where the configuration involving atom N5 is pyramidal, this distance is 1.395 (3) Å. By contrast, the mean values for bonds of types C_{aryl}–NC₂, involving planar N atoms, and C_{aryl}–NHC, involving pyramidal N atoms, are 1.371 and 1.419 Å, respectively (Allen *et al.*, 1987). The remaining bond lengths in (I)–(III) show no unusual values.

The supramolecular structures of (I)–(III) all have different dimensionality. In (I), the two independent molecules are linked by a pair of C–H···O hydrogen bonds (Table 1). Atom C145 in the type 1 molecule at (x, y, z) acts as a hydrogen-

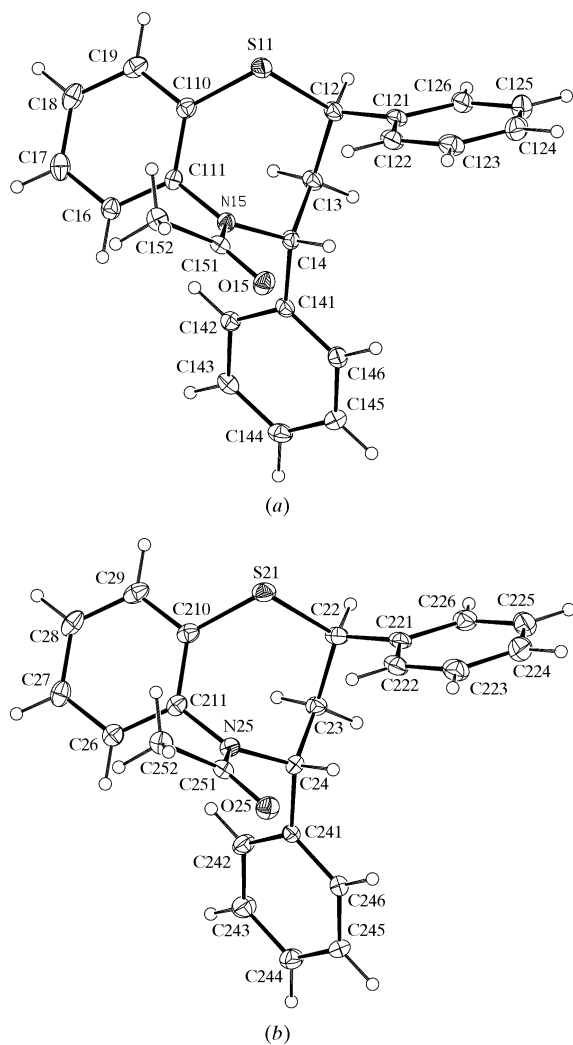


Figure 1
The two independent molecules of (I), showing the atom-labelling schemes: (a) molecule 1 and (b) molecule 2. Displacement ellipsoids are drawn at the 30% probability level.

bond donor to carbonyl atom O25 in the type 2 molecule at (1 – x, 1 – y, 1 – z), while atom C245 at (1 – x, 1 – y, 1 – z) in turn acts as a donor to carbonyl atom O15 at (x, y, z). In this manner, an approximately centrosymmetric $R_2^2(16)$ dimer is formed (Fig. 4). This dimeric aggregate is centred at approximately (0.75, 0.37, 0.75), and this alone precludes the possibility of any additional symmetry. While such an aggregate would normally have been selected as the asymmetric unit, in this instance the asymmetric unit was selected so that each of the independent molecules had the *R,R* configuration. The $R_2^2(16)$ dimer contains one *R,R* molecule and one *S,S* molecule. There are four of these dimeric units in each unit cell, but there are no direction-specific interactions between adjacent dimers.

