

Hydrogen-bonded dimers, chains and rings in six differently substituted 2-vinyltetrahydro-1,4-epoxy-1-benzazepines

Lina M. Acosta,^a Alirio Palma,^a Ali Bahsas,^b Justo Cobo^c
and Christopher Glidewell^{d*}

^aLaboratorio de Síntesis Orgánica, Escuela de Química, Universidad Industrial de Santander, AA 678 Bucaramanga, Colombia, ^bLaboratorio de RMN, Grupo de Productos Naturales, Departamento de Química, Universidad de los Andes, Mérida 5101, Venezuela, ^cDepartamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and ^dSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

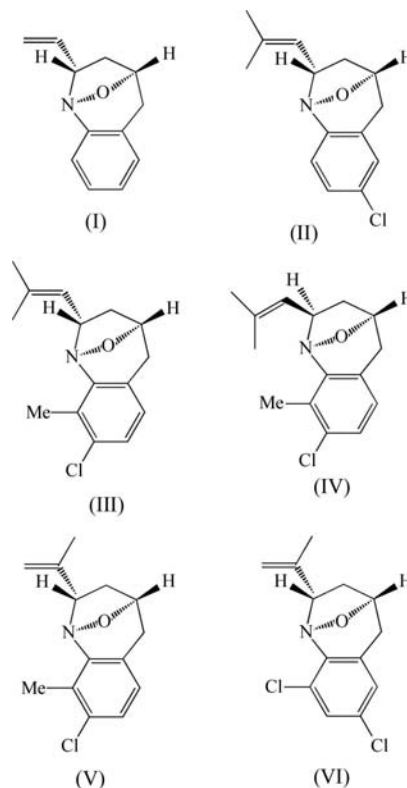
Received 8 March 2010
Accepted 9 March 2010
Online 16 March 2010

In (2*SR*,4*RS*)-2-*exo*-vinyl-2,3,4,5-tetrahydro-1*H*-1,4-epoxy-1-benzazepine, C₁₂H₁₃NO, (I), the molecules are linked by two independent C—H···π(arene) hydrogen bonds to form sheets, such that all of the molecules in a given sheet are of the same configuration. The molecules of (2*SR*,4*RS*)-7-chloro-2-*exo*-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1,4-epoxy-1-benzazepine, C₁₄H₁₆ClNO, (II), are linked by a C—H···O hydrogen bond into *C*(4) chains, where all the molecules in a given chain are of the same configuration, whereas the molecules of (2*SR*,4*RS*)-8-chloro-9-methyl-2-*exo*-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1,4-epoxy-1-benzazepine, C₁₅H₁₈ClNO, (III), are linked into centrosymmetric dimers by pairs of symmetry-related C—H···π(arene) hydrogen bonds. (2*RS*,4*RS*)-8-Chloro-9-methyl-2-*endo*-(2-methylprop-1-enyl)-2,3,4,5-tetrahydro-1*H*-1,4-epoxy-1-benzazepine, C₁₅H₁₈ClNO, (IV), is a diastereoisomer of (III) and, as for (II), a single C—H···O hydrogen bond links the molecules into *C*(4) chains, each containing molecules of a single configuration. The structure of (2*SR*,4*RS*)-8-chloro-9-methyl-2-*exo*-(prop-1-en-2-yl)-2,3,4,5-tetrahydro-1*H*-1,4-epoxy-1-benzazepine, C₁₄H₁₆ClNO, (V), contains a C—H···O hydrogen bond which links pairs of molecules into centrosymmetric *R*₂²(6) dimers. (2*SR*,4*RS*)-7,9-Dichloro-2-*exo*-(prop-1-en-2-yl)-2,3,4,5-tetrahydro-1*H*-1,4-epoxy-1-benzazepine, C₁₃H₁₃Cl₂NO, (VI), is an inversion twin containing both the (2*S*,4*R*) and (2*R*,4*S*) enantiomers in the space group *P*₂₁, and a C—H···O hydrogen bond links molecules of a given configuration into simple *C*(3) chains.

