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Sterically shielded pyramidal amino groups in two 4,4′-(arylmethylene)-bis(6-allyl-3-chloro-2-methylaniline) derivatives

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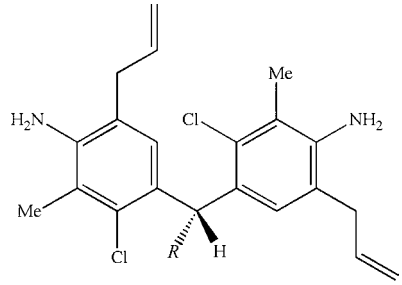
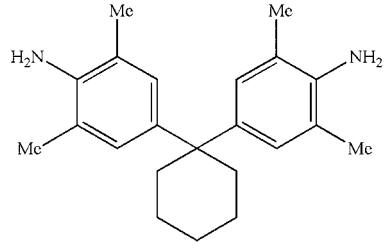
4,4′-(Phenylmethylene)bis(6-allyl-3-chloro-2-methylaniline), $C_{27}H_{28}Cl_2N_2$, (I), and 4,4′-(2-thienylmethylene)bis(6-allyl-3-chloro-2-methylaniline), $C_{25}H_{26}Cl_2N_2S$, (II), adopt similar molecular conformations, although the thienyl group in (II) exhibits orientational disorder over two sets of sites with occupancies of 0.614 (3) and 0.386 (3). The amino groups in both compounds are pyramidal. A single N—H···N hydrogen bond links the molecules of (I) into cyclic centrosymmetric dimers. Molecules of (II) are linked by an ordered C—H···π(arene) hydrogen bond to form cyclic centrosymmetric dimers, and these dimers are linked into statistically interrupted chains by a second C—H···π(arene) hydrogen bond involving a donor in the minor component of the disordered thienyl unit.

Comment

We have recently investigated the synthetic utility of 2-allylanilines as building blocks in heterocyclic synthesis (Palma *et al.*, 2004; Gómez Ayala *et al.*, 2006; Yépez *et al.*, 2006). On the other hand, it is well known that condensation of substituted anilines with aromatic or heteroaromatic aldehydes produces aldimines. These in turn can react with thioglycollic acid to give 4-thiazolidinones (Singh *et al.*, 1981), which exhibit a wide range of biological activities. Prompted by the possibility of preparing new bioactive 4-thiazolidinone derivatives, we have investigated the reactivity of aldimines with thioglycollic acid. However, we found that under the reaction conditions employed, these reactions did not produce the expected 4-thiazolidinones. Instead, we observed the formation of two unexpected new compounds arising from the self-condensation of the aldimines, and these have been identified as 4,4′-(phenylmethylene)bis(6-allyl-3-chloro-2-methylaniline), (I), and 4,4′-(2-thienylmethylene)bis(6-allyl-3-chloro-2-methylaniline), (II), and we report here their molecular and supramolecular structures (Figs. 1 and 2).



(I) R = phenyl
(II) R = 2-thienyl



(III)

While the molecules of compound (I) are fully ordered (Fig. 1), those of (II) exhibit orientational disorder of the 2-thienyl substituent, corresponding to a rotation about the C1—C32 bond (Fig. 2), with unequal populations in the two conformers with refined values of 0.614 (3) and 0.386 (3). With the exception of the orientation of the unsubstituted phenyl group in compound (I), as compared to that of the thienyl group in compound (II), the rest of the skeletal conformation is very similar in the two compounds, as indicated by the leading torsion angles defining the orientation of the substituted aryl rings (Table 1). Thus, the torsion angles defining the orientation of the C11–C16 ring are very similar in both compounds; likewise the corresponding angles defining the orientation of the C21–C26 ring are very similar in the two compounds. However, while the C18—C19—C20 allyl group adopts an almost identical conformation in each compound, the torsion angles defining the orientation of the the C28—C29—C30 allyl groups have opposite signs in the two compounds. Thus, the Ar_2C unit (where Ar represents the substituted aryl ring) does not exhibit even approximate internal symmetry.