In (II), the molecules are linked by two C–H···O hydrogen bonds (Table 2) into a chain of rings. Atom C24 in the molecule at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O5 in the molecule at (1 – x, –y, 1 – z), so forming an $R_2^2(22)$ ring centred at ($\frac{1}{2}$, 0, $\frac{1}{2}$), while atom C44 at

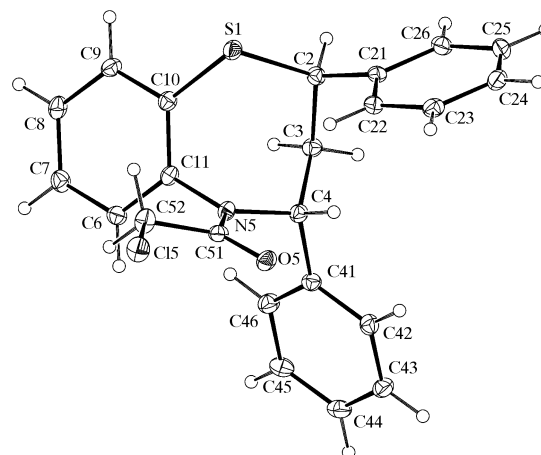


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

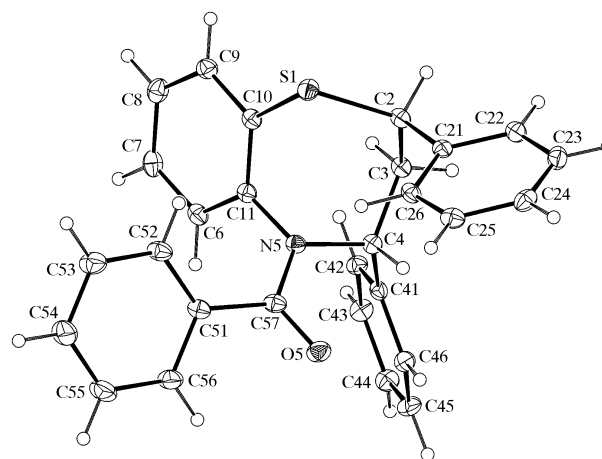


Figure 3
The molecule of (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

(x, y, z) acts as a donor to atom O5 at $(1 - x, 1 - y, 1 - z)$, thus forming an $R_2^2(18)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Propagation of these two hydrogen bonds then generates a chain of rings along $(\frac{1}{2}, y, \frac{1}{2})$, with $R_2^2(18)$ rings centred at $(\frac{1}{2}, n + \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) and $R_2^2(22)$ rings centred at $(\frac{1}{2}, n, \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 5). Two chains of this type pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

As in (II), the supramolecular structure of (III) is again dictated by two intermolecular C—H...O hydrogen bonds (Table 3), but now their effect is to generate a sheet structure, in contrast with the chain of rings in (II). The stronger of these two hydrogen bonds gives rise to a chain running parallel to the [010] direction. Atom C23 in the molecule at (x, y, z) acts

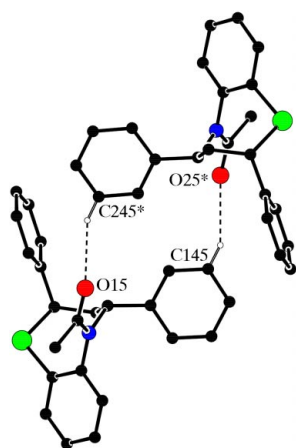


Figure 4

Part of the crystal structure of (I), showing the formation of a hydrogen-bonded $R_2^2(16)$ dimer. For clarity, the unit-cell box and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

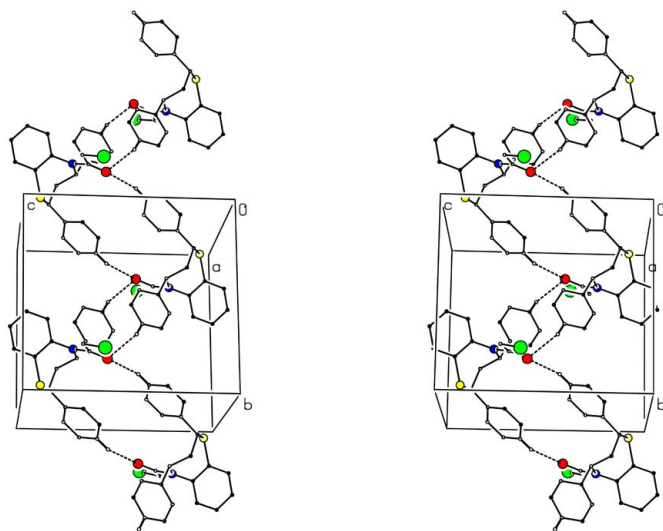


Figure 5

A stereoview of part of the crystal structure of (II), showing the formation of a chain of alternating $R_2^2(18)$ and $R_2^2(22)$ rings along [010]. For clarity, H atoms not involved in the motif shown have been omitted.

