Acta Cryst. (1996). B52, 369–375

The Crystal Packing Modes of Three Sterically Overcrowded Imidazole Derivatives

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(*Received 10 November 1994; accepted 14 August 1995*)

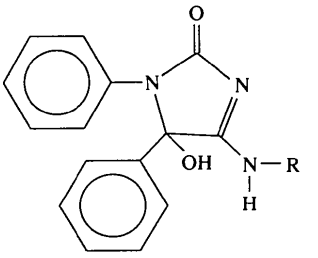
Abstract

The crystal packing of racemic 4-cyclohexylamino-5-hydroxy-1,5-diphenyl-Δ^3-imidazolin-2-one resembles the bilayered packing arrangements with alternating hydrophilic and hydrophobic layers observed in the crystal structures of lipids. The hydrophobic layers of the imidazolinone are built up individually by phenyl and cyclohexyl groups. In contrast, the corresponding 4-*tert*-butylamino derivative crystallizes optically resolved in a non-bilayer layer structure. This crystal packing is similar to the host-lattice of the inclusion compound formed by 9-(4-*tert*-butylphenyl)fluoren-9-ol and dioxane [Csöregh, Weber, Nassimbeni, Gallardo, Dörpinghaus, Ertan & Bourne (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 1775–1781]. The major building units of 4-*tert*-butylamino-1,5-diphenylimidazole are centrosymmetrical dimers in which the molecules display a 'yin-and-yang'-like self-complementarity. The dimers pack in columns, which form a distorted hexagonal pattern.

1. Introduction

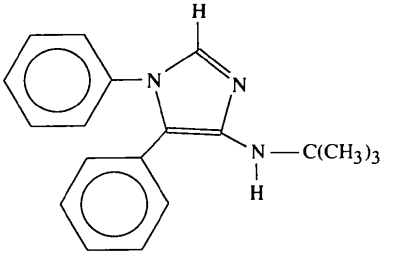
Starting with the pioneering work of Kitaigorodskii (1961), the two- and three-dimensional packing behaviour of very different compound classes has been analysed and systematized. Among them are hydrocarbons (Gavezzotti & Filippini, 1992), as well as hydrogen-bonded systems such as amides (Berkovitch-Yellin & Leiserowitz, 1980; Berkovitch-Yellin, Ariel & Leiserowitz, 1983; Dado, Desper, Holmgren, Rito & Gellman, 1992), urea derivatives (Etter, Urbančzyk-Lipkowska, Zia-Ebrahimi & Panunto, 1990; Chang, West, Fowler & Lauher, 1993) and carboxylic acids (Berkovitch-Yellin & Leiserowitz, 1982). Due to the many possible hydrogen-bonding schemes that polyols can form, their systematization has been unsuccessful, with two exceptions (André, Luger, Rosengarten & Fuhrhop, 1993; André, 1995).

Here the packing characteristics of three imidazole compounds, differing slightly in their structural formulae, will be described and discussed. Both 4-cyclohexylamino-5-hydroxy-1,5-diphenyl-Δ^3-imidazolin-2-one (1) and 4-*tert*-butylamino-5-hydroxy-1,5-diphenyl-Δ^3-imidazolin-2–one (2) have a hydroxyl group and a neighbouring secondary amine group in the 1,3-position which can act as hydrogen-bond donors; furthermore, they exhibit a carbonyl function and an unsubsituted imidazole N atom which can act as acceptors. Compound (1) possesses a cyclohexyl group, whereas (2) has a *tert*-butyl group at the corresponding position. 4-*tert*-Butylamino-1,5-diphenylimidazole (3) is similar to (2), but lacks the carbonyl function and the hydroxyl group.



(1) $R = C_6H_{11}$

(2) $R = C(CH_3)_3$



(3)

2. Experimental

2.1. *Synthesis*

Compound (1) was synthesized as follows: to a solution of 1.283 mg of pentacarbonyl(4-cyclohexylamino-1,5-diphenyl-Δ^4-imidazol-2-ylidene)tungsten (Rieger, Lotz, Kernbach, Schröder, André & Fehlhammer, 1994) in 100 ml of acetone (2.00 mmol) was added a hydrous solution of $KMnO_4$ (3.32 g in 20 ml, 21.00 mmol), resulting in the spontaneous formation of manganese