In each compound, the two amino N atoms, *viz.* N14 and N24, have markedly pyramidal geometry and, consistent with this, the C—N distances are close to the mean value for C(aryl)—NH_2 bonds having a pyramidal N atom (1.394 Å; Allen *et al.*, 1987), rather longer than the mean value for such bonds having a planar N atom (1.355 Å). Despite this, the orientation of the amino groups is such that the lone-pair orbital on each N atom is approximately orthogonal to the plane of the adjacent aryl ring. However, the shielding effect

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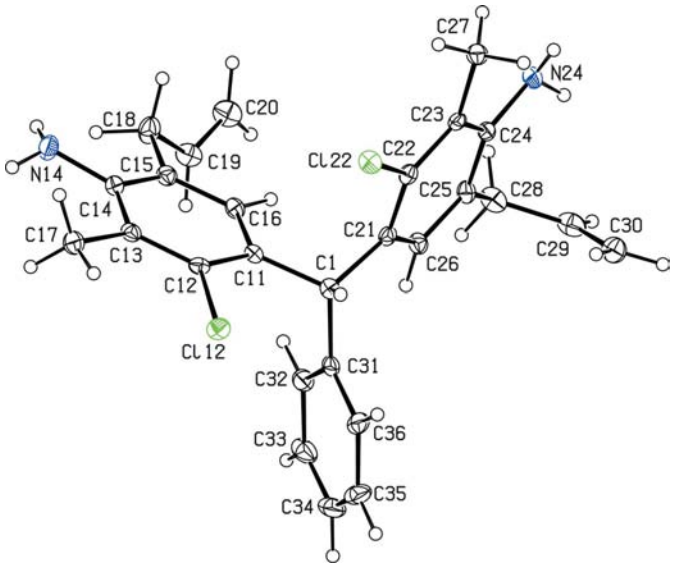

Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

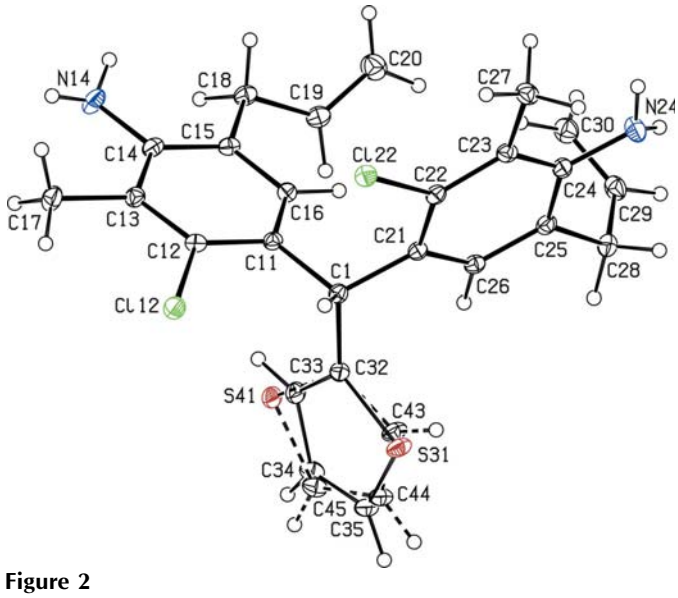

Figure 2
The molecular structure of compound (II), showing the two orientations of the thienyl substituent, with occupancies of 0.614 (3) and 0.386 (3), and the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

of the two adjacent substituents, namely the methyl and allyl groups, means that the participation of the amino groups in intermolecular hydrogen-bond formation is restricted: only one of the four N—H bonds in (I), and none of those in (II), is involved in hydrogen-bond formation (Table 2).