as a hydrogen-bond donor to carbonyl atom O5 in the molecule at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$, so producing a $C(10)$ chain, generated by the 2_1 screw axis along $(\frac{1}{4}, y, \frac{3}{4})$ (Fig. 6). Four of these chains pass through each unit cell; two, lying in the domain $-0.02 < x < 0.52$, are generated by screw axes at $x = \frac{1}{4}$, while the other two, lying in the domain $0.48 < x < 1.02$, are generated by screw axes at $x = \frac{3}{4}$. Within each domain, the

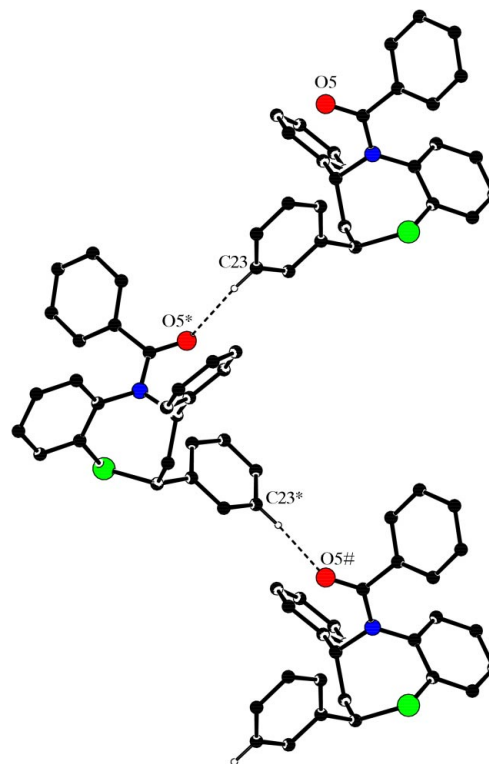


Figure 6

Part of the crystal structure of (III), showing the formation of a $C(10)$ chain along [010]. For clarity, the unit-cell box and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(x, 1 + y, z)$, respectively.

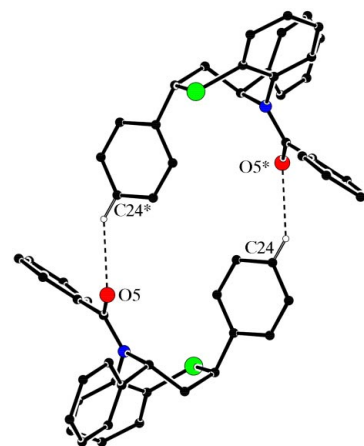


Figure 7

Part of the crystal structure of (III), showing the formation of an $R_2^2(22)$ dimer. For clarity, the unit-cell box and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(\frac{1}{2} - x, \frac{1}{2} - y, 2 - z)$.

$C(10)$ chains are linked into sheets by the second of the $C-H \cdots O$ hydrogen bonds. Atom C24 in the molecule at (x, y, z) , which lies in the $C(10)$ chain along $(\frac{1}{4}, y, \frac{3}{4})$, acts as a hydrogen-bond donor to carbonyl atom O5 in the molecule at $(\frac{1}{2} - x, \frac{1}{2} - y, 2 - z)$, which lies in the $C(10)$ chain along $(\frac{1}{4}, y, \frac{3}{4})$, so forming a centrosymmetric $R_2^2(22)$ ring centred at $(\frac{1}{4}, \frac{1}{4}, 1)$ (Fig. 7). The combination of the $R_2^2(22)$ rings and the $C(10)$ chains generates a (100) sheet built from $R_2^2(22)$ and $R_6^4(30)$ rings alternating in a chessboard fashion (Fig. 8). Two sheets of this type pass through each unit cell, one in each domain of x as defined above, but there are no direction-specific interactions between adjacent sheets. Despite the presence of at least three independent aryl rings in each of (I)–(III), there are neither $C-H \cdots \pi(\text{arene})$ hydrogen bonds nor aromatic $\pi-\pi$ stacking interactions present in any of their structures.

