The (1RS,2RS,7RS,8RS)- and (1RS,2SR,7SR,8RS)-diastereoisomers of 8,9,11,12-tetrachloro-N-ethyl-tricyclo[6.2.2.0²,⁷]dodeca-9,11-diene-1,10-dicarboximide

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Two racemic diastereoisomers, $C_{16}H_{15}Cl_4NO_2$, of the title 1,4-photoadduct of N-ethyltetrachlorophthalimide with cyclohexene have been isolated and their stereostructures determined.

Comment

The photochemistry of phthalimides has been studied extensively and has been reviewed by Kanaoka (1978), Coyle (1984) and Oelgemöller & Griesbeck (2002). Schwack (1987), Suau et al. (1989) and Kubo et al. (1989) have all reported the photoinduced para-cycloaddition of alkenes to various N-substituted phthalimides to yield products analogous to the title compounds. However, the spectroscopic methods used for product structure elucidation left the precise product stereochemistries unresolved. The stereochemistries of two related diastereomeric 1,4-cycloadducts, (I) and (II), formed by photoreaction of N-ethyl-3,4,5,6-tetrachlorophthalimide with cyclohexene, are reported here.
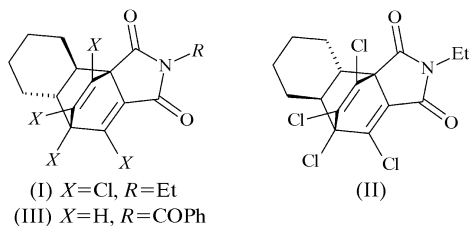
(I) X=Cl, R=Et
(III) X=H, R=COPh
(II)

Fig. 1 shows the (1R,2R,7R,8R)-enantiomer of the major photoadduct, (I), isolated from irradiation of N-ethyltetrachlorophthalimide in the presence of cyclohexene. The (1R,2S,7S,8R)-enantiomer of the minor photoadduct, (II), is shown in Fig. 2. Corresponding bond lengths and angles for (I) and (II) are generally similar, and most have values that are

typical of their types. Exceptions include the C9—C10—C14 angles of 135.5 (3) and 135.0 (2)° for (I) and (II), respectively. Also notable are the Cl1—C8 bonds of 1.768 (3) and 1.770 (2) Å in (I) and (II), respectively; these are significantly longer than the remaining C—Cl bonds, which range from 1.704 (2) to 1.714 (4) Å. While the distances to atoms Cl3 and Cl4 are typical of those in Cl—C≡C—Cl fragments, those to Cl2 are short for their type (mean value 1.734 Å; Allen et al., 1987). Those to Cl1, on the other hand, are typical of Cl—C(C)₂—C(C)₂—Cl bonds, but are much shorter than isolated Cl—C(C)₃ bonds.

From Figs. 1 and 2 it is clear that the difference between the isomers is the disposition of the H atoms at the stereogenic centres at C2 and C7. The torsion angles given in Table 3 confirm this. Also present in Table 3 are the corresponding values for N-benzoyltricyclododecadienedicarboximide, (III), in the same enantiomeric form as (I) and (II), whose structure has been described by McSweeney et al. (2005). Adduct (III), which is formed as a single diastereoisomer by the photoaddition of cyclohexene to N-benzoylphthalimide, is wholly analogous to (I) and (II), apart from the N-substituent and the absence of Cl atoms. The crystals of (I), (II) and (III) are all alike in being racemic with enantiomers that differ in the configurations at C1 and C8 in the product molecules. These differences arise because there are two equally probable choices for the 1,4-atom pair of the parent phthalimide at which addition to the cyclohexene can take place. The data in
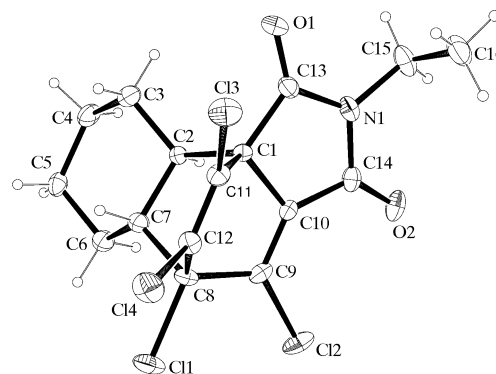

Figure 1
The molecule of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small circles of arbitrary radii.
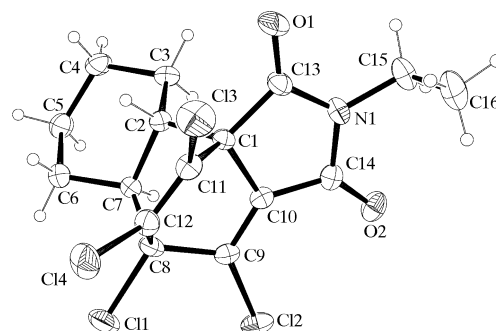

Figure 2
The molecule of (II). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small circles of arbitrary radii.