Accordingly, the supramolecular aggregation in both compounds is fairly simple. In compound (I), two molecules related by inversion are linked by paired N—H···N hydrogen bonds (Table 2), in which atom N14 acts as hydrogen-bond donor and atom N24 acts as hydrogen-bond acceptor, so forming a centrosymmetric $R_2^2(24)$ (Bernstein *et al.*, 1995) motif centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 3). There are no direction-specific interactions between these dimers. In particular, N—H···π(arene) and C—H···π(arene) hydrogen bonds and aromatic π–π stacking interactions are all absent.

There are no hydrogen bonds in compound (II) involving the amino groups, either as donors or as acceptors. Instead, the supramolecular aggregation depends upon two C—H···π(arene) hydrogen bonds, one of which involves a C—H bond in the minor component of the disordered thienyl group, so adding an element of statistical uncertainty to the aggregation. Fully ordered atom C20 in the molecule at (x, y, z) acts as hydrogen-bond donor to the C11–C16 ring in the molecule at $(1 - x, 1 - y, 1 - z)$, so generating a cyclic centrosymmetric dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 4). Partially occupied atom C44 forms a second hydrogen bond (Table 2), the role of which is to link the ordered dimers stacked along $(n + \frac{1}{2}, \frac{1}{2}, n + \frac{1}{2})$, where n represents an integer. Atom C44 in the molecule at (x, y, z), which is part of the dimer centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, acts as donor to the C21–C26 ring in the molecule at $(-x, 1 - y, -z)$, which itself forms part of the dimer centred at $(-\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$. Since atom C44 lies in the minor component of the disordered thienyl group, with occupancy 0.386 (3), then a pair of molecules such as those at (x, y, z) and $(-x, 1 - y, -z)$ could be linked by two, one or zero C—H···π(arene) hydrogen bonds, depending upon the local orientation of the two thienyl groups concerned. Hence, the resulting chain is best regarded as a statistically interrupted chain running parallel to the [101] direction, in that the likelihood that a continuous chain of centrosymmetric rings will be formed must be extremely low. There are no direction-specific interactions between adjacent chains.

It is noteworthy that only one of the N—H bonds in (I) participates in hydrogen-bond formation, while neither of the amino N atoms in (II) is within hydrogen-bonding range of any plausible donor or acceptor. The amino groups in 1,1-bis(4-amino-3,5-dimethylphenyl)cyclohexane, (III) [Cambridge Structural Database (CSD; Allen, 2002) refcode YAFNUO; Hanton *et al.*, 1992] are similarly subject to steric shielding. These groups are also markedly pyramidal, but only one of the four N—H bonds participates in the formation of N—H···N hydrogen bonds, although two others form N—H···π(arene) hydrogen bonds. It was suggested (Hanton *et al.*, 1992) that the assumption of pyramidal geometry at the amino N atoms in (III) was a response to the deficit of conventional hydrogen-bond acceptors in this compound. The behaviour of compound (II) reported here does not support this suggestion.

When the flanking substituents have sufficient steric bulk, for example *tert*-butyl groups, even fairly acidic phenolic hydroxyl groups sometimes fail to participate in any hydrogen-bond formation (Rezende *et al.*, 2005; Lutz & Spek, 2005). Thus, a survey (Lutz & Spek, 2005) of the August 2005 release of the CSD identified 53 examples of 2,6-di-*tert*-butylphenol derivatives for which H-atom coordinates had been deposited for fully ordered structures, and in 29 of these the shielded hydroxyl group formed no hydrogen bonds to any

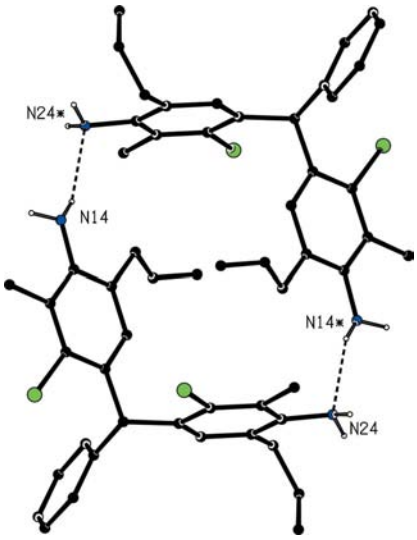

Figure 3
Part of the crystal structure of compound (I), showing the formation of a centrosymmetric $R_2^2(24)$ dimer. For the sake of clarity, H atoms bonded to C atoms have been omitted, as has the unit-cell outline. Atoms marked with an asterisk (*) are at the symmetry position $(1-x, 1-y, 1-z)$.