Table 1. *Experimental details*

	(1)	(2)	(3)
Crystal data			
Chemical formula	$C_{21}H_{23}N_3O_2$	$C_{19}H_{21}N_3O_2$	$C_{19}H_{21}N_3$
Chemical formula weight	349.43	323.39	291.40
Cell setting	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_12_12_1$	$P2_1/a$
a (Å)	34.845 (9)	8.321 (2)	16.607 (2)
b (Å)	10.013 (4)	12.411 (4)	11.427 (3)
c (Å)	10.918 (4)	17.008 (6)	9.668 (2)
β (°)	90.0	90.0	114.38 (2)
V (Å^3)	3809 (2)	1756.4 (9)	1671.1 (6)
Z	8	4	4
D_x (Mg m^{-3})	1.218	1.223	1.158
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
Wavelength (Å)	1.5418	1.5418	1.5418
No. of reflections for cell parameters	53	24	40
θ range (°)	22.51–25.95	20.28–26.91	20.24–36.16
μ (mm^{-1})	0.646	0.659	0.546
Temperature (K)	293	293	293
Crystal form	Needle	Block	Hexagonal plates
Crystal size (mm)	0.50 × 0.30 × 0.08	0.90 × 0.68 × 0.37	0.60 × 0.40 × 0.30
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Stoe four-circle	Stoe four-circle	Stoe four-circle
Data collection method	ω–2θ	ω–2θ	ω–2θ
Absorption correction	None	None	None
No. of measured reflections	2895	1691	2950
No. of independent reflections	2854	1691	2772
No. of observed reflections	1823	1625	2536
Criterion for observed reflections	$F > 2\sigma(F)$	$F > 2\sigma(F)$	$F > 2\sigma(F)$
R_{int}	0.094	–	0.008
θ_{max} (°)	63.93	64.0	63.98
Range of h, k, l	$0 \rightarrow h \rightarrow 40$	$0 \rightarrow h \rightarrow 9$	$0 \rightarrow h \rightarrow 19$
	$0 \rightarrow k \rightarrow 11$	$0 \rightarrow k \rightarrow 14$	$0 \rightarrow k \rightarrow 13$
	$0 \rightarrow l \rightarrow 12$	$0 \rightarrow l \rightarrow 19$	$0 \rightarrow l \rightarrow 11$
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 90 min	Every 90 min	Every 90 min
Intensity decay (%)	12	4	4
Refinement			
Refinement on	F	F	F
R	0.061	0.035	0.038
wR	0.038	0.033	0.037
S	1.84	4.06	4.52
No. of reflections used in refinement	1823	1625	2536
No. of parameters used	328	290	284
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined except H(161), H(162) and H(163), which were placed in calculated positions and held fixed	All H-atom parameters refined
Weighting scheme	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$	0.051	0.058	0.049
$\Delta\rho_{max}$ (e Å^{-3})	0.267	0.177	0.175
$\Delta\rho_{min}$ (e Å^{-3})	−0.268	−0.120	−0.124
Extinction method	13 reflections excluded	2 reflections excluded	Zachariasen (1968)
Extinction coefficient	1.68 (7)	0.6 (1)	1.5 (2)
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol IV, Tables 2.2B and 2.3.1)	*International Tables for X-ray Crystallography* (1974, Vol IV, Tables 2.2B and 2.3.1)	*International Tables for X-ray Crystallography* (1974, Vol IV, Tables 2.2B and 2.3.1)

dioxide. $Fe(NO_3)_3.9H_2O$ (0.994 g) was added gradually with concomitant gas evolution and warming. After stirring the solution at room temperature for 7 days, the solution turned colourless. MnO_2 was filtered off, extracted with methanol and the filtrate was concentrated. The resulting light yellow solid was transferred to a chromatography column charged with SiO_2 (2 × 20 cm) and eluted with diethylether/petroleum ether (1:1), yielding 577 mg (83%) of (1), m.p. 473 K. Compound (2) (m.p. 468 K) was synthesized analogously to (1), with a yield of 82% and starting with pentacarbonyl(4-*tert*-butylamino-1,5-phenyl-Δ^4-imidazolin-2-ylidene)chromium (Rieger *et al.*, 1994).

Compound (3) was synthesized from pentacarbonyl(4-*tert*-butylamino-1,5-diphenyl-Δ^4-imidazolin-2-ylidene)chromium by the removal of the pentacarbonylchromium complex using pyridine, as described previously (Rieger *et al.*, 1994).

2.2. *Crystal structure determination*

Single crystals of each compound suitable for X-ray diffraction studies were grown by evaporation of the solvents listed in Table 1.

Data for all the compounds were collected on a Stoe four-circle diffractometer with Ni-filtered Cu $K\alpha$ radiation and were corrected for Lorentz and polarization effects, but no absorption correction was performed. The structures were solved by direct methods with *SHELXS*86 (Sheldrick, 1985).

