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# Two 2,2-dihalo-*N*-(1-phenylethyl)-cyclopropane-1-carboxamides

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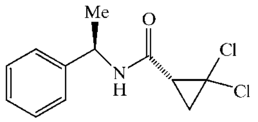
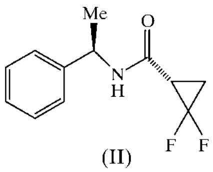
The crystal structures of (1*R*,1′*S*)-2′,2′-dichloro-*N*-(1-phenylethyl)cyclopropane-1′-carboxamide, $C_{12}H_{13}Cl_2NO$, (I), and (1*R*,1′*R*)-2′,2′-difluoro-*N*-(1-phenylethyl)cyclopropane-1′-carboxamide, $C_{12}H_{13}F_2NO$, (II), have been determined. Both crystals contain two independent molecules with different conformations of the phenylethyl groups. In the crystals of both compounds, the molecules are linked together by N—H···O hydrogen bonds, thus forming chains in the *a* direction.

## Comment

The title compounds, (I) and (II), have been synthesized as intermediate products in the synthesis of novel ferroelectric liquid crystals with optically active dihalo-substituted cyclopropanecarboxylic acids in their side chain (Miyazawa & de Meijere, 2001). An X-ray structural study has confirmed the absolute configuration of the molecules, which was proposed on the basis of chemical information.



(I)



(II)

The structures of (I) and (II) are similar but not isostructural. The structures of both compounds contain two independent molecules, and the conformations of these molecules are different. However, in (II) the two independent molecules differ mainly by the orientation of the phenyl ring, whereas in (I) the conformation around the N—C7 bonds in the two molecules is also different (Fig. 1). The replacement of chlorine substitutents in the cyclopropane cycle of (I) with the more electronegative fluorine substitutents in (II) results in a predictable (*e.g.* Allen, 1980; Cremer & Kraka, 1985) increase in the asymmetry of the three-membered ring, with a significant elongation of the distal bond C10—C11 (C30—C31) and a shortening of the vicinal bonds C12—C10 (C32—C30) and C12—C11 (C32—C31) (Tables 1 and 3).

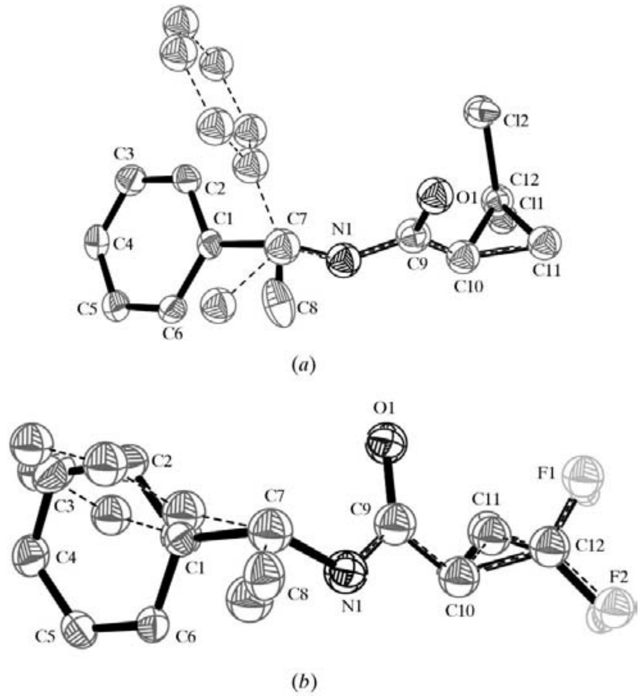


**Figure 1**
The overlapping of the two independent molecules of (*a*) (I) and (*b*) (II). Displacement ellipsoids are shown at the 50% probability level, and H atoms have been omitted for clarity.

