

For all compounds, data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1996). Program(s) used to solve structures: *SHELXS97* (Sheldrick, 1997) for (1) and (2); *SHELXS* (Sheldrick, 1990) for (3). For all compounds, program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLUTON92* (Spek, 1992a) and *PLATON92* (Spek, 1992b)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1061). Services for accessing these data are described at the back of the journal.

## References

- Babu, A. M., Weakley, T. J. R. & Murthy, M. R. N. (1998). *Z. Kristallogr.* **213**, 321–322.
- Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
- Harms, K. & Wocadlo, S. (1996). *XCAD4. Program for the Lp Correction of Enraf-Nonius Four-Circle Diffractometer Data*. University of Marburg, Germany.
- Keller, H. L., Kucharczyk, D. & Küppers, H. (1982). *Z. Kristallogr.* **158**, 221–224.
- Küppers, H. (1973). *Acta Cryst.* **B29**, 318–327.
- McAuley, A. & Nancollas, G. H. (1960). *Trans. Faraday Soc.* **56**, 1165–1171.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Spek, A. L. (1992a). *PLATON92. Program for Molecular Geometry*. University of Utrecht, The Netherlands.
- Spek, A. L. (1992b). *PLUTON92. Program for Molecular Graphics*. University of Utrecht, The Netherlands.
- Vijayalakshmi, J. & Srinivasan, R. (1983). *Acta Cryst.* **C39**, 908–909.
- Yasada, M., Yamasaki, K. & Ohtaki, H. (1960). *Bull. Chem. Soc. Jpn.* **33**, 1067–1070.

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## Twisted Structure of a Substituted 2-Chloro-3-(4-chloro-2-methyl-1,3-oxazol-5-yl)-1H-indole

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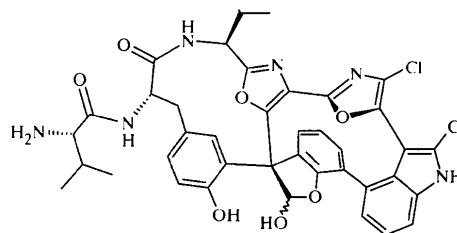
### Abstract

2,2,2-Trichloroethyl 2-chloro-3-(4-chloro-2-methyl-1,3-oxazol-5-yl)-1H-indole-1-carboxylate,  $C_{15}H_9Cl_5N_2O_3$ , the first synthetic example of an oxazolyindole with a

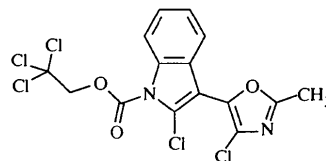
Cl atom at the *ortho* position of each ring, exhibits a dihedral angle of  $45.6(1)^\circ$  between the heteroaromatic ring systems.

### Comment

The natural product diazonamide A, isolated from the marine ascidian *Diazona chinensis*, exhibits interesting biological activity and possesses a unique structure (see Scheme below). Four adjacent heterocyclic rings, viz one oxazole, one chlorooxazole, one chloroindole and one benzofuran, are fixed in one macrocyclic ring of a bicyclic framework in such a way that any appreciable overlap of the conjugated heterocycles is prevented; e.g. the chlorooxazole and the chloroindole ring subtend an interplanar angle of  $60^\circ$  (Lindquist *et al.*, 1991). In order to elucidate to what extent this torsion is attributed to the macrocyclic arrangement of the four rings or the repulsive effect of the two *ortho*-chloro substituents, we focused our interest, with respect to the total synthesis of diazonamide A, on 2-chloro-3-(4-chloro-2-methyl-1,3-oxazol-5-yl)-1H-indole-1-carboxylic acid 2,2,2-trichloroethyl ester, (1), the first synthetic example of an oxazolyindole with one *ortho*-Cl atom on each heterocyclic ring.



Diazonamide A



(1)

Generally, X-ray structure analyses of molecules consisting of two five-membered heterocyclic rings connected to each other by a single bond and each bearing a substituent *ortho* to that bond are rare (Secondo *et al.*, 1996). The crystal structure determination of the new oxazolyindole (1) (Fig. 1) reveals that both heterocyclic rings are planar and that the molecular dimensions are similar to those of other oxazoles (Ambats & Marsh, 1965) and indoles (Chadwick, 1984). The two heterocyclic rings of (1), however, are twisted with respect to each other by a dihedral angle of  $45.6(1)^\circ$ . The distance

of 3.409 (1) Å between the two Cl atoms Cl16 and Cl17 corresponds to the theoretical sum of the van der Waals radii of Cl atoms (1.76 + 1.76 Å; Bondi, 1964). In order to reduce the loss of resonance caused by the torsion of the two heteroaromatic rings, each of the repelling Cl atoms is oppositely twisted out of the plane of the corresponding heterocycle [for oxazole, Cl16 is displaced by 0.06 (1) Å; for indole, Cl17 is displaced by 0.08 (1) Å]. The C—C bond distance of 1.445 (2) Å between C3 and C10 connecting the two heterocyclic systems indicates a certain degree of conjugation. The comparatively lower extent of torsion [45.6 (1)°] found in the dichloro-oxazolyindole (1) implies that the interplanar angle of 60° found in diazomamide A is attributable to both the repelling Cl atoms and the formation of the macrocyclic ring.