The conventional full-matrix least-squares refinements were performed with *Xtal*2.2 (Hall & Stewart, 1987). The function minimized was $\Sigma 1/\sigma^2(|F_o| - |F_c|)^2$, with $\sigma^2(F_o)$ from counting statistics. All non-H atoms of (1), (2) and (3) were refined with anisotropic displacement parameters; all H atoms were located in difference-Fourier maps and refined with isotropic displacement parameters. The geometry of H(161), H(162) and H(163) of (2) was too poor to be accepted. Therefore, their coordinates were calculated and held fixed during the final refinement cyles. Some low-order reflections (13 of 1, two of 2), with F_c considerably larger than F_o, probably due to severe extinction, were excluded from the final refinement cycles.

No attempts were made to determine the absolute configuration of the measured specimen of (2), crystallizing optically resolved.

3. Results and discussion

Fractional coordinates of the non-H atoms of (1), (2) and (3) are given in Tables 2–4.* Dihedral angles between the phenyl rings and the imidazole moiety are given in Table 5. The geometries of the hydrogen-bonding schemes of (1), (2) and (3) are given in Table 6, where a summary of the roman numerals used in the text for the denotion of the symmetry operations can also be found. Perspective views of the molecular structures are shown in Figs. 1–3. The crystal packings and hydrogen-bonding patterns of (1) and (2) are depicted in Figs. 4 and 5. Figs. 6(*a*) and (*b*) show the analogous crystal packing of (2) and an inclusion compound. The packing arrangement of (3) is displayed in Fig. 7.

3.1. *Molecular structures*

In spite of the non-aromaticity of the imidazole rings in (1) and (2), all imidazole moieties are planar; the maximum deviation from the least-squares plane amounts to 0.005 Å. The cyclohexyl ring of (1) assumes an almost undistorted chair form.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	U_{eq}
N(1)	0.36960 (8)	0.0666 (3)	0.5122 (2)	0.046 (2)
C(2)	0.35479 (9)	0.1053 (3)	0.4024 (3)	0.046 (2)
N(3)	0.33846 (7)	0.2327 (3)	0.4109 (2)	0.042 (2)
C(4)	0.34333 (8)	0.2707 (3)	0.5251 (3)	0.040 (2)
C(5)	0.36425 (9)	0.1701 (3)	0.6051 (3)	0.043 (2)
C(6)	0.3940 (1)	−0.0478 (3)	0.5285 (3)	0.056 (2)
C(7)	0.4266 (1)	−0.0609 (5)	0.4569 (4)	0.091 (3)
C(8)	0.4502 (2)	−0.1700 (9)	0.4763 (8)	0.137 (6)
C(9)	0.4414 (2)	−0.2617 (8)	0.5657 (9)	0.136 (6)
C(10)	0.4100 (2)	−0.2485 (5)	0.6384 (6)	0.106 (4)
C(11)	0.3852 (2)	−0.1392 (4)	0.6199 (4)	0.077 (3)
O(12)	0.35610 (6)	0.0395 (2)	0.3080 (2)	0.056 (2)
N(13)	0.33041 (8)	0.3830 (3)	0.5728 (3)	0.047 (2)
C(14)	0.30814 (9)	0.4835 (3)	0.5040 (3)	0.044 (2)
C(15)	0.2791 (1)	0.5478 (4)	0.5886 (4)	0.066 (3)
C(16)	0.2563 (1)	0.6558 (6)	0.5204 (6)	0.093 (4)
C(17)	0.2823 (2)	0.7594 (5)	0.4618 (6)	0.096 (4)
C(18)	0.3117 (2)	0.6923 (5)	0.3790 (5)	0.085 (3)
C(19)	0.3347 (1)	0.5869 (4)	0.4483 (4)	0.058 (2)
O(20)	0.34019 (6)	0.1179 (2)	0.6969 (2)	0.049 (1)
C(21)	0.40272 (9)	0.2188 (3)	0.6541 (3)	0.044 (2)
C(22)	0.4216 (1)	0.3230 (4)	0.6000 (4)	0.063 (3)
C(23)	0.4576 (1)	0.3643 (5)	0.6399 (4)	0.077 (3)
C(24)	0.4739 (1)	0.2994 (6)	0.7371 (4)	0.083 (3)
C(25)	0.4560 (1)	0.1939 (5)	0.7926 (4)	0.082 (3)
C(26)	0.4205 (1)	0.1546 (5)	0.7511 (3)	0.065 (3)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	*y*	*z*	U_{eq}
N(1)	−0.0783 (3)	1.1434 (2)	0.8377 (1)	0.035 (1)
C(2)	−0.0473 (4)	1.2334 (2)	0.7929 (2)	0.040 (2)
N(3)	−0.0410 (3)	1.2093 (2)	0.7138 (1)	0.041 (1)
C(4)	−0.0676 (4)	1.1058 (2)	0.7077 (2)	0.035 (1)
C(5)	−0.0968 (3)	1.0496 (2)	0.7872 (2)	0.033 (1)
C(6)	−0.0950 (4)	1.1431 (2)	0.9218 (2)	0.039 (2)
C(7)	−0.1827 (4)	1.2234 (3)	0.9581 (2)	0.049 (2)
C(8)	−0.1918 (5)	1.2274 (3)	1.0400 (2)	0.065 (2)
C(9)	−0.1185 (5)	1.1508 (4)	1.0842 (2)	0.072 (3)
C(10)	−0.0373 (6)	1.0688 (4)	1.0476 (2)	0.077 (3)
C(11)	−0.0220 (5)	1.0647 (3)	0.9658 (2)	0.058 (2)
O(12)	−0.0276 (3)	1.3245 (1)	0.8191 (1)	0.051 (1)
N(13)	−0.0643 (3)	1.0489 (2)	0.6423 (1)	0.039 (1)
C(14)	−0.0108 (5)	1.0876 (2)	0.5640 (2)	0.046 (2)
C(15)	−0.114 (1)	1.1787 (5)	0.5371 (3)	0.107 (5)
C(16)	0.1617 (6)	1.1218 (4)	0.5704 (3)	0.105 (4)
C(17)	−0.0241 (6)	0.9919 (3)	0.5086 (2)	0.061 (2)
O(20)	0.0297 (3)	0.9774 (2)	0.8026 (1)	0.038 (1)
C(21)	−0.2632 (3)	1.0002 (2)	0.7929 (2)	0.034 (1)
C(22)	−0.3989 (4)	1.0623 (3)	0.7797 (2)	0.055 (2)
C(23)	−0.5509 (4)	1.0181 (3)	0.7820 (3)	0.068 (3)
C(24)	−0.5694 (4)	0.9084 (3)	0.7977 (2)	0.063 (2)
C(25)	−0.4370 (5)	0.8472 (3)	0.8114 (2)	0.053 (2)
C(26)	−0.2843 (4)	0.8913 (2)	0.8092 (2)	0.040 (2)