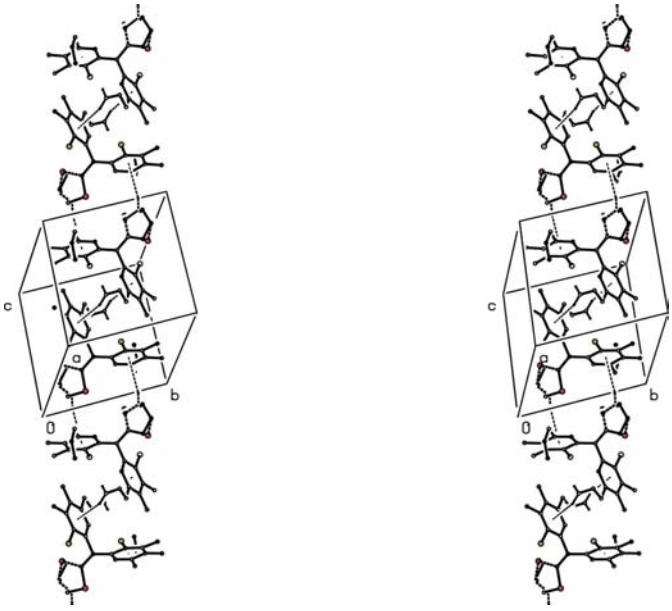

Figure 4
A stereoview of part of the crystal structure of compound (II), showing the formation of a statistically interrupted chain of rings along [101]. For the sake of clarity, H atoms bonded to C or N atoms which are not involved in the motifs shown have been omitted, and all possible C—H···π(arene) hydrogen bonds involving atom C44 have been included.

acceptor. In a total of 90 structures containing 2,6-di-*tert*-butylphenol units, none contained O···O distances consistent with the formation of hydrogen bonds between pairs of shielded hydroxyl groups.

Experimental

Thioglycollic acid (2 mmol) and a catalytic quantity of boron trifluoride etherate were added to a solution of the corresponding (*E*)-6-allyl-3-chloro-2-methyl-*N*-(aryl-2-ylmethylene)aniline (1 mmol) in toluene (10 ml). The reaction mixtures were heated under reflux, with stirring, for 6–8 h. Each mixture was brought to pH = 8 using aqueous sodium carbonate solution, and then extracted with ethyl acetate (2 × 50 ml). The organic extracts were dried over anhydrous sodium sulfate and then concentrated under reduced pressure to give the crude products, which were purified by column chromatography on silica gel using heptane–ethyl acetate (5:1 to 1:1 *v*/*v*) as eluent. Crystallization from heptane gave crystals suitable for single-crystal X-ray diffraction. Compound (I): yellow crystals, yield 33%, m.p. 405–406 K; MS (70 eV) *m*/*z* (%): 450 (M^+, 100), 415 (24), 409 (34), 373 (79), 270 (31), 234 (23); analysis found: C 71.9, H 6.2, N 6.3%; $C_{27}H_{28}Cl_2N_2$ requires: C 71.8, H 6.3, N 6.2%. Compound (II): colourless crystals, yield 25%, m.p. 412–413 K; MS (70 eV) (*m*/*z* (%): 456 (M^+, 100), 421 (28), 415 (30), 379 (20), 373 (6), 339 (9), 276 (64), 240 (18); analysis found: C 65.6, H 5.8, N 6.2%; $C_{25}H_{26}Cl_2N_2S$ requires: C 65.6, H 5.7, N 6.1%.

