

4',5',6',7'-Tetrachlorospiro[cyclohex-2-ene-1,2'-indan]-1',3'-dione

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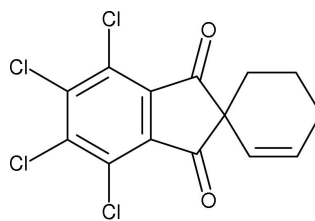
Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
Disorder in main residue
 R factor = 0.070
 wR factor = 0.198
Data-to-parameter ratio = 17.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

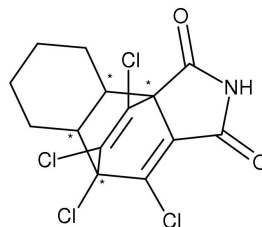
The title compound, $\text{C}_{14}\text{H}_8\text{Cl}_4\text{O}_2$, has been isolated following irradiation of a dichloromethane solution of *N*-acetyltetrachlorophthalimide and cyclohexene. The structure refinement is slightly compromised by the disorder over two positions of equal occupancy of a methylene group β to the spiro C atom.

Comment

The photochemistry of phthalimides has been extensively investigated over the past three decades and has yielded a rich diversity of molecular transformations, which have been reviewed by Kanaoka (1978), Coyle (1984) and Oelgemöller & Griesbeck (2002). Unsymmetrical 1,4-cycloaddition occurs across the benzo ring of *N*-benzoylphthalimide on irradiation in the presence of cyclohexene (McSweeney *et al.*, 2005), and similar 1,4-photocycloaddition occurs between *N*-ethyl-3,4,5,6-tetrachlorophthalimide and cyclohexene (Grimley *et al.*, 2005). The title compound, (I), and *rel*-(2*S*,7*R*)-8,9,11,12-tetrachlorotricyclo[6.2.2.0^{2,7}]dodeca-9,11-diene-1,10-dicarboximide, (II), are products of the photochemical reaction between *N*-acetyl-3,4,5,6-tetrachlorophthalimide, (III), and cyclohexene in dichloromethane. Compound (II) is simply a further example of a compound resulting from 1,4-cycloaddition but (I), the structure of which is presented here, is more unusual.



(I)



(II)

Formation of (I) most likely occurs *via* a sequence involving photoinitiated electron transfer/allylic proton transfer from cyclohexene to *N*-acetyltetrachlorophthalimide followed by radical coupling, to yield the corresponding cyclohexenyl carbinol. Subsequent thermal ring opening to give the corre-

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spending acyclic imido ketone, followed by enolization and ring closure with elimination of acetamide, would yield the observed dione (I).

The molecule of (I) is shown in Fig. 1. The majority of the bond lengths and angles are as expected for a molecule of this kind, but some data relating to particular features of the molecular geometry are given in Table 1.

In the course of refinement, the methylene group β to the spiro C atom was found to be disordered over two sites of equal occupancy, C13A and C13B. It is to this disorder, and possible limitations in modelling it, that the surprising variation in the length of the bonds to C13A and C13B and the unusual C13B–C14–C1 angle of $119.3(6)^\circ$ are attributed. Prolonged and ultimately wholly unsuccessful attempts were made to investigate an alternative model for the disorder in this part of the molecule, in which the entire cyclohexene ring was disordered over two orientations related by rotation through 180° about the vector between atoms C1 and C12. The relevant torsion angles in Table 1 show that atoms C13A and C13B each lie at the apex of a triangular flap which adopts two orientations, one tilted above and one below the plane of the other atoms in the cyclohexene ring. Other torsion angles in Table 1 reveal that the five-membered ring defined by C1–C3/C8/C9 is puckered, with pucker parameters (Cremer & Pople, 1975) of $Q_2 = 0.117(5) \text{ \AA}$ and $\varphi_2 = 348(2)^\circ$ corresponding most closely to a twist conformation with twist about the C9–C1 bond.

The packing of the molecules of (I) in the unit cell (Fig. 2) brings about overlap of the rings defined by atoms C3–C8 related in pairs by crystallographic centres of symmetry (symmetry code: $1 - x, 1 - y, 1 - z$), in which the distance between the ring centroids, the perpendicular distance between the rings and the lateral displacement or slippage of the rings are 3.983, 3.624 and 1.652 \AA , respectively. There are no other intermolecular contacts of any significance.

Experimental

Compound (I) was one of three products of the irradiation through Pyrex for 30 h of *N*-acetyl-3,4,5,6-tetrachlorophthalimide, (III), (3.08 g, 9.4 mmol) and cyclohexene (15.80 g, 192.7 mmol) in dichloromethane (300 ml). The solvents were removed under vacuum and the resulting mixture separated using a Chromatotron and a 4 mm plate. The eluent was a mixture of dichloromethane and light petroleum (b.p. 313–333 K) (2:98, increased stepwise to 60:40). This gave, in order of recovery from the plate, firstly compound (I), a yellow crystalline solid (15 mg, 5%), m.p. 401–404 K (from chloroform–light petroleum b.p. 363–373 K) [IR (ν_{max} , cm^{-1}): 2938 (aliphatic CH), 1749 (C=O), 1533 (C=C), 1284 and 1207; ^1H NMR (270 MHz, CDCl_3 , δ , p.p.m.): 6.3 (1H, *t* of *d*, $J = 9.9 \text{ Hz}$, $J = 7.7 \text{ Hz}$), 5.3 (1H, *d*, $J = 9.9 \text{ Hz}$) and 2.2–1.3 (6H, *m*, aliphatic H); ^{13}C NMR (CDCl_3 , δ , p.p.m.): 197.1 (carbonyl C) 142.0, 135.6, 135.1, 131.1, 119.8 (unsaturated C), 56.7 (quaternary C), 28.7, 23.9 and 17.7 (aliphatic C)], secondly a mixture of a minor product and (III) as a brown oil (25 mg), thirdly unreacted (III) (2.80 g, 8.6 mmol), identified by comparison of its IR spectrum with that of an authentic sample, and finally the 1,4-adduct, *rel*-(2*S*,7*R*)-8,9,11,12-tetrachlorotricyclo-[6.2.2.0^{2,7}]dodeca-9,11-diene-1,10-dicarboximide, (II), (46 mg, 15%).