The phenyl rings are inclined to the imidazole ring at various angles. As shown by the torsion angles C(2)—N(1)—C(6)—C(7) and N(1)—C(5)—C(21)—C(22) lying in the ranges 43–53 and 45–89°, respectively, there is less orientational variety for phenyl ring I than II in the three imidazole derivatives (Table 5).

* Lists of atomic coordinates, anisotropic displacement parameters, complete geometry and structure factors have been deposited with the IUCr (Reference: KA0029). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (3)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
N(1)	0.84525 (7)	0.0925 (1)	0.9136 (1)	0.0417 (5)
C(2)	0.79589 (9)	0.0887 (1)	0.7613 (2)	0.0479 (5)
N(3)	0.82493 (7)	0.1589 (1)	0.6841 (1)	0.0484 (4)
C(4)	0.89792 (8)	0.2127 (1)	0.7934 (2)	0.0427 (4)
C(5)	0.91236 (8)	0.1745 (1)	0.9367 (1)	0.0391 (1)
C(6)	0.82150 (8)	0.0348 (1)	1.0231 (2)	0.0445 (4)
C(7)	0.7966 (1)	−0.0817 (1)	1.0013 (2)	0.0615 (6)
C(8)	0.7675 (1)	−0.1348 (2)	1.1009 (2)	0.0765 (7)
C(9)	0.7646 (1)	−0.0743 (2)	1.2219 (2)	0.0741 (7)
C(10)	0.7917 (1)	0.0403 (2)	1.2454 (2)	0.0650 (6)
C(11)	0.8202 (1)	0.0956 (1)	1.1458 (2)	0.0540 (5)
N(13)	0.94647 (9)	0.2972 (1)	0.7567 (1)	0.0529 (4)
C(14)	0.9651 (1)	0.2883 (1)	0.6198 (2)	0.0548 (5)
C(15)	0.9880 (2)	0.1633 (2)	0.5926 (3)	0.0976 (8)
C(16)	0.8850 (2)	0.3336 (2)	0.4832 (2)	0.0734 (7)
C(17)	1.0439 (1)	0.3694 (2)	0.6507 (3)	0.0790 (8)
C(21)	0.98465 (8)	0.2046 (1)	1.0831 (1)	0.0405 (4)
C(22)	1.03331 (9)	0.1195 (1)	1.1884 (2)	0.0487 (5)
C(23)	1.1044 (1)	0.1516 (2)	1.3210 (2)	0.0599 (6)
C(24)	1.1289 (1)	0.2674 (2)	1.3501 (2)	0.0650 (6)
C(25)	1.0811 (1)	0.3524 (2)	1.2478 (2)	0.0659 (6)
C(26)	1.0088 (1)	0.3215 (1)	1.1158 (2)	0.0538 (5)