Comment

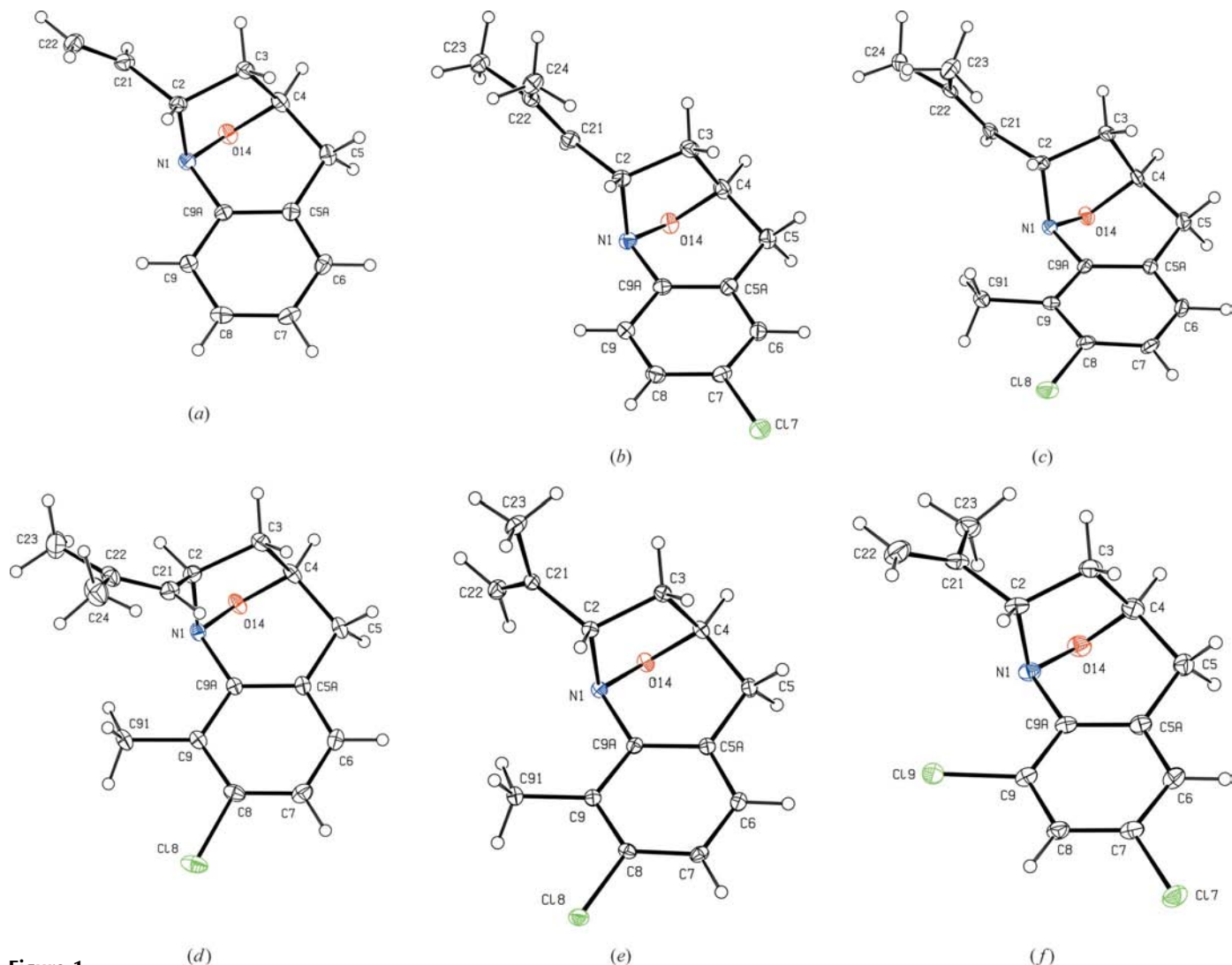
We report here the structures of six differently-substituted 2-vinyl-2,3,4,5-tetrahydro-1*H*-1,4-epoxy-1-benzazepines, (I)–

(VI) (Fig. 1), which exhibit interesting variations in their intermolecular hydrogen-bonding arrangements. The work reported here is a continuation of a wider structural study of substituted tetrahydroepoxybenzazepines (Acosta *et al.*, 2008, 2010; Blanco *et al.*, 2008; Gómez *et al.*, 2008, 2009, 2010), and the underlying synthetic rationale and the potential applications of these compounds have already been discussed (Acosta *et al.*, 2008).