Compound (I)

Crystal data

$C_{27}H_{28}Cl_2N_2$
M_r = 451.41
Triclinic, $P\overline{1}$
a = 8.9868 (2) Å
b = 10.8718 (4) Å
c = 12.4359 (4) Å
α = 94.333 (2)°
β = 93.634 (3)°
γ = 102.490 (2)°
V = 1178.90 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 120 K
0.08 × 0.08 × 0.06 mm

Data collection

Bruker–Nonius APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.971, T_{max} = 0.983
15045 measured reflections
4344 independent reflections
3431 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.128
S = 1.08
4344 reflections
294 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Compound (II)

Crystal data

$C_{25}H_{26}Cl_2N_2S$
M_r = 457.44
Triclinic, $P\overline{1}$
a = 8.7263 (2) Å
b = 10.6766 (2) Å
c = 12.2691 (3) Å
α = 77.1100 (10)°
β = 87.7930 (10)°
γ = 82.367 (2)°
V = 1104.35 (4) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.40 mm^{-1}
T = 120 K
0.08 × 0.06 × 0.05 mm

Data collection

Bruker–Nonius APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.959, T_{max} = 0.980
16485 measured reflections
5043 independent reflections
4375 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Table 1
Selected geometric parameters (Å, °) for (I) and (II).

Parameter	(I)	(II)
C14—N14	1.390 (4)	1.396 (2)
C24—N24	1.408 (4)	1.400 (2)
C21—C1—C11—C12	−145.7 (3)	−145.13 (15)
C14—C15—C18—C19	−149.5 (3)	−161.73 (16)
C15—C18—C19—C20	−128.9 (4)	−130.1 (2)
C11—C1—C21—C22	73.4 (3)	77.66 (19)
C24—C25—C28—C29	76.8 (4)	−78.3 (2)
C25—C28—C29—C30	10.7 (5)	−12.8 (2)
C11—C1—C31—C32	50.7 (4)	
C21—C1—C31—C32	−76.2 (4)	
C11—C1—C32—S31		−173.47 (12)
C11—C1—C32—S41		−5.5 (2)

Table 2
Hydrogen-bond parameters (Å, °) for (I) and (II).

*Cg*1 is the centroid of the C11–C16 ring and *Cg*2 is the centroid of the C21–C26 ring.

Compound	*D*—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
(I)	N14—H14*A*···N24^{i}	0.86 (3)	2.79 (2)	3.186 (4)(3)	155 (3)
(II)	C20—H20*A*···*Cg*1^{i}	0.95	2.90	3.718 (2)	145
	C44—H44···*Cg*2^{ii}	0.95	2.88	3.772 (18)	156

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.086$
$S = 1.10$
5043 reflections
298 parameters
10 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

It was apparent from an early stage in the structure analysis that the thienyl group in compound (II) was disordered over two sets of atomic sites having unequal occupancy and related to one another by a 180° rotation about the C1—C32 bond (Fig. 2). To model this disorder, the bonded distances and the 1,3 nonbonded distances in the minor component were set equal to the corresponding distances in the major component, subject in each case to an s.u. value of 0.005 Å. In addition, the anisotropic displacement parameters of the pairs of partial-occupancy atoms occupying essentially the same physical space were set to be equal. On this basis, the site-occupancy factors for the major and minor components of the thienyl substituent refined to 0.614 (3) and 0.386 (3), respectively. All H atoms were located in difference maps. H atoms bonded to C atoms were then treated as riding atoms, with C—H = 1.00 (aliphatic CH), 0.99 (CH_2), 0.98 (CH_3) or 0.95 Å (all other C—H types), and with U_{iso}(H) = kU_{eq}(C), where $k = 1.5$ for the methyl groups, which were permitted to rotate but not to tilt, and $k = 1.2$ for all other H atoms bonded to C atoms. The coordinates of the H atoms bonded to N atoms were refined subject to a distance restraint of 0.86 (1) Å and with U_{iso}(H) = $1.2U_{eq}$(N).

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3211). Services for accessing these data are described at the back of the journal.

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