Table 3 correspond, therefore, for (I) and (II) to the molecule selected as the asymmetric unit, but for (III) to the enantiomer of the molecule selected as the asymmetric unit of the structure as described by McSweeney *et al.* (2005). The torsion angles about the C1—C2 and C7—C8 bonds clearly show the structural difference between diastereoisomers (I) and (II). These values also show that the isomeric form of (III) is the same as that of (I) and different from that of (II). The stereochemical relationship between (I) and (II) is also evident in the puckering parameters (Cremer & Pople, 1975) associated with the cyclohexane ring defined by atoms C2–C7. The parameters, with those for (II) in square brackets, are $Q = 0.575$ (4) Å [0.628 (3) Å], $\theta = 13.1$ (4)° [166.6 (3)°] and $\varphi = 337.3$ (16)° [151.6 (11)°]. In terms of θ and φ, these are related as required for inversion of the conformation of the ring consistent with the different configurations at C2 and C7 for the two diastereoisomers.

The packing of the molecules of (I) creates layers parallel to (100) and, for the choice of origin used in the refinement, centred on $x = 0$ (Fig. 3), within which the C6—H6···O2 hydrogen bonds (Table 1) create centrosymmetric dimers, such as that shown in the centre of the cell. Further short contacts [Cl3···O2iii; symmetry code: (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$] are found between the dimers and within the layer of molecules. In (II), the molecules are found in layers parallel to ($\bar{1}$02), interconnected as shown in Fig. 4 by the hydrogen bonds given in Table 2.

The racemic nature of (III) and of the isomers (I) and (II), a prerequisite for the refinement of the structures in centrosymmetric space groups, is a natural consequence of the manner in which the compounds have been formed by *para*-cycloaddition of achiral reactants. There are four possible racemic products, *viz.* two involving *trans* ring junctions across
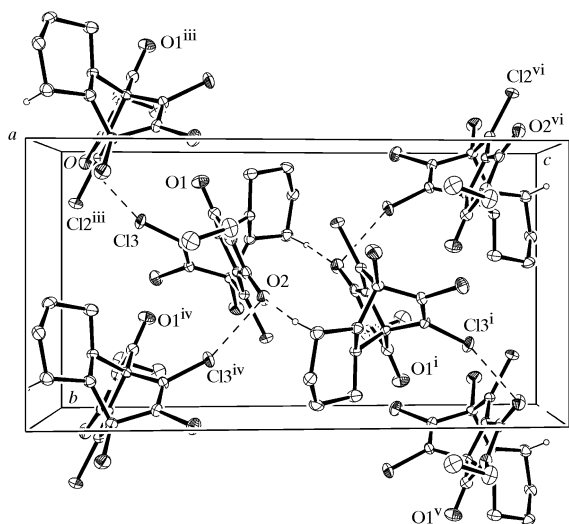
Figure 4
A layer of molecules of (II). Displacement ellipsoids are drawn at the 20% probability level and H atoms involved in C—H···O and C—H···Cl contacts (dashed lines) are shown as small circles of arbitrary radii. Selected atoms are labelled. [Symmetry codes: (ii) $-x, -y + 1, -z$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$; (viii) $x + 1, -y + \frac{3}{2}, z + \frac{1}{2}$; (ix) $-x + 2, -y + 1, -z + 1$.]

the C2—C7 bond and two involving *cis* junctions across the C2—C7 bond arising from 1,4-addition across the aromatic ring, which must of necessity be *cis*. Formation of a single unsymmetrical diastereoisomer from *N*-benzoylphthalimide suggests a favoured approach by the cyclohexene to the excited phthalimide, possibly involving minimization, in the transition state, of steric interactions between the *N*-benzoyl-imide ring and the cyclohexene. For *N*-ethyltetrachlorophthalimide, on the other hand, two diastereoisomers are formed, presumably reflecting lesser differentiation between the reaction pathways arising from the presence of the Cl atoms and the sterically less demanding ethyl group. The stereochemistry at the C2—C7 ring junction in both cases is the outcome of overall *trans* addition across the cyclohexene double bond.