In the light of the very different supramolecular structures adopted by (I)–(III), it seemed of interest to re-examine the supramolecular structure of (IV) using space group $P2_1/n$, with $Z' = 1$, and the atomic coordinates established by Laavanya *et al.* (2002), where the atom labelling is identical to that employed in (I)–(III). There are, in fact, three $C-H \cdots \pi(\text{arene})$ hydrogen bonds, all with $H \cdots$ centroid distances

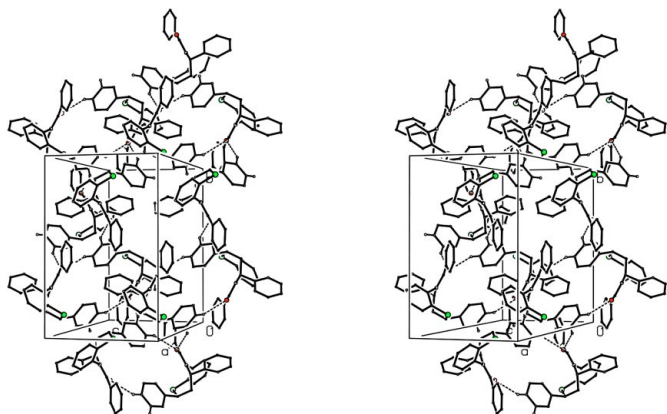


Figure 8

A stereoview of part of the crystal structure of (III), showing the formation of a (100) sheet built from alternating $R_2^2(22)$ and $R_6^4(30)$ rings. For clarity, H atoms not involved in the motif shown have been omitted.

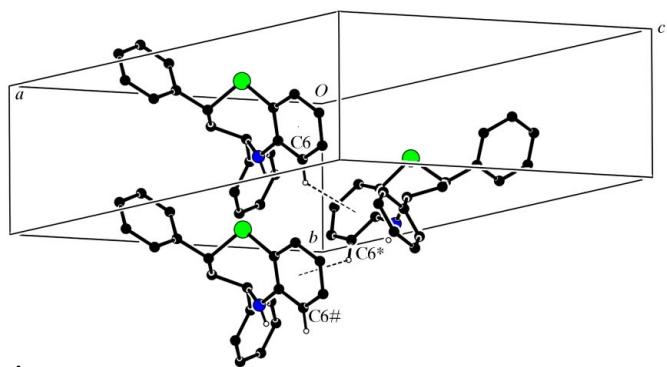


Figure 9

Part of the crystal structure of (IV) (Laavanya *et al.*, 2002), showing the formation of a $C-H \cdots \pi(\text{arene})$ chain along $(\frac{1}{4}, y, \frac{1}{4})$. For clarity, H atoms bonded to C atoms but not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ and $(x, 1 + y, z)$, respectively.

of less than 3.0 Å (Table 4), which were not noted in the original report but which together link the molecules of (IV) into a continuous three-dimensional framework.

In the first of these interactions, atom C6 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the C6–C11 ring in the molecule at $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, so producing a [010] chain generated by the 2_1 screw axis along $(\frac{1}{4}, y, \frac{1}{4})$ (Fig. 9). In a similar way, atom C21 at (x, y, z) acts as a donor to the C20–C25 ring (original atom numbering) in the molecule at $(\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, so producing a second [010] chain, this time generated by the screw axis along $(\frac{3}{4}, y, \frac{1}{4})$. The combination of these two chains then generates a (001) sheet in the form of a (4,4)-net (Batten & Robson, 1998), lying in the domain $-0.04 < z < 0.54$ (Fig. 10); a second sheet, related to the first by inversion, lies in the domain $0.46 < z < 1.04$.