Compounds (I)–(V) (see scheme and Fig. 1) all crystallize as racemic mixtures in centrosymmetric space groups. In each of (I)–(V), the reference molecule was selected as having the *R* configuration at atom C4, and on this basis the reference molecules have the *S* configuration at atom C2 in (I)–(III) and (V), but in (IV) the reference molecule has the *R* configuration at C2, so that (III) and (IV) are, in fact, diastereoisomers. In addition, (II) and (V) are positional isomers. By contrast, (VI) crystallizes as an inversion twin in the Sohnke space group *P*₂₁. For the crystal selected for data collection, the twin fractions were found to be unequal, *viz.* 0.39 (7) for the (2*S*,4*R*) form and 0.61 (7) for the (2*R*,4*S*) form, although the deviations from 0.5 are not large compared with the experimental uncertainty. As the synthesis of these compounds involves no reagent or solvent capable of imparting any enantiomeric bias, it is to be expected that (VI), as well as (I)–(V), was synthesized as a true racemic mixture, and it is therefore possible that this compound crystallizes with somewhat different twin fractions in the various individual crystals.

The ring-puckering parameters (Cremer & Pople, 1975) for (I)–(VI) (Table 1) show that the overall shape of the fused heterocyclic system varies very little, regardless of the number


Figure 1

The molecular structures of (a) (I), (b) (II), (c) (III), (d) (IV), (e) (V) and (f) (VI), showing the atom-labelling schemes. The (2*R*,4*R*) enantiomer is shown for (IV) and the (2*S*,4*R*) enantiomers for the remainder. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

and location of the methyl groups in the vinyl substituent or the configuration at atom C2. On the other hand, the orientation of the vinyl group relative to the fused bicyclic system, as defined by the N1–C2–C21–C22 torsion angle (Table 1), shows considerable variation, in particular between diastereoisomers (III) and (IV), as expected from the different configurations at C2, but less expectedly for the prop-1-en-2-yl derivatives (V) and (VI).

The supramolecular aggregation in (I)–(VI) depends upon C–H···O and C–H··· π (arene) hydrogen bonds (Table 2), but (I) is the only example in this group where the crystal structure contains two independent C–H··· π (arene) hydrogen bonds.

In (I), the hydrogen bond having atom C6 as the donor links molecules related by the 2_1 screw axis along $(\frac{1}{4}, y, \frac{1}{4})$, while the hydrogen bond in which atom C22 acts as the donor links molecules related by the 2_1 screw axis along $(\frac{3}{4}, y, \frac{1}{2})$, so forming two chain motifs, both running parallel to the [010] direction but in opposite senses. The combination of these

chains generates a sheet lying parallel to (001) in the domain $0 < z < \frac{1}{2}$ (Fig. 2) in which all of the molecules have the (2*S*,4*R*) configuration. A second sheet, lying in the domain $\frac{1}{2} < z < 1.0$, is related to the first sheet by inversion and contains only molecules with the (2*R*,4*S*) configuration. Within the sheet, each aryl ring accepts one hydrogen bond on each face and the angle subtended at ring centroid Cg1 (ring C5a/C6–C9/C9a) of the reference molecule by the two H···Cg contacts, H6ⁱ···Cg1···H22ⁱⁱ, is 167° [symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$]. Between adjacent sheets, the only direction-specific interaction is a C–H···O contact (Table 2) with an H···O distance which is long and a C–H···O angle which is small, so that this contact cannot realistically be regarded as a structurally significant hydrogen bond. Aromatic π – π stacking interactions are absent from the structure of (I), because of the presence of C–H··· π (arene) hydrogen bonds on each face of the aryl ring, so that the supramolecular aggregation in (I) is two-dimensional.

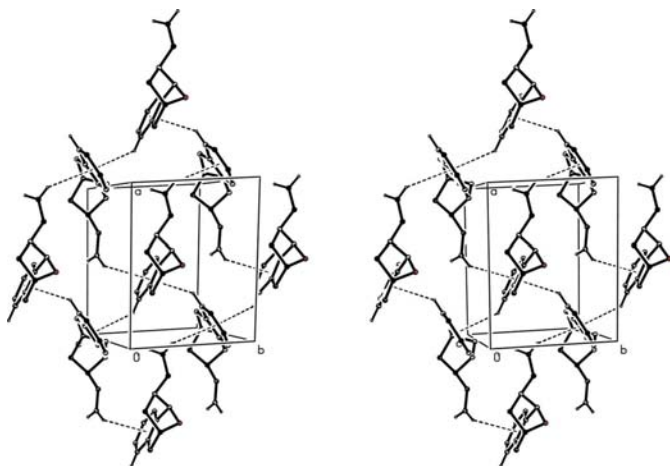


Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded sheet parallel to (001). Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted.