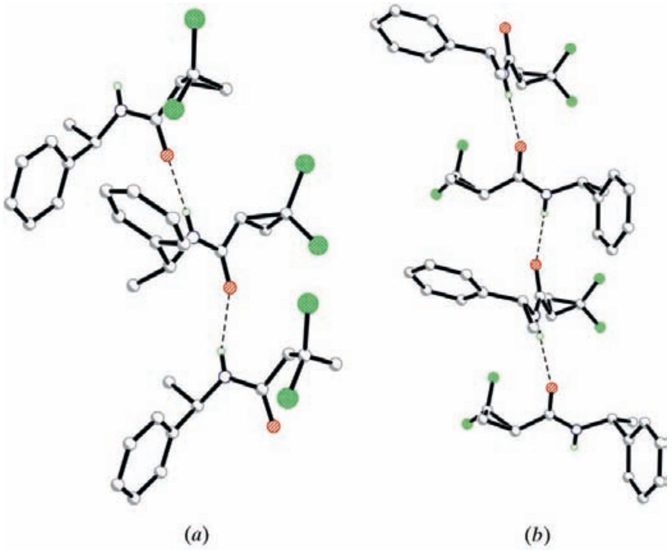


**Figure 2**
The arrangement of the molecules in hydrogen-bonded chains in (*a*) (I) and (*b*) (II).

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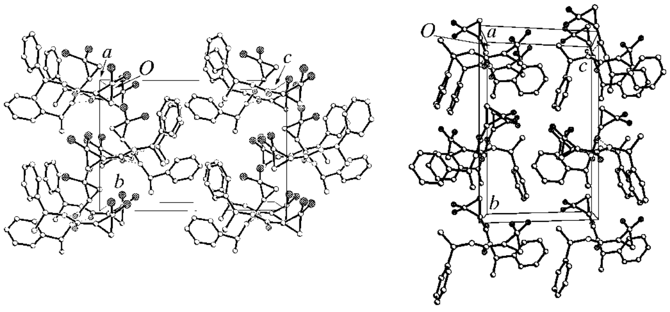
In the crystals of (I) and (II), the molecules of both compounds form infinite chains along the *a* axis, and the molecules in these chains are connected by strong N—H⋯O hydrogen bonds (Tables 2 and 4). However, because the molecules of (I) and (II) have different configurations, the molecular arrangements in the chains are also different (Fig. 2). In (I), the phenyl rings and methyl groups of adjacent molecules are in close proximity, whereas in (II), the C11 methylene groups of the cyclopropane rings are located between the benzene rings. As a result, the chains in (I) are packed together so as to form hydrophobic areas in which the phenylethyl groups are located (Fig. 3), which is not the case in (II).



(*a*) (*b*)

**Figure 3**
The packing diagrams of (*a*) (I) and (*b*) (II), viewed along the *a* axis in each case.

## Experimental

Crystals of (I) and (II) (Miyazanwas & de Meijere, 2001) were obtained by the slow evaporation of solutions in hexane/methanol and hexane/diethyl ether, respectively.

### Compound (I)

*Crystal data*

$C_{12}H_{13}Cl_2NO$
$M_r = 258.13$
Monoclinic, $P2_1$
$a = 9.4157\ (3)$ Å
$b = 9.6893\ (3)$ Å
$c = 13.9473\ (4)$ Å
$\beta = 92.91\ (1)^\circ$
$V = 1270.8\ (1)$ Å$^3$
$Z = 4$
$D_x = 1.349$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 999 reflections
$\theta = 10.3$–$20.8^\circ$
$\mu = 0.49$ mm$^{-1}$
$T = 100\ (2)$ K
Plate, colourless
0.48 × 0.20 × 0.06 mm

*Data collection*

Bruker SMART CCD 1K diffractometer
ω scans
Absorption correction: multi-scan *SADABS* (Sheldrick, 1998)
$T_{\min} = 0.799$, $T_{\max} = 0.971$
12 790 measured reflections
6176 independent reflections
5373 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 30.4^\circ$
$h = -13 \rightarrow 12$
$k = -13 \rightarrow 11$
$l = -19 \rightarrow 18$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.071$
$S = 1.02$
6176 reflections
393 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.21$ e Å$^{-3}$
Absolute structure: Flack (1983)
Flack parameter = −0.01 (4)

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

| | | | |
|---|---|---|---|
| Cl1—C12 | 1.7661 (18) | C7—C8 | 1.524 (3) |
| Cl2—C12 | 1.7532 (19) | C9—C10 | 1.506 (2) |
| Cl3—C32 | 1.769 (2) | C10—C12 | 1.509 (3) |
| Cl4—C32 | 1.7524 (19) | C10—C11 | 1.512 (3) |
| O1—C9 | 1.236 (2) | C11—C12 | 1.482 (3) |
| O2—C29 | 1.238 (2) | C29—C30 | 1.502 (3) |
| N1—C9 | 1.341 (2) | C30—C32 | 1.506 (3) |
| N1—C7 | 1.478 (2) | C30—C31 | 1.523 (3) |
| N2—C29 | 1.341 (2) | C31—C32 | 1.485 (3) |
| N2—C27 | 1.471 (2) | | |
| | | | |
| C9—N1—C7 | 121.88 (16) | Cl2—C12—Cl1 | 111.01 (10) |
| C29—N2—C27 | 120.91 (15) | O2—C29—N2 | 123.17 (17) |
| O1—C9—N1 | 123.83 (16) | O2—C29—C30 | 122.52 (17) |
| O1—C9—C10 | 122.38 (16) | N2—C29—C30 | 114.31 (15) |
| N1—C9—C10 | 113.76 (15) | C29—C30—C32 | 119.10 (15) |
| C9—C10—C12 | 119.31 (15) | C29—C30—C31 | 118.25 (16) |
| C9—C10—C11 | 119.40 (16) | C32—C30—C31 | 58.73 (12) |
| C12—C10—C11 | 58.74 (12) | C32—C31—C30 | 60.07 (13) |
| C12—C11—C10 | 60.51 (12) | C31—C32—C30 | 61.21 (13) |
| C11—C12—C10 | 60.75 (12) | Cl4—C32—Cl3 | 111.76 (11) |
| | | | |
| C9—N1—C7—C1 | 152.73 (18) | C29—N2—C27—C21 | 78.3 (2) |
| C9—N1—C7—C8 | −80.9 (2) | C29—N2—C27—C28 | −158.78 (17) |
| C6—C1—C7—N1 | 84.2 (2) | C22—C21—C27—N2 | −150.49 (18) |
| C2—C1—C7—N1 | −92.5 (2) | C26—C21—C27—N2 | 33.6 (2) |