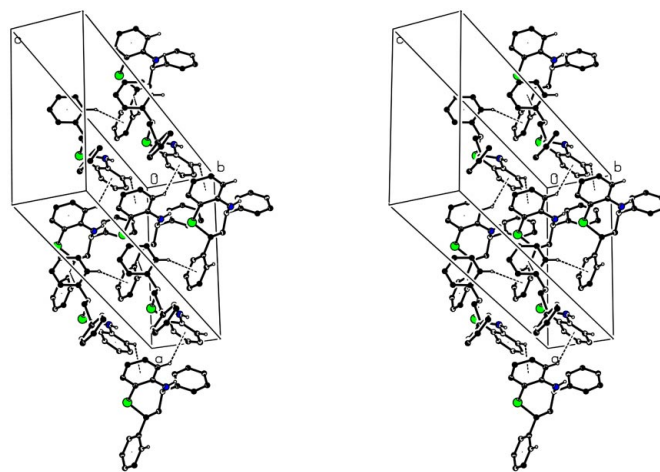


Figure 10

A stereoview of part of the crystal structure of (IV), showing the formation of a (001) sheet. For clarity, H atoms not involved in the motif shown have been omitted.

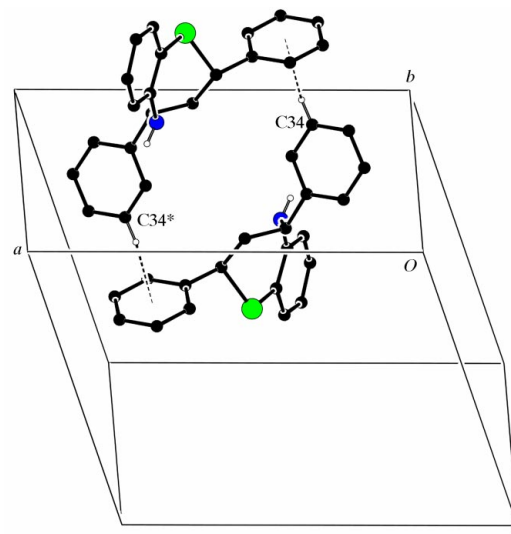


Figure 11

Part of the crystal structure of (IV), showing the formation of the centrosymmetric motif that links the (001) sheets. For clarity, H atoms bonded to C atoms but not involved in the motif shown have been omitted. The atom marked with an asterisk (*) is at the symmetry position $(1 - x, 1 - y, -z)$.

The third C—H $\cdots\pi$ (arene) hydrogen bond links adjacent (001) sheets; atom C34 in the molecule at (x, y, z), which lies in the domain $-0.04 < z < 0.54$, acts as a hydrogen-bond donor to ring C20—C25 in the molecule at $(1 - x, 1 - y, -z)$, which lies in the domain $-0.54 < z < 0.04$. The resulting centrosymmetric motif (Fig. 11) thus serves to link sheets in different domains and in this manner to link all of the (001) sheets into a single framework.

It is also timely to re-evaluate the intermolecular N—H \cdots S interaction in (IV). This interaction was originally discounted (Laavanya *et al.*, 2002) as insignificant on the grounds that the shortest intermolecular N \cdots S distance (Table 4) is in excess of the 3.3 Å sum of the van der Waals radii (Bondi, 1964). However, an analysis (Allen *et al.*, 1997) of hydrogen bonds having two-coordinate S as the acceptor, using data retrieved from the Cambridge Structural Database (Allen, 2002), indicated mean H \cdots S, N \cdots S and N—H \cdots S parameters in such bonds where S is bonded to two C atoms of 2.74 (2) Å, 3.58 (3) Å and 145 (3)° respectively. Accordingly, if the N—H \cdots S contact in (IV) is not considered to be a significant intermolecular interaction, it is more soundly rejected on the grounds of the long H \cdots S distance and the small N—H \cdots S angle than on the grounds of the N \cdots S distance.

In summary, we have shown that the very closely related series of compounds (I)–(IV) exhibit supramolecular aggregation in zero, one, two and three dimensions, respectively, and that while in (I)–(III) the aggregation depends solely on C—H \cdots O hydrogen bonds, in (IV) it depends solely on C—H $\cdots\pi$ (arene) hydrogen bonds. The occurrence of such differences resulting from very modest changes in molecular constitution undoubtedly presents a considerable challenge for computational methods that seek to predict, whether from first principles or otherwise, the crystal structures of simple molecular compounds (Lommerse *et al.*, 2000; Motherwell *et al.*, 2002).