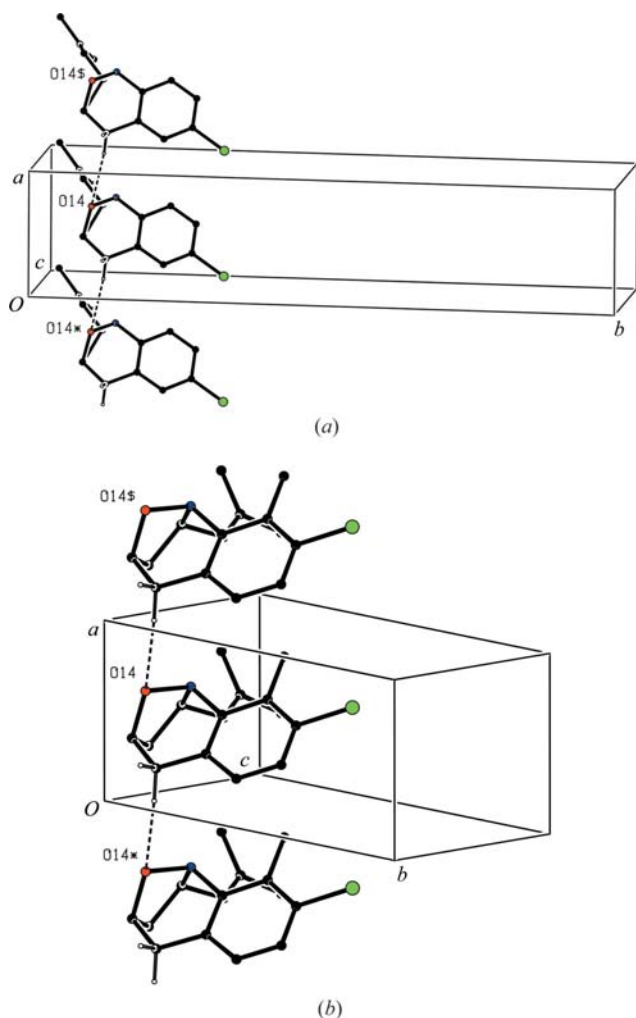


Figure 3
Parts of the crystal structures of (a) (II) and (b) (IV), showing the formation of C(4) chains along [100]. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*) or a dollar sign (\$) are at the symmetry positions $(-1+x, y, z)$ and $(1+x, y, z)$, respectively.

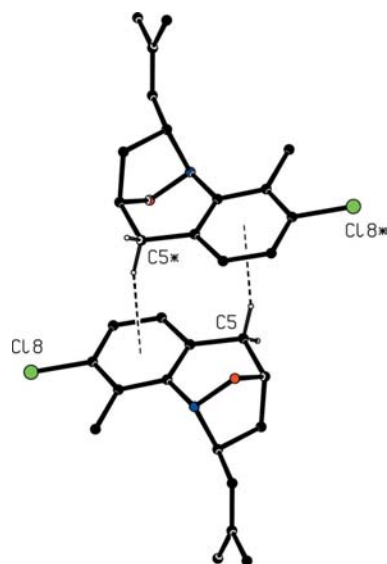


Figure 4
Part of the crystal structure of (III), showing the formation of a hydrogen-bonded dimer built from paired C—H \cdots π (arene) hydrogen bonds (dashed lines). For the sake of clarity, the unit-cell outline and H atoms bonded to C atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(2-x, 1-y, 1-z)$.

In contrast with the crystal structure of (I), those of (II)–(VI) each contain only a single hydrogen bond, all of the C—H \cdots O type apart from (III), where the hydrogen bond is of the C—H \cdots π (arene) type (Table 2). As found for (I), aromatic π – π stacking interactions are absent from the structures of all of (II)–(VI).