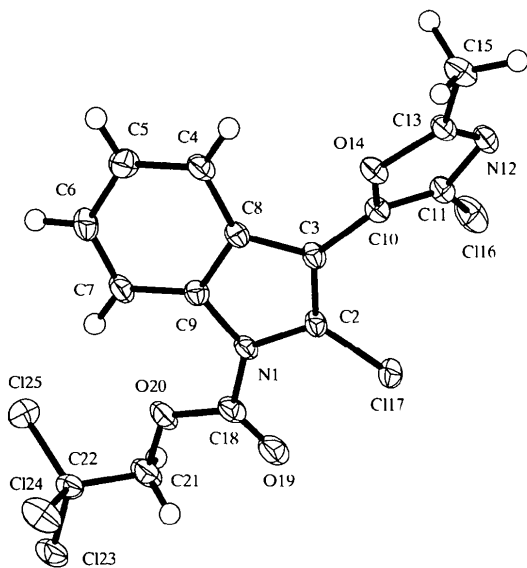


Fig. 1. The molecular structure of (1) showing 50% probability displacement ellipsoids.

## Experimental

A mixture of 2-chloro-3-cyanocarbonylindole-1-carboxylic acid 2,2,2-trichloroethyl ester (0.5 mmol) (Radspieler & Liebscher, 1997), acetaldehyde (1 mmol) and boron trifluoride–diethyl ether complex (1 mmol) was treated with gaseous hydrogen chloride. After 24 h of stirring, the solution was quenched with water, extracted and purified by column chromatography. Crystals [m.p. 401 (1) K] suitable for X-ray analysis were obtained from hexane–methylene chloride solution.

### Crystal data

C<sub>15</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>3</sub>  
M<sub>r</sub> = 442.49

Mo Kα radiation  
λ = 0.71073 Å

Monoclinic

P2<sub>1</sub>/c

a = 10.835 (2) Å

b = 20.834 (3) Å

c = 7.850 (2) Å

β = 103.00 (2)°

V = 1726.7 (6) Å<sup>3</sup>

Z = 4

D<sub>r</sub> = 1.702 Mg m<sup>-3</sup>

D<sub>m</sub> not measured

Cell parameters from 5000 reflections

θ = 1.94–24.2°

μ = 0.858 mm<sup>-1</sup>

T = 200 (2) K

Plate

0.48 × 0.38 × 0.20 mm

Colourless

### Data collection

Stoe IPDS diffractometer

Scans: φ rotation, φ increment = 1.4°, 157 exposures

Absorption correction:

numerical integration from crystal shape (XRED1.08; Stoe & Cie, 1997)

T<sub>min</sub> = 0.731, T<sub>max</sub> = 0.866

11 329 measured reflections

3163 independent reflections

2690 reflections with

I > 2σ(I)

R<sub>int</sub> = 0.033

θ<sub>max</sub> = 25.5°

h = -13 → 13

k = -25 → 25

l = -9 → 9

### Refinement

Refinement on F<sup>2</sup>

R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.029

wR(F<sup>2</sup>) = 0.078

S = 1.033

3161 reflections

262 parameters

All H atoms refined

w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0471P)<sup>2</sup> + 0.5240P]

where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3

(Δ/σ)<sub>max</sub> = 0.001

Δρ<sub>max</sub> = 0.581 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.346 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Data are 98.9% complete to a 2θ value of 51°. The program XSHAPE1.02 (Stoe & Cie, 1997) was applied for crystal optimization before a numerical absorption correction, implemented in XRED1.08 (Stoe & Cie, 1997). More than 200 strong reflections with four symmetry equivalents in each case were used for optimization. XSHAPE is based on the program HABITUS (Herrendorf, 1993)

Data collection: IPDS2.75 (Stoe & Cie, 1997). Cell refinement: IPDS2.75. Data reduction: IPDS2.75. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: XSTEP2.16 (Stoe & Cie, 1997). Software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1281). Services for accessing these data are described at the back of the journal.

## References

- Ambats, I. & Marsh, R. E. (1965). *Acta Cryst.* **19**, 942–948.  
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.  
Chadwick, D. J. (1984). *Comprehensive Heterocyclic Chemistry*, Vol. 4, edited by A. R. Katritzky & C. W. Rees, pp. 155–164. Oxford: Pergamon Press.