Table 5. *Torsion angles describing the twist between the phenyl and the imidazole rings in (1), (2) and (3)*

Compound	Torsion angle(°)*	
(1)	C(2)—N(1)—C(6)—C(7)	53.0 (5)
	N(1)—C(5)—C(21)—C(22)	89.6 (4)
(2)	C(2)—N(1)—C(6)—C(7)	43.0 (4)
	N(1)—C(5)—C(21)—C(22)	54.9 (4)
(3)	C(2)—N(1)—C(6)—C(7)	48.9 (2)
	N(1)—C(5)—C(21)—C(22)	45.0 (2)

* The first two and the last two atoms of each torsion angle belong to the imidazole and phenyl ring, respectively.

Table 6. *Hydrogen-bond geometries* for (1), (2) and (3)*

D—H···*A*	*D*···H	H—*A*	*D*···*A*	*D*—H···*A*
(1)				
N(13)—H···O(12^{ii})	0.89 (3)	1.97 (3)	2.828 (4)	162 (3)
O(20)—H···N(3^{ii})	1.02 (4)	1.76 (4)	2.775 (3)	173 (3)
(2)				
N(13)—H···O(12^{iii})	0.96 (4)	2.17 (4)	2.962 (3)	140 (3)
O(20)—H···O(12^{iii})	0.71 (3)	2.10 (3)	2.808 (3)	177 (3)
C(26)—H···N(3^{iii})	0.90 (3)	2.68 (3)	3.547 (4)	163 (2)
(3)				
C(24)—H···N(3^{iv})	0.97 (2)	2.65 (2)	3.614 (2)	177 (2)

Symmetry codes: (i) x, y, z; (ii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $\frac{1}{2}+x, \frac{1}{2}-y, 1+z$; (v) $-\frac{1}{2}-x, 2-y, \frac{1}{2}+z$; (vi) $-\frac{1}{2}-x, 2-y, -\frac{1}{2}+z$; (vii) $2-x, -y, 2-z$; (viii) $x-\frac{1}{2}, \frac{1}{2}-y, z$. * Calculated using *PLATON* (Spek, 1990).

The third torsion angle needed to describe the conformation of the compounds, namely N(3)—C(4)—N(13)—C(14), is 0.2 (8)° in (1), 8.0 (5)° in (2) and −38.8 (2)° in (3). The orientation of the *tert*-butyl group, therefore, is not quite the same in (2) and (3).

The amine H atom is *trans* with respect to N(3) in all three compounds. The corresponding *cis* form, which allows for the formation of hydrogen-bonded dimers (see below), cannot be adopted since it implies steric congestion involving the bulky residues on N(13) and the phenyl rings on the imidazole.

3.2. *Hydrogen-bonding schemes and crystal packing*

The molecules of (1) are arranged with their longest molecular axis along the *a* axis in such a manner that the cyclohexyl and phenyl groups only interact with like

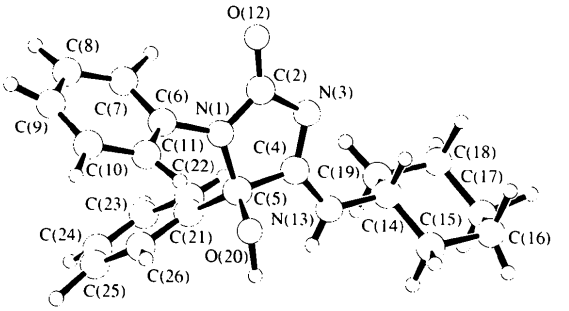


Fig. 1. Molecular structure of (1), showing the atomic numbering scheme. Phenyl rings I and II are defined by C(6)–C(11) and C(21)–C(26), respectively.