In each of (II) and (IV), molecules related by translation are linked by C—H \cdots O hydrogen bonding to form simple C(4) chains (Bernstein *et al.*, 1995) running parallel to the [100] direction (Fig. 3), but it is clear that, although the same donor and acceptor atoms are involved in these two structures, the mutual orientations of the molecules within the chains are different, as are the dimensions of the C—H \cdots O hydrogen bonds. These differences may be associated with either or both of the differences in the molecular configurations, *viz.* (2*SR*,4*RS*) for (II) and (2*RS*,4*RS*) for (IV), and in the space groups, *viz.* *P*2₁/*c* for (II) and *P* $\bar{1}$ for (IV). In the structure of (II) there are four chains passing through each unit cell, but in the structure of (IV) there are only two. In any specific chain, all of the molecules have the same configuration. As there are no direction-specific interactions between the chains in (II) and (IV), these hydrogen-bonded structures are both one-dimensional.

The hydrogen-bonded structures of (III) and (V), by contrast, both consist of centrosymmetric dimers, built from pairs of symmetry-related C—H \cdots π (arene) hydrogen bonds in (III) (Fig. 4) and from pairs of symmetry-related C—H \cdots O hydrogen bonds in (V), so forming an *R*₂²(6) ring having a chair-type conformation (Fig. 5). Within each of these dimers, the two molecules involved are of the opposite configuration and the hydrogen-bonded aggregation in (III) and (V) is thus finite, or zero-dimensional.

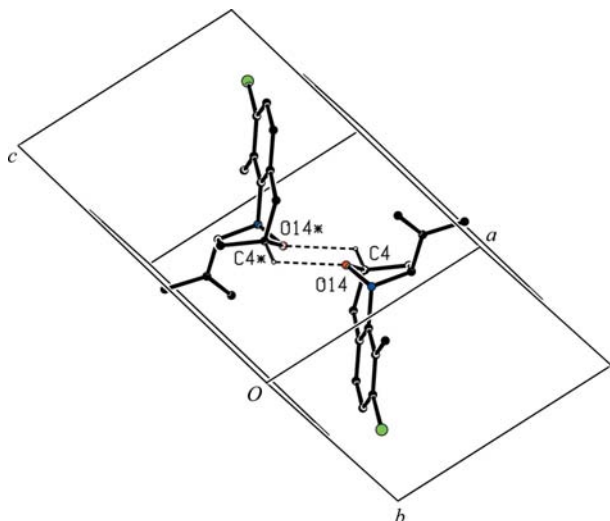


Figure 5
Part of the crystal structure of (IV), showing the formation of a hydrogen-bonded dimer built from paired C—H...O hydrogen bonds (dashed lines). For the sake of clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$.

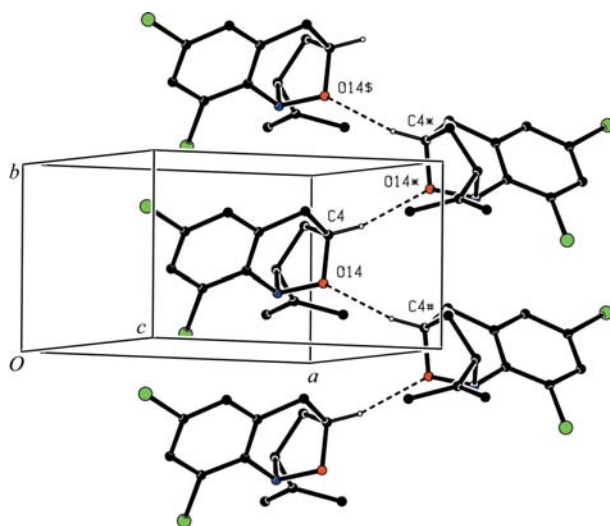


Figure 6
Part of the crystal structure of (VI), showing the formation of a $C(3)$ chain parallel to $[010]$. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), a hash symbol (#) or a dollar sign (\$) are at the symmetry positions $(2 - x, \frac{1}{2} + y, 1 - z)$, $(2 - x, -\frac{1}{2} + y, 1 - z)$ and $(x, 1 + y, z)$, respectively.

The single hydrogen bond in the structure of (VI) utilizes the same donor and acceptor atoms as that in (V), but rather than forming a cyclic dimer as in (V), in (VI) this hydrogen bond now generates a $C(3)$ chain running parallel to the $[010]$ direction and linking molecules related by the 2_1 screw axis along $(1, y, \frac{1}{2})$ (Fig. 6). Again, therefore, the hydrogen-bonded structure is one-dimensional and all the molecules in a specific chain are of the same configuration.