Experimental

Irradiation through Pyrex for 15 h of a solution of *N*-ethyl-3,4,5,6-tetrachlorophthalimide (2.0 g, 6.4 mmol) and cyclohexene (27.2 g, 0.33 mol) in acetonitrile (300 ml) resulted in the formation of two products. After removal of solvents under vacuum, flash chromatography on silica gel, with diethyl ether–light petroleum (b.p. 313–333 K) (3:97 increased stepwise to 7:93) as eluant, yielded in order of recovery from the column: (i) unreacted *N*-ethyltetrachlorophthalimide (576 mg. 1.8 mmol), identified by comparison of its IR spectrum with that of a known sample; (ii) compound (I); (iii) compound (II). Compound (I) is a white crystalline solid [yield 510 mg, 28%; m.p. 443–445 K (from light petroleum, b.p. 333–353 K)]. Analysis found: C 48.1, H 3.7, N 3.2, Cl 36.2%; $C_{16}H_{15}Cl_4NO_2$ requires C 48.6, H 3.8, N 3.5, Cl 35.9%. λ_{max} (MeCN) 208 ($\varepsilon = 13\,758$ dm^3 mol^{-1} cm^{-1}) and 242 nm (15 539); ν_{max} 1768 and 1709 cm^{-1} (C=O); ^{1}H NMR (270 MHz, CDCl$_3$): δ 3.7 (2H, *q*, N–CH$_2$), 2.25 (lH, *m*), 0.8–2.1 (9H, complex multiplets), 1.2 (3H, *t*, Me); ^{13}C NMR (67.8 MHz, CDCl$_3$): δ 168.3, 162.2, 147.0, 133.0, 129.1, 125.6, 78.3, 58.4, 57.3, 51.7, 34.3, 29.3, 28.7, 27.0, 26.6, 13.4; *m/e*: 393 (M^+,

Figure 3
A layer of molecules of (I). Displacement ellipsoids are drawn at the 20% probability level and H atoms involved in C—H···O contacts (shorter dashed lines) are shown as small circles of arbitrary radii. The longer dashed lines represent short contacts mentioned in the *Comment*. Selected atoms are labelled. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $x, -y + \frac{3}{2}, z + \frac{1}{2}$; (vi) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.]
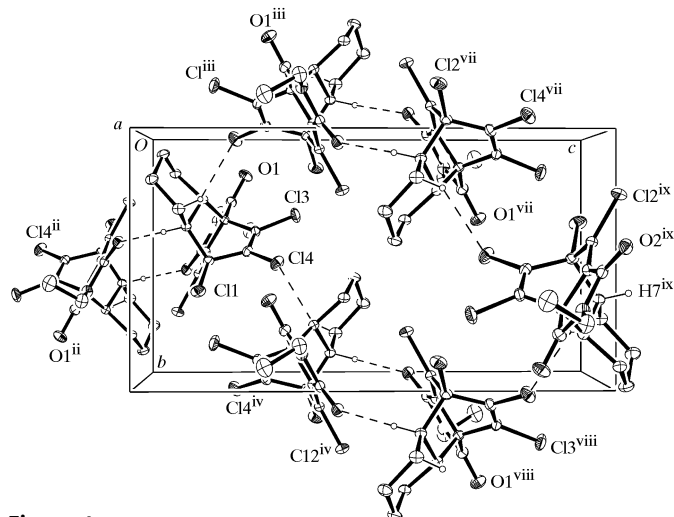
1%), 362 (18), 360 (54), 358 (55), 329 (37), 327 (77), 325 (59), 318 (10), 316 (33), 314 (65), 312 (52), 294 (12), 292 (340), 290 (36), 82 (70), 67 (l00), 69 (24), 54 (44), 41 (26). Compound (II) is a white crystalline solid [yield 277 mg, 15%; m.p. 431–432 K (from light petroleum, b.p. 333–353 K)]. Analysis found: C 49.3, H 3.9, N 3.3, Cl 33.4%; $C_{16}H_{15}Cl_4NO_2$ requires: C 48.6, H 3.8, N 3.5, Cl 35.9%. λ_{max} 207 (ε = 9344 $dm^3\ mol^{-1}\ cm^{-1}$) and 242 nm (11 844); ν_{max} 1769 and 1708 cm^{-1} (C=O), 1664 and 1587 cm^{-1} (C=C); ^{1}H NMR (270 MHz; CDCl₃): δ 3.7 (2H, q, J = 6 Hz, N–CH₂–), 2.2 (2H, m), 1.9 (2H, m), 1.6 (2H, m), 1.0–1.5 (4H, m), 1.2 (3H, t, J = 7 Hz, Me); ^{13}C NMR (67.8 MHz; CDCl₃): δ 168.1, 161.5, 139.0, 138.5, 135.1, 123.5, 78.5, 58.9, 58.8, 57.9, 53.4, 34.4, 29.2, 27.0, 26.9, 13.3; m/e: 393 (M^+, 3%), 362 (13), 360 (43), 358 (44), 329 (18), 327 (33), 325 (26), 318 (10), 316 (33), 314 (62), 312 (49), 294 (16), 292 (40), 290 (43), 82 (73), 69 (14), 67 (100), 54 (38), 41 (43).