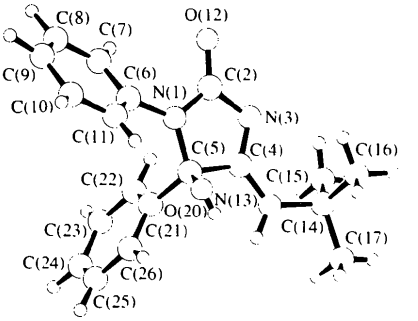


Fig. 2. Molecular structure of (2), showing the atomic numbering scheme. Phenyl rings I and II are defined by C(6)–C(11) and C(21)–C(26), respectively.

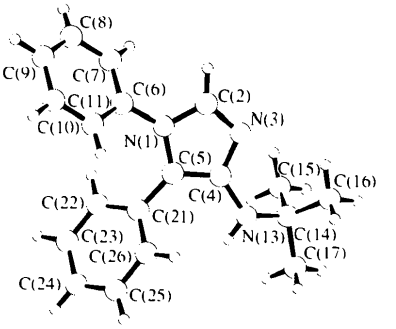


Fig. 3. Molecular structure of (3), showing the atomic numbering scheme. Phenyl rings I and II are defined by C(6)–C(11) and C(21)–C(26), respectively.

moieties (Fig. 4). Therefore, no 'mixed' interactions exist within the crystal packing. In contrast, in the crystal structure of the related 1-(4-bromobenzyl)-2,5-dimethyl-4-morpholino-5-phenyl-4,5-dihydroimidazole (Destro, 1979) there is no strict separation between phenyl rings and the morpholine moieties.

The domains within the cell of (1) exhibiting hydrogen-bonded polar moieties (see below) are separated by hydrophobic layers individually formed by phenyl and cyclohexyl groups. Therefore, the crystal packing of (1) is essentially analogous to bilayered packing arrangements formed by lipid compounds. Here polar and apolar hydrophobic molecular domains also occur in alternating layers (Pascher, Lundmark, Nyholm & Sundell, 1992).

All potential hydrogen-bond donors and acceptors of (1) are involved in its hydrogen-bonding scheme: the hydroxyl group and the amine N atom donate a hydrogen bond to N(3) and to the carbonyl group, respectively, lying on the same glide-plane-related molecule II. Since the lone pair of the N(13) atom can interact with the imidazolinone's π-system, the hydrogen bonds involving N(13) and O(12) are of the resonance-assisted type (Gilli, Bertolasi, Ferreti & Gilli, 1993) and generate endless chains. It is noteworthy that a N—H···O=C hydrogen bond is found. This is namely the dominant hydrogen-bonding pattern found in the crystal structures of secondary amides (*cf.* footnote 17d of Etter, 1990), where the C=O and N—H moieties are not separated by several bonds as is the case in (1).

The resonance-assisted endless hydrogen-bond chains running in the z direction close to $x = \frac{1}{4}$ and in the $\bar{z}$ direction close to $x = \frac{3}{4}$ generate a net zero dipole moment for the crystal. In contrast to (1), (2) crystallizes as a conglomerate [space group $P2_12_12_1$ (Jacques, Collet & Wilen, 1981)]. Since the synthesis of (2) is assumed to be stereochemically unselective, it can be reasonably concluded that the optical resolution is a consequence of its very elegant crystal packing. This

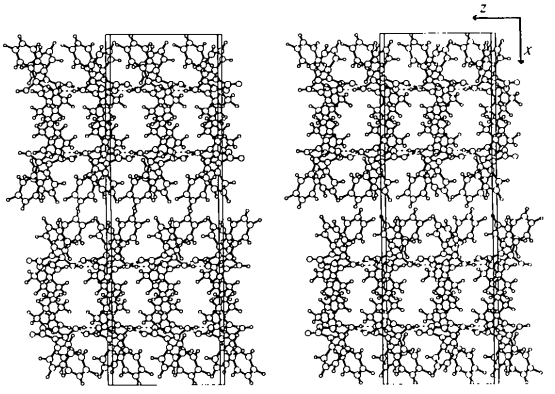


Fig. 4. *SCHAKAL88* Plot (Keller, 1989) of the crystal packing of (1). The viewing direction is [0$\bar{1}$0]. Polar and apolar domains occur in alternating layers within the cell.

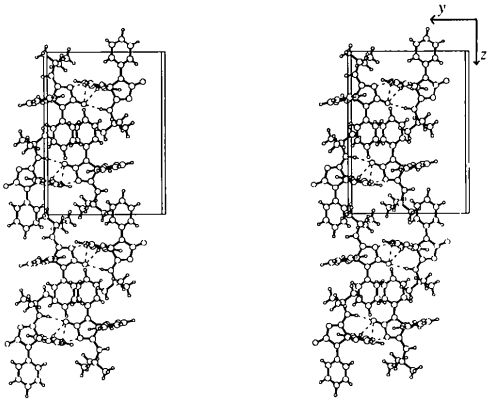


Fig. 5. The crystal packing of (2) viewed along [$\bar{1}$00].