In each of (I), (II), (IV) and (VI), the molecules within a given hydrogen-bonded aggregate, whether the sheet in (I) or

the chains in (II), (IV) and (VI), all have the same configuration, whereas in (III) and (V) the hydrogen-bonded dimers both contain pairs of molecules having opposite configurations. Hence, the hydrogen bonding appears to mediate molecular-scale enantiomeric sorting in (I), (II), (IV) and (VI), but enantiomeric pairing in (III) and (V). Within the structures of each of (II)–(IV), atom C5 acts as the hydrogen-bond donor. However, in (II) and (IV), where C—H...O hydrogen bonds are present, these involve the bisectonal H atom at C5, denoted H5B, and chain motifs result, but in (III), where a C—H... π (arene) hydrogen bond is present, this involves the axial H atom at C5, denoted H5A, and a ring motif results. Similarly, although the same combination of hydrogen-bond donor and acceptor is present in the structures of (V) and (VI), in (V) this interaction gives rise to a ring motif, whereas in (VI) a chain results, so that the hydrogen-bonded structures of (V) and (VI) are of different dimensionalities. These subtle differences in the hydrogen-bonding patterns do not appear to have any simple or readily-accessible explanations.

Experimental

For the preparation of (I)–(VI), sodium tungstate dihydrate (5–10 mol%), followed by 30% aqueous hydrogen peroxide solution (0.30 mol), were added to a stirred solution of the appropriately substituted 2-allyl-*N*-alkenylaniline (0.10 mol) in methanol (30 ml). The resulting mixtures were then stirred at ambient temperature for either 8 h [for (I) and (II)] or 72 h [for each of (III)–(VI)]. Each mixture was then filtered and the solvent removed under reduced pressure. Toluene (30 ml) was added to the solid residue and the resulting solution was heated at 355–360 K for 5–7 h. After cooling each solution to ambient temperature, the solvent was removed under reduced pressure and the crude product was purified by chromatography on silica gel using heptane–ethyl acetate (compositions in the range from 90:1 to 10:1 *v/v*) as eluent. Crystallization from methanol–dichloromethane (1:1 *v/v*) gave colourless crystals of (I)–(VI) suitable for single-crystal X-ray diffraction.

Analyses: for (I), yield 58%, m.p. 335–336 K; MS (70 eV) m/z (%): 187 (M^+ , 31), 170 (18), 157 (10), 130 (22), 105 (38), 104 (100), 78 (36). For (II), yield 49%, m.p. 350–351 K; MS (70 eV) m/z (%): 249 [M^+ (^{35}Cl), 43], 232 (29), 164 (9), 139 (100), 104 (33), 77 (30). For (III), yield 45%, m.p. 367–368 K; MS (70 eV) m/z (%): 263 [M^+ (^{35}Cl), 45], 246 (27), 178 (12), 153 (100), 144 (39), 118 (36), 103 (18), 91 (36). For (IV), yield 25%, m.p. 380–381 K; MS (70 eV) m/z (%): 263 [M^+ (^{35}Cl), 64], 246 (33), 178 (15), 153 (100), 144 (39), 118 (36), 103 (18), 91 (39). For (V), yield 65%, m.p. 375–376 K; MS (70 eV) m/z (%): 249 [M^+ (^{35}Cl), 59], 166 (9), 153 (100), 141 (36), 118 (29), 91 (33), 77 (24). For (VI), yield 63%, m.p. 370–371 K; MS (70 eV) m/z (%): 269 [M^+ (^{35}Cl), 61], 172 (100), 151 (30), 138 (61), 123 (33), 102 (30), 75 (36).

Compound (I)

Crystal data

$\text{C}_{12}\text{H}_{13}\text{NO}$	$V = 960.8 (2) \text{ \AA}^3$
$M_r = 187.23$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 9.8070 (13) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$b = 7.3982 (7) \text{ \AA}$	$T = 120 \text{ K}$
$c = 13.738 (2) \text{ \AA}$	$0.31 \times 0.29 \times 0.20 \text{ mm}$
$\beta = 105.441 (11)^\circ$	

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.969$, $T_{\max} = 0.984$

13902 measured reflections
2200 independent reflections
1488 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.054$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.107$
 $S = 1.06$
2200 reflections
127 parameters

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.17 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$