**Table 2**
Hydrogen-bonding geometry (Å, °) for (I).

| *D*—H⋯*A* | *D*—H | H⋯*A* | *D*⋯*A* | *D*—H⋯*A* |
|---|---|---|---|---|
| N1—H1N⋯O2$^{\rm i}$ | 0.84 (3) | 2.11 (3) | 2.909 (2) | 158 (3) |
| N2—H2N⋯O1$^{\rm ii}$ | 0.83 (3) | 2.12 (3) | 2.927 (2) | 163 (2) |

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

### Compound (II)

*Crystal data*

$C_{12}H_{13}F_2NO$
$M_r = 225.23$
Monoclinic, $P2_1$
$a = 9.2402\ (4)$ Å
$b = 14.2669\ (5)$ Å
$c = 9.3542\ (4)$ Å
$\beta = 109.33\ (1)^\circ$
$V = 1163.6\ (1)$ Å$^3$
$Z = 4$
$D_x = 1.286$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 998 reflections
$\theta = 10.2$–$20.8^\circ$
$\mu = 0.10$ mm$^{-1}$
$T = 120\ (2)$ K
Plate, colourless
0.42 × 0.22 × 0.04 mm

*Data collection*

Bruker SMART CCD 1K diffractometer
ω scans
11 953 measured reflections
5647 independent reflections
3738 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$
$\theta_{\max} = 30.3^\circ$
$h = -12 \rightarrow 13$
$k = -20 \rightarrow 17$
$l = -12 \rightarrow 12$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.084$
$S = 0.99$
5647 reflections
393 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.034P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.15$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.22$ e Å$^{-3}$
Absolute structure: Flack (1983)
Flack parameter = 1.0 (5)

**Table 3**
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| F1—C12 | 1.354 (3) | N2—C27 | 1.466 (3) |
| F2—C12 | 1.350 (3) | C9—C10 | 1.493 (3) |
| F3—C32 | 1.350 (3) | C10—C12 | 1.476 (3) |
| F4—C32 | 1.361 (2) | C10—C11 | 1.549 (3) |
| O1—C9 | 1.238 (2) | C11—C12 | 1.436 (4) |
| O2—C29 | 1.239 (2) | C29—C30 | 1.499 (3) |
| N1—C9 | 1.336 (3) | C30—C32 | 1.474 (3) |
| N1—C7 | 1.467 (3) | C30—C31 | 1.547 (3) |
| N2—C29 | 1.333 (3) | C31—C32 | 1.450 (3) |
| | | | |
| C9—N1—C7 | 122.16 (19) | C11—C12—C10 | 64.28 (17) |
| C29—N2—C27 | 123.78 (19) | O2—C29—N2 | 123.5 (2) |
| O1—C9—N1 | 122.85 (19) | O2—C29—C30 | 121.7 (2) |
| O1—C9—C10 | 121.45 (18) | N2—C29—C30 | 114.75 (19) |
| N1—C9—C10 | 115.70 (19) | C32—C30—C29 | 119.3 (2) |
| C12—C10—C9 | 119.69 (19) | C32—C30—C31 | 57.31 (15) |
| C12—C10—C11 | 56.63 (16) | C29—C30—C31 | 117.4 (2) |
| C9—C10—C11 | 117.8 (2) | C32—C31—C30 | 58.81 (16) |
| C12—C11—C10 | 59.09 (16) | F3—C32—F4 | 107.82 (17) |
| F2—C12—F1 | 107.82 (18) | C31—C32—C30 | 63.88 (16) |
| | | | |
| C9—N1—C7—C1 | 89.8 (2) | C29—N2—C27—C28 | −157.5 (2) |
| C9—N1—C7—C8 | −145.3 (2) | C29—N2—C27—C21 | 76.8 (3) |
| C2—C1—C7—N1 | −125.6 (2) | C22—C21—C27—N2 | 3.4 (3) |
| C6—C1—C7—N1 | 53.8 (2) | C26—C21—C27—N2 | −174.6 (2) |

The absolute configuration of (I) was confirmed by the Flack (1983) parameter, and that of (II) was set by reference to the configuration at C7 in compound (I). Refined C—H distances were in the ranges 0.89 (2)–1.08 (3) and 0.88 (2)–1.03 (3) Å for (I) and (II), respectively.

**Table 4**
Hydrogen-bonding geometry (Å, °) for (II).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1N···O2$^{\rm i}$ | 0.79 (2) | 2.10 (2) | 2.884 (2) | 171 (2) |
| N2—H2N···O1 | 0.82 (2) | 2.02 (3) | 2.840 (2) | 177 (2) |

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

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997) and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1205). Services for accessing these data are described at the back of the journal.

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