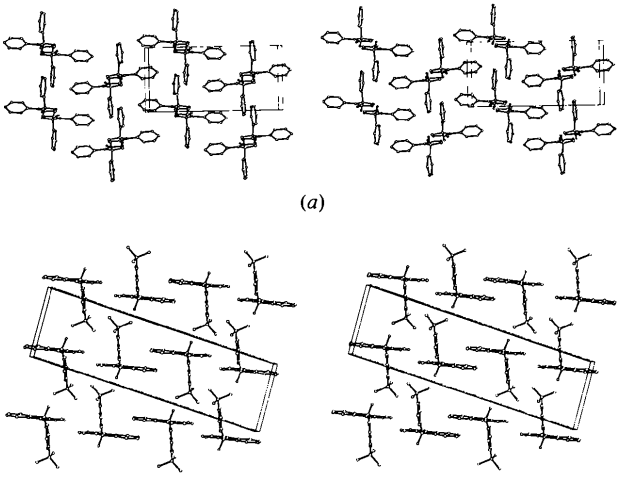


Fig. 6. (*a*) Analogous crystal packing of (2) and (*b*) the host lattice of 9-(4-*tert*-butylphenyl)fluoren-9-ol:dioxane (1:1). For clarity, the H atoms were omitted in both structures. In order to show the essential point, (2) is stripped of its amino-*tert*-butyl moiety and the dioxane guest molecules occurring in the large cavities are not displayed in (*b*).

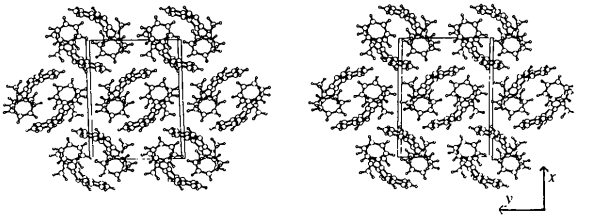


Fig. 7. The crystal packing of (3). The viewing direction is [00$\bar{1}$]. Note the centrosymmetric dimers exhibiting a 'yin-and-yang'-like phenotype.

packing can be regarded as an orthogonally interconnected layer structure (Fig. 5). The imidazolinone and phenyl rings I are twisted against each other, but not to such an extent that one could regard them as forming part of a layer lying approximately in the *bc* plane. This layer is completed by another imidazolinone–phenyl I pair generated by the 2_1 axis along **b**. The layer is highly corrugated due to the twist angle between the imidazoline and phenyl I and the offset of the second imidazolinone-phenyl I pair along **a**. The two phenyl II rings pertaining to each layer are perpendicular to the layer, one phenyl II ring pointing up and the other down, as a consequence of the twofold screw axis generating the layer. Each unit cell contains two of these layers having the idealized form of a parallelogram with axes of approximately 7.9 and 11.6 Å and symmetry related by the 2_1 axis along **a**. The phenyl II rings interconnect each layer to two other layers by interacting with perpendicularly oriented phenyl I rings pertaining to the latter layers. These interactions are of the edge-plane type (Williams & Xiao, 1993).

Phenyl I_I interacts with phenyl II_V and phenyl II_I with phenyl I_{VI}, producing an identical centroid–centroid distance of 5.13 Å. This value is compatible with the distances found in tetraarylporphyrines (Byrn, Curtis, Khan, Sawin, Tsumuri & Strouse, 1990).

The crystal packing of (2) shows remarkable similarity to the host lattice of the inclusion compound formed by 9-(4-*tert*-butylphenyl)fluoren-9-ol and dioxane (Csöregh, Weber *et al.*, 1993). The common motif of both structures becomes visible when (2) is stripped of its amino-*tert*-butyl moiety (Figs. 7*a* and *b*). As discussed above, (2) can be thought of as a corrugated layer structure. The layer pattern found in (2) and in the host lattice is formed by a pair of molecules with phenyl moieties perpendicular to the layer in alternating directions. The fluoren residues of the inclusion compound are almost completely planar. The offset between two molecules of this motif is larger – and opposite in direction – than in (2), but the general packing pattern of the two compounds remains identical.