Experimental

Compounds (I)–(III) were prepared by acylation of (IV) (Laavanya *et al.*, 2002) with acetic anhydride, chloroacetyl chloride and benzoyl chloride, respectively, in the presence of triethylamine in dry benzene under reflux conditions. Analyses found for (I): C 77.0, H 6.1, N 3.7%; C₂₃H₂₁NOS requires: C 76.8, H 5.9, N 3.9%; found for (II): C 70.2, H 5.0, N 3.6%; C₂₃H₂₀CINOS requires: C 70.1, H 5.1, N 3.6%; found for (III): C 79.5, H 5.6, N 3.3%; C₂₈H₂₃NOS requires: C 79.8, H 5.5, N 3.3%. Crystals of (I)–(III) suitable for single-crystal X-ray diffraction were grown from solutions in ethanol; m.p.: (I) 401–404 K, (II) 393–397 K, and (III) 445–449 K.

Compound (I)

Crystal data

C₂₃H₂₁NOS
 $M_r = 359.48$
 Monoclinic, $P2_1/c$
 $a = 20.3579$ (4) Å
 $b = 8.3014$ (1) Å
 $c = 22.2513$ (4) Å
 $\beta = 93.865$ (1)°
 $V = 3751.90$ (11) Å³
 $Z = 8$

$D_x = 1.273$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8274 reflections
 $\theta = 3.0$ – 27.1 °
 $\mu = 0.18$ mm⁻¹
 $T = 120$ (2) K
 Plate, colourless
 $0.20 \times 0.04 \times 0.03$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)
 $T_{\min} = 0.954$, $T_{\max} = 0.994$
 51 290 measured reflections
 8274 independent reflections

4659 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.109$
 $\theta_{\max} = 27.1$ °
 $h = -25 \rightarrow 26$
 $k = -10 \rightarrow 9$
 $l = -26 \rightarrow 28$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.125$
 $S = 1.00$
 8274 reflections
 471 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 0.0549P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.22$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C145—H145 \cdots O25 ⁱ	0.95	2.47	3.336 (3)	152
C245—H245 \cdots O15 ⁱ	0.95	2.41	3.268 (3)	150

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C24—H24 \cdots O5 ⁱⁱ	0.95	2.42	3.295 (3)	153
C44—H44 \cdots O5 ⁱ	0.95	2.48	3.364 (2)	154

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

Compound (II)

Crystal data

C₂₃H₂₀CINOS
 $M_r = 393.92$
 Monoclinic, $P2_1/n$
 $a = 12.6348$ (4) Å
 $b = 11.9337$ (5) Å
 $c = 12.7904$ (5) Å
 $\beta = 92.549$ (2)°
 $V = 1926.63$ (13) Å³
 $Z = 4$

$D_x = 1.358$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4418 reflections
 $\theta = 3.2$ – 27.5 °
 $\mu = 0.32$ mm⁻¹
 $T = 120$ (2) K
 Plate, colourless
 $0.28 \times 0.24 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)
 $T_{\min} = 0.926$, $T_{\max} = 0.987$
 26 344 measured reflections
 4418 independent reflections

2950 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.081$
 $\theta_{\max} = 27.5$ °
 $h = -16 \rightarrow 16$
 $k = -15 \rightarrow 15$
 $l = -16 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.098$
 $S = 1.00$
 4418 reflections
 244 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0478P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.22$ e Å⁻³
 $\Delta\rho_{\min} = -0.37$ e Å⁻³

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C23—H23...O5 ⁱⁱⁱ	0.95	2.49	3.347 (2)	150
C24—H24...O5 ^{iv}	0.95	2.53	3.295 (2)	138

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

Table 4
Hydrogen bonds and short intermolecular contact parameters (Å, °) for (IV).