Compound (I)

Crystal data

$C_{16}H_{15}Cl_4NO_2$
$M_r = 395.09$
Monoclinic, $P2_1/c$
$a = 10.705\ (17)$ Å
$b = 9.269\ (12)$ Å
$c = 17.53\ (3)$ Å
$\beta = 97.83\ (13)°$
$V = 1723\ (5)$ Å³
$Z = 4$

$D_x = 1.523$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
$\theta = 10.0–12.3°$
$\mu = 0.69$ mm⁻¹
$T = 298\ (2)$ K
Prism, colourless
$0.60 \times 0.32 \times 0.25$ mm

Data collection

Nicolet $P3$ four-circle diffractometer
θ–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.606$, $T_{max} = 0.841$
5280 measured reflections
5047 independent reflections
2697 reflections with $I > 2\sigma(I)$

$R_{int} = 0.036$
$\theta_{max} = 30.1°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 13$
$l = -24 \rightarrow 24$
2 standard reflections
every 50 reflections
intensity decay: 0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.159$
$S = 1.00$
5047 reflections
209 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.59$ e Å⁻³
$\Delta\rho_{min} = -0.27$ e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C6—H6B⋯O2^i	0.97	2.53	3.434 (7)	154

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

Compound (II)

Crystal data

$C_{16}H_{15}Cl_4NO_2$
$M_r = 395.09$
Monoclinic, $P2_1/c$
$a = 10.937\ (7)$ Å
$b = 9.228\ (4)$ Å
$c = 17.100\ (6)$ Å
$\beta = 94.83\ (4)°$
$V = 1719.7\ (15)$ Å³
$Z = 4$

$D_x = 1.526$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
$\theta = 11.1–13.2°$
$\mu = 0.70$ mm⁻¹
$T = 298\ (2)$ K
Block, colourless
$0.60 \times 0.60 \times 0.38$ mm

Data collection

Nicolet $P3$ four-circle diffractometer
θ–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.567$, $T_{max} = 0.768$
5269 measured reflections
5043 independent reflections
3191 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$

$\theta_{max} = 30.1°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 13$
$l = -24 \rightarrow 24$
2 standard reflections
every 50 reflections
intensity decay: 0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.134$
$S = 1.04$
5043 reflections
209 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0612P)^2 + 0.2253P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.63$ e Å⁻³
$\Delta\rho_{min} = -0.33$ e Å⁻³

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C7—H7⋯O2^{ii}	0.98	2.49	3.428 (3)	161
C6—H6A⋯Cl4^{iii}	0.97	2.81	3.669 (3)	147

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

Table 3
Selected torsion angles (°) for (I)–(III).

	(I)	(II)	(III)^a
C10—C1—C2—C3	−160.5 (3)	−85.4 (2)	−159.1 (4)
C11—C1—C2—C3	85.8 (4)	160.6 (2)	86.5 (4)
C13—C1—C2—C3	−48.9 (4)	31.3 (3)	−48.3 (5)
C10—C1—C2—C7	68.6 (3)	39.8 (2)	69.5 (3)
C11—C1—C2—C7	−45.1 (4)	−74.1 (2)	−44.9 (4)
C13—C1—C2—C7	−179.7 (3)	156.59 (19)	−179.7 (3)
C1—C2—C7—C6	−154.6 (3)	154.62 (19)	−155.5 (3)
C3—C2—C7—C6	67.8 (4)	−72.1 (2)	65.8 (4)
C1—C2—C7—C8	−16.6 (3)	22.7 (2)	−18.0 (4)
C3—C2—C7—C8	−154.1 (3)	155.98 (19)	−156.7 (3)
C2—C7—C8—C12	68.7 (3)	39.5 (2)	69.7 (4)
C6—C7—C8—C12	−159.6 (3)	−85.4 (3)	−158.8 (4)
C2—C7—C8—C9	−43.9 (3)	−73.4 (2)	−44.1 (4)
C6—C7—C8—C9	87.7 (4)	161.7 (2)	87.4 (4)

Note: (*a*) the values given are for the enantiomer of the molecule selected as the asymmetric unit of the racemic structure described by McSweeney *et al.* (2005).

In the final stages of refinement, H atoms were introduced in calculated positions, with C—H distances of 0.96, 0.97 and 0.98 Å for methyl, methylene and tertiary H atoms, respectively, and refined using a riding model with U_{iso}(H) values of $1.5U_{eq}$(C) for methyl H atoms and $1.2U_{eq}$(C) otherwise. The rotational orientation of the methyl groups was also refined.

For both compounds, data collection: *Nicolet P3 Software* (Nicolet, 1980); cell refinement: *Nicolet P3 Software*; data reduction: *RDNIC* (Howie, 1980); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); publication software: *SHELXL97* and *PLATON* (Spek, 2003).

organic compounds

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1384). Services for accessing these data are described at the back of the journal.

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