However, the crystal packing of (2) is completely distinct from the packing arrangement of (1). Indeed, there are hydrophobic layers in (2) formed by *tert*-butyl and phenyl I moieties, but the hydrophobic phenyl II rings and the polar residues involved in hydrogen bonds share a common layer. Thus, the 'bilayer' crystal packing observed in racemic (1) is not reproduced in optically resolved (2). In contrast to (1), N(3) of (2) does not accept a hydrogen bond from O(20), but from C(26). Its C···N distance is of the order of magnitude given by Berkovitch-Yellin & Leiserowitz (1984). $O(12)_{III}$ accepts two hydrogen bonds, namely from $N(13)_I$ and $O(20)_I$. Therefore, the hydrogen bonds occur within a layer, whereas the phenyl I–phenyl II interactions are interlayer oriented. The hydrogen-bonding pattern of (2) is described by graph set $R_2^1(7)$, neglecting the C—H···N bond (Etter, MacDonald & Bernstein, 1990). This hydrogen-bonding scheme resembles the $R_2^1(6)$ pattern common to many urea derivatives (Etter, Urbańczyk-Lipkowska *et al.*, 1990; Chang *et al.*, 1993) where the carbonyl O atom accepts two hydrogen bonds, one each from the two amide N atoms of one neighbouring molecule. Thus, (2) behaves as a 'pseudo-urea' with respect to the hydrogen bonding.

Remarkably, neither (1) nor (2) exhibit a hydrogen bond between their hydroxyl groups. In principle, the OH groups of (1) and (2) are able to induce the formation of hydrogen-bonded tetrameric aggregates of graph set $R_4^4(8)$, as found in 9-methyl-9-fluorenol (Csöregh, Czugler & Weber, 1993) and in other sterically crowded monoalcohols (Puff, Braun & Reuter, 1991; Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992; Ferguson, Gallagher, Murphy, Spalding, Glidewell & Holden, 1992). The lack of such O—H···O bonds in (1) and (2) can be attributed to the fact that no hydrogen bonds can be formed in such tetramers between the amino group and the carbonyl function or N(3). A hydrogen-bonding scheme without the participation of these functional groups must be regarded as detrimental to the formation of tetramers (Etter, 1991).

It should be emphasized that the general connectivities of the hydrogen-bonding schemes of (1) and (2) do follow known patterns. However, the highly elegant interconnected layer structure of (2), which probably caused its optical resolution, was not predictable from current knowledge.

While in (1) and (2) the hydrogen-bonding schemes can be formed with only one molecule per asymmetric unit, this is not always possible. For monoalcohols, hydrogen bonding can often only be achieved through the presence of more than one independent molecule (Brock & Duncan, 1994). Due to the availability of more than one functional group potentially forming hydrogen bonds, (1) and (2) do not have to behave this way, *i.e.* there is no need to crystallize with more than one independent molecule.

Looking along the *c* direction the molecular packing of (3) is best described as a hexagonal columnar arrangement (Fig. 7). The smallest building unit of these columns is not the asymmetric unit consisting of one molecule, but rather a molecular dimer. It is formed between the molecule in the asymmetric unit and its centrosymmetrical counterpart at $2-x, -y, 2-z$, showing a 'yin-and-yang'-like self-complementarity (Fig. 7). The intradimer centroid-to-centroid distance of 5.46 Å between phenyl I_I and phenyl II_{VII} equals the intercentroid distance of phenyl I_I and phenyl II_{VIII} involved in intercolumnar interactions. Since the cross section of the dimers in the *ab* plane is not circular but elliptical with radii of approximately 2.2 and 5.9 Å, the hexagonal lattice built by these columns is distorted.

An intercolumnar C—H···N bond is found between C(24) and N(3). There is, however, no hydrogen

bond between the only potential hydrogen-bond donor and acceptor of (3), namely N(13) and N(3), respectively. Additionally, no N—H···phenyl interactions are observed; H(13)'s shortest distance of 3.5 Å to a phenyl centroid is considerably longer than normally accepted in organic compounds (Hanton, Hunter & Purvis, 1992; Viswamitra, Radhakrishnan, Bandekar & Desiraju, 1993).

Hydrogen-bonded dimers of graph set $R_2^2(8)$ involving an amine hydrogen and a pyrimidine N atom are found in the crystal structure of 2-amino-4-chloro-6-methylpyrimidine (Etter, 1991; MacDonald & Whitesides, 1995). Analogous dimers satisfying the hydrogen-bonding propensities of H(13) and N(3) could also be formed by (3), but only if the amine H atom was in a *cis* arrangement with respect to N(3). However, this conformation is not accessible due to steric hindrance, as stated above. Thus, intrinsic molecular properties prevent the molecules of (3) from adopting a favourable hydrogen-bonding motif.

This work was supported by the Fonds der Chemischen Industrie.

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