Herrendorf, W. (1993). PhD thesis, University of Karlsruhe, Germany.  
 Lindquist, N., Fencial, W., van Duynne, G. D. & Clardy, J. (1991). *J. Am. Chem. Soc.* **113**, 2303–2304.  
 Radspieler, A. & Liebscher, J. (1997). Unpublished results.  
 Secondo, P. M., Hester, C. A., Collier, H. L., Baughman, R. G. & Cordes, A. W. (1996). *Acta Cryst.* **C52**, 2882–2883.  
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.  
 Stoe & Cie (1997). Programs *IPDS2.75*, *XRED1.08*, *XSHAPE1.02* and *XSTEP2.16*. Stoe & Cie, Darmstadt, Germany.

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## Dinitrobenzoate Derivative of a Chiral Arylcyclopentane

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### Abstract

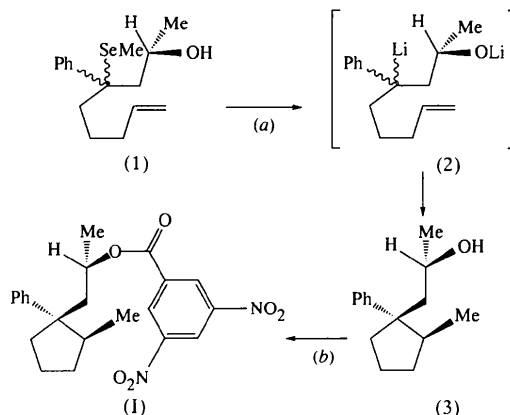
The structure of (2*S*)-1-[(1*S*,2*R*)-2-methyl-1-phenylcyclopentyl]-2-propyl 3,5-dinitrobenzoate, C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>, (I), has been determined and the observed conformation is discussed. The observed proximity of the phenyl and dinitrobenzoate moieties can be explained by intramolecular electrostatic forces. Compound (I) was synthesized by carbocyclization followed by acylation with 3,5-dinitrobenzoyl chloride.

### Comment

$\omega$ -Alkenylbenzylolithiums, readily available from the corresponding selenides and butyllithium, possess a very high propensity to cyclize in cyclopentyl-methyl-lithiums and to produce, after hydrolysis, 1-phenyl-2-methylcyclopentanes in high yield (Krief & Barbeaux, 1987). The control of the relative stereochemistry is very high; the cyclopentyl derivative possessing *cis* stereochemistry between the phenyl and methyl groups is obtained when the reaction is carried out in alkanes or in ether, whereas the *trans* stereoisomer is obtained in tetrahydrofuran. We have, therefore, studied the asymmetric version of this reaction (Krief & Bousbaa, 1996).

We have performed the carbocyclization reaction on the organolithium derivative (2) bearing a remote chi-

ral centre in a suitable position to promote diastereofacial differentiation. Using proper reaction conditions (reaction *a*), we were able to obtain compound (3) in high yield (90%) and in high diastereoisomeric ratio (82%). To establish unambiguously the stereochemistry of this major reaction product, the three-dimensional structure of its 3,5-dinitrobenzoate derivative, (I), obtained by reaction (*b*), was determined by single-crystal X-ray diffraction.



- (a) (i) 1.1 eq. MeLi–LiBr–ether, 293 K, 5 min;  
 (ii) 1.1 eq. *tert*-BuLi–pentane, ether, 253 K, 1 h;  
 (iii) MeOH, 253 K;  
 (b) Cl(CO)Ph(NO<sub>2</sub>)<sub>2</sub>, DMAP, pyridine, 298 K, 1 h.

The configuration of compound (I) (Fig. 1) is 1*S*,2*R*,7*S* because the stereochemistry of the C7 atom is known to be *S*. Indeed, compound (I) was derived from the enantiomerically pure compound (1), itself synthesized using 2(*S*)-propylene oxide (Krief & Bousbaa, 1996). The thermal agitation parameters of the carbonyl O2 atom and the atoms of the nitro groups (N1, N2, O3–O6) are very high; this situation is discussed in the *Experimental* section. The five-membered ring (C1–C5) is in an ‘envelope’ conformation, with the C2 atom pointing out of the plane defined by the four other atoms. However, the characteristic sequence of values of the corresponding torsion angles ( $\omega_1$ ,  $-\omega_1$ ,  $\omega_2$ , 0,  $-\omega_2$ ; Dunitz, 1979) is only fairly well observed (Table 1). In particular, there is a difference of 13° between the absolute values of torsion angles C2–C3–C4–C5 and C2–C1–C5–C4. This could be the result of steric interactions between the C6 and C15 atoms, linked in *cis* positions relative to the adjacent C1 and C2 atoms, respectively.

Despite the flexibility of the chain of atoms C1–C6–C7–O1, the phenyl and dinitrobenzoate substituents are close to each other; the distance between the centroids of the rings is 4.88 Å and the planes defined by the two cycles form an angle of 55.96(13) Å [this situation imposes a ‘*gauche*’ conformation on the C9–C1–C6–C7 and C1–C6–C7–O1 chains