Compound (II)**Crystal data**

$\text{C}_{14}\text{H}_{16}\text{ClNO}$
 $M_r = 249.73$
Monoclinic, $P2_1/c$
 $a = 5.6445 (5) \text{ \AA}$
 $b = 25.744 (3) \text{ \AA}$
 $c = 8.3894 (11) \text{ \AA}$
 $\beta = 95.124 (9)^\circ$

$V = 1214.2 (2) \text{ \AA}^3$
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.30 \text{ mm}^{-1}$
 $T = 120 \text{ K}$
 $0.44 \times 0.24 \times 0.20 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.895$, $T_{\max} = 0.943$

15979 measured reflections
2783 independent reflections
1929 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.129$
 $S = 1.08$
2783 reflections
156 parameters

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.30 \text{ e } \text{\AA}^{-3}$

Compound (III)**Crystal data**

$\text{C}_{15}\text{H}_{18}\text{ClNO}$
 $M_r = 263.75$
Monoclinic, $P2_1/n$
 $a = 11.0631 (7) \text{ \AA}$
 $b = 5.7212 (5) \text{ \AA}$
 $c = 21.203 (6) \text{ \AA}$
 $\beta = 102.587 (16)^\circ$

$V = 1309.8 (4) \text{ \AA}^3$
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.28 \text{ mm}^{-1}$
 $T = 120 \text{ K}$
 $0.40 \times 0.19 \times 0.12 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.869$, $T_{\max} = 0.967$

16325 measured reflections
2306 independent reflections
1661 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.105$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.155$
 $S = 1.11$
2306 reflections
166 parameters

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.43 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.39 \text{ e } \text{\AA}^{-3}$

Compound (IV)**Crystal data**

$\text{C}_{15}\text{H}_{18}\text{ClNO}$
 $M_r = 263.75$
Triclinic, $P\bar{1}$
 $a = 5.2890 (9) \text{ \AA}$
 $b = 9.3076 (16) \text{ \AA}$
 $c = 13.551 (3) \text{ \AA}$
 $\alpha = 94.554 (15)^\circ$
 $\beta = 94.684 (15)^\circ$

$\gamma = 97.298 (14)^\circ$
 $V = 656.7 (2) \text{ \AA}^3$
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.28 \text{ mm}^{-1}$
 $T = 120 \text{ K}$
 $0.32 \times 0.26 \times 0.11 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.932$, $T_{\max} = 0.970$

16228 measured reflections
3005 independent reflections
2348 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.113$
 $S = 1.11$
3005 reflections

166 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.36 \text{ e } \text{\AA}^{-3}$

Compound (V)**Crystal data**

$\text{C}_{14}\text{H}_{16}\text{ClNO}$
 $M_r = 249.73$
Monoclinic, $P2_1/n$
 $a = 8.6828 (11) \text{ \AA}$
 $b = 10.1456 (6) \text{ \AA}$
 $c = 14.2976 (16) \text{ \AA}$
 $\beta = 107.587 (9)^\circ$

$V = 1200.6 (2) \text{ \AA}^3$
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.30 \text{ mm}^{-1}$
 $T = 120 \text{ K}$
 $0.50 \times 0.17 \times 0.14 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.844$, $T_{\max} = 0.959$

14152 measured reflections
2759 independent reflections
2083 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.093$
 $S = 1.07$
2759 reflections

156 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.31 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.28 \text{ e } \text{\AA}^{-3}$

Compound (VI)**Crystal data**

$\text{C}_{13}\text{H}_{13}\text{Cl}_2\text{NO}$
 $M_r = 270.14$
Monoclinic, $P2_1$
 $a = 10.4753 (13) \text{ \AA}$
 $b = 5.4759 (8) \text{ \AA}$
 $c = 10.9632 (12) \text{ \AA}$
 $\beta = 105.791 (13)^\circ$

$V = 605.13 (13) \text{ \AA}^3$
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.52 \text{ mm}^{-1}$
 $T = 120 \text{ K}$
 $0.30 \times 0.25 \times 0.16 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.826$, $T_{\max} = 0.922$

10313 measured reflections
2751 independent reflections
2385 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.053$

Table 1

Selected geometric parameters (Å, °) for (I)–(VI).

Ring-puckering parameters refer to the atom sequences O14–N1–C2–C3–C4 and O14–N1–C9a–C5a–C5–C4, respectively.