Original atom numbering (Laavanya *et al.*, 2002). *Cg1* and *Cg2* are the centroids of the C6—C11 and C20—C25 rings, respectively.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C6—H6... <i>Cg1</i> ^v	0.98	2.82	3.521 (3)	129
C21—H21... <i>Cg2</i> ^{vi}	0.94	2.99	3.746 (3)	139
C34—H34... <i>Cg2</i> ^{vii}	0.91	2.98	3.669 (4)	133
N5—H5...S1 ^{viii}	0.82 (2)	3.05 (2)	3.490 (3)	116 (2)

Symmetry codes: (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vii) $1 - x, 1 - y, -z$; (viii) $x, 1 + y, z$.

Compound (III)

Crystal data

C ₂₈ H ₂₃ NOS	<i>D</i> _x = 1.309 Mg m ⁻³
<i>M</i> _r = 421.53	Mo <i>K</i> α radiation
Monoclinic, <i>C2/c</i>	Cell parameters from 4894 reflections
<i>a</i> = 30.1891 (8) Å	<i>θ</i> = 3.0–27.5°
<i>b</i> = 14.8005 (3) Å	<i>μ</i> = 0.17 mm ⁻¹
<i>c</i> = 9.7965 (3) Å	<i>T</i> = 120 (2) K
<i>β</i> = 102.2570 (16)°	Block, colourless
<i>V</i> = 4277.43 (19) Å ³	0.36 × 0.26 × 0.16 mm
<i>Z</i> = 8	

Data collection

Nonius KappaCCD diffractometer	3535 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>φ</i> scans, and <i>ω</i> scans with <i>κ</i> offsets	<i>R</i> _{int} = 0.060
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)	<i>θ</i> _{max} = 27.5°
<i>T</i> _{min} = 0.937, <i>T</i> _{max} = 0.973	<i>h</i> = -39 → 35
21 732 measured reflections	<i>k</i> = -19 → 18
4894 independent reflections	<i>l</i> = -11 → 12

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 1.1026P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	(<i>Δ</i> / <i>σ</i>) _{max} < 0.001
<i>S</i> = 1.03	<i>Δρ</i> _{max} = 0.21 e Å ⁻³
4894 reflections	<i>Δρ</i> _{min} = -0.38 e Å ⁻³
280 parameters	
H-atom parameters constrained	

For (I) and (II), space groups *P2₁/c* and *P2₁/n*, respectively, were uniquely assigned from the systematic absences. For (III), the systematic absences permitted *Cc* and *C2/c* as possible space groups; *C2/c* was selected and confirmed by successful structure analysis. All H atoms were located from difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.99 (CH₂) and 1.00 Å (aliphatic CH). Examination of the refined structure of (I) for possible additional symmetry using *ADDSYM* in *PLATON* (Spek, 2003) showed that none could be detected.

For all compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski &

Table 5
Selected torsion angles (°) for (I)–(IV).

Torsion angle	(I)		(II)	(III)	(IV)
	Mol. 1	Mol. 2			
<i>x</i>	1	2	nil	nil	nil
Sx1—Cx10—Cx11—Xx5	-7.2 (3)	-6.3 (2)	-2.6 (2)	-8.6 (2)	0.7 (3)
Cx11—Cx10—Sx1—Cx2	64.1 (2)	63.2 (2)	62.6 (2)	60.3 (2)	32.2 (2)
Cx10—Cx11—Xx5—Cx4	-71.8 (3)	-72.0 (3)	-74.3 (2)	-75.1 (2)	38.4 (3)
Sx1—Cx2—Cx3—Cx4	-64.6 (2)	-64.5 (2)	-63.4 (2)	-70.7 (2)	45.9 (3)
Xx5—Cx4—Cx3—Cx2	64.1 (2)	64.2 (2)	66.3 (2)	58.1 (2)	45.3 (3)
Cx10—Sx1—Cx2—Cx3	-18.1 (2)	-18.4 (2)	-20.8 (2)	-9.0 (2)	-83.4 (2)
Cx11—Xx5—Cx4—Cx3	33.1 (3)	32.9 (3)	30.4 (2)	42.3 (2)	-96.3 (3)

Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants that have provided computing facilities for this work.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1057). Services for accessing these data are described at the back of the journal.

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