Ring-puckering parameters					
Compound	Five-membered ring		Six-membered ring		
	Q_2	φ_2	Q	θ	φ
(I)	0.449 (2)	196.9 (2)	0.629 (2)	53.8 (2)	345.3 (2)
(II)	0.445 (2)	198.4 (3)	0.613 (2)	51.1 (2)	344.1 (3)
(III)	0.449 (3)	199.1 (5)	0.631 (3)	55.6 (3)	345.3 (4)
(IV)	0.445 (2)	198.8 (3)	0.623 (2)	52.7 (2)	347.9 (2)
(V)	0.435 (2)	193.5 (3)	0.621 (2)	52.4 (2)	345.2 (2)
(VI)	0.434 (3)	196.6 (4)	0.618 (3)	53.5 (3)	344.5 (3)

Torsion angles N1–C2–C21–C22

(I)	126.62 (16)
(II)	146.9 (2)
(III)	144.9 (3)
(IV)	–108.4 (2)
(V)	–6.3 (2)
(VI)	115.5 (3)

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.045$$

$$wR(F^2) = 0.115$$

$$S = 1.05$$

2751 reflections

156 parameters

1 restraint

H-atom parameters constrained

$$\Delta\rho_{\max} = 0.42 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.56 \text{ e } \text{Å}^{-3}$$

Absolute structure: Flack (1983),

with 1223 Friedel pairs

Flack parameter: 0.61 (7)

All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C–H = 0.95 (aromatic or alkenyl H), 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (aliphatic CH), and with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$, where $k = 1.5$ for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms. When the initial refinement for (VI) appeared to be complete, the value of the Flack x parameter (Flack, 1983), $x = 0.59$ (8), indicated that the refinement should be handled as an inversion twin, leading to twin fractions of 0.39 (7) for the (2*S*,4*R*) form and 0.61 (7) for the (2*R*,4*S*) form.

For all compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

The authors thank the Servicios Técnicos de Investigación of the Universidad de Jaén and the staff for the data collection. JC thanks the Consejería de Innovación, Ciencia y

Table 2

Parameters (Å, °) for hydrogen bonds and short intermolecular contacts in (I)–(VI).

Cg1 represents the centroid of the C5a/C6–C9/C9a ring.

Compound	$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
(I)	C4–H4 \cdots O14 ⁱ	1.00	2.60	3.209 (2)	119
	C6–H6 \cdots Cg1 ⁱⁱ	0.95	2.83	3.6158 (17)	141
	C22–H22B \cdots Cg1 ⁱⁱⁱ	0.95	2.78	3.5289 (17)	136
(II)	C5–H5B \cdots O14 ^{iv}	0.99	2.58	3.570 (3)	174
(III)	C5–H5A \cdots Cg1 ^v	0.99	2.79	3.730 (4)	158
(IV)	C5–H5B \cdots O14 ^{iv}	0.99	2.39	3.358 (3)	166
(V)	C4–H4 \cdots O14 ^{vi}	1.00	2.57	3.202 (2)	121
(VI)	C4–H4 \cdots O14 ^{vii}	1.00	2.48	3.389 (4)	151

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

Empresa (Junta de Andalucía, Spain), the Universidad de Jaén (project reference UJA_07_16_33) and the Ministerio de Ciencia e Innovación (project reference SAF2008-04685-C02-02) for financial support. AP and LMA thank COLCIENCIAS for financial support (grant No. 1102-408-20563).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3373). Services for accessing these data are described at the back of the journal.

References

- Acosta, L. M., Bahsas, A., Palma, A., Cobo, J., Low, J. N. & Glidewell, C. (2008). *Acta Cryst.* **C64**, o514–o518.
- Acosta, L. M., Palma, A., Bahsas, A., Cobo, J. & Glidewell, C. (2010). *Acta Cryst.* **C66**, o206–o208.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Blanco, M. C., Raysth, W., Palma, A., Cobo, J., Low, J. N. & Glidewell, C. (2008). *Acta Cryst.* **C64**, o524–o528.
- Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Duisenberg, A. J. M., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.
- Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gómez, S. L., Palma, A., Cobo, J. & Glidewell, C. (2010). In preparation.
- Gómez, S. L., Raysth, W., Palma, A., Cobo, J., Low, J. N. & Glidewell, C. (2008). *Acta Cryst.* **C64**, o519–o523.
- Gómez, S. L., Sanabria, C. M., Palma, A., Bahsas, A., Cobo, J. & Glidewell, C. (2009). *Acta Cryst.* **C65**, o465–o469.
- Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.