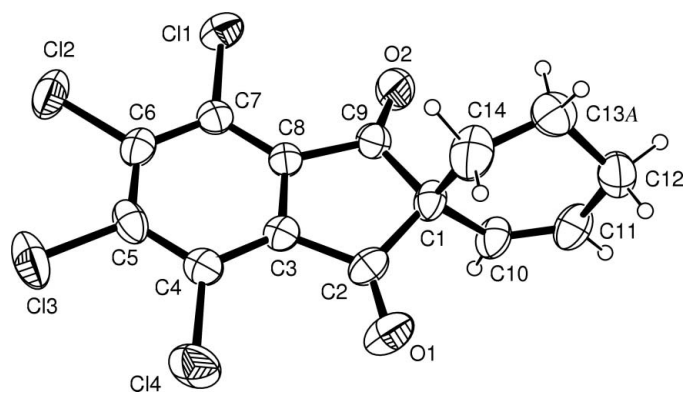


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small circles of arbitrary radii. The only component of the disorder noted elsewhere which is shown here is that which is compatible with C13A.

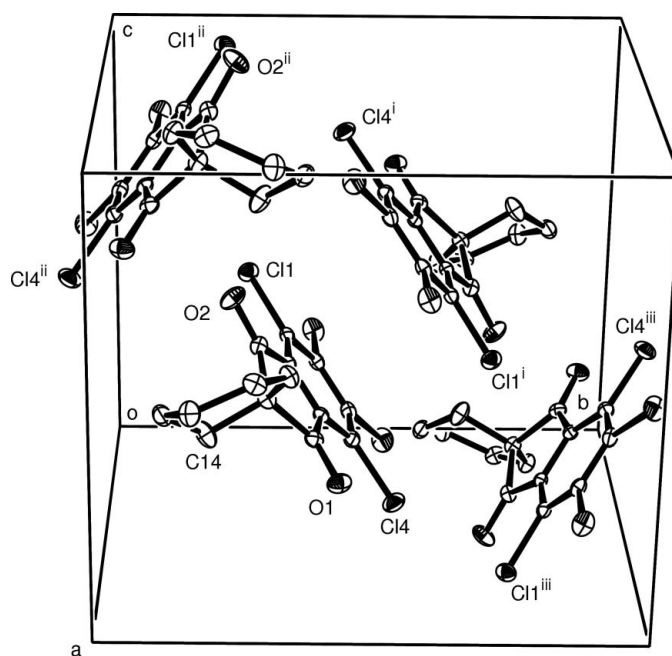


Figure 2
The unit-cell contents of (I). Displacement ellipsoids are drawn at the 10% probability level and H atoms have been omitted for clarity. Selected atoms are labelled. Atom C13A is the only representative of the disorder noted elsewhere which is shown here. [Symmetry codes (i) $1 - x, 1 - y, 1 - z$; (ii) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

Crystal data

$\text{C}_{14}\text{H}_8\text{Cl}_4\text{O}_2$
 $M_r = 350.00$
Monoclinic, $P2_1/c$
 $a = 10.707(6) \text{ \AA}$
 $b = 12.103(8) \text{ \AA}$
 $c = 10.800(6) \text{ \AA}$
 $\beta = 91.25(5)^\circ$
 $V = 1399.2(14) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.662 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
 $\theta = 7.7\text{--}10.6^\circ$
 $\mu = 0.84 \text{ mm}^{-1}$
 $T = 298(2) \text{ K}$
Block, yellow
 $0.60 \times 0.60 \times 0.20 \text{ mm}$

Data collection

Nicolet P3 four-circle diffractometer	1634 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$\theta_{\max} = 27.6^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 13$
$T_{\min} = 0.565$, $T_{\max} = 0.845$	$k = 0 \rightarrow 15$
3222 measured reflections	$l = -14 \rightarrow 14$
3222 independent reflections	2 standard reflections every 50 reflections
	intensity decay: none

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.070$	$w = 1/[\sigma^2(F_o^2) + (0.102P)^2]$
$wR(F^2) = 0.198$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{\max} < 0.001$
3222 reflections	$\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$
190 parameters	$\Delta\rho_{\min} = -0.31 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

C1–C10	1.521 (6)	C12–C13A	1.519 (8)
C1–C9	1.524 (6)	C12–C13B	1.495 (8)
C1–C14	1.525 (6)	C13A–C14	1.441 (8)
C1–C2	1.525 (6)	C13B–C14	1.449 (8)
C10–C1–C9	112.0 (4)	C14–C1–C2	108.4 (4)
C10–C1–C14	112.4 (4)	C14–C13A–C12	114.8 (7)
C9–C1–C14	108.0 (4)	C14–C13B–C12	115.8 (7)
C10–C1–C2	112.7 (4)	C13A–C14–C1	115.1 (6)
C9–C1–C2	102.8 (3)	C13B–C14–C1	119.3 (6)
C9–C1–C2–C3	–10.3 (4)	C1–C10–C11–C12	–2.4 (9)
C1–C2–C3–C8	5.1 (4)	C10–C11–C12–C13A	–16.1 (9)
C2–C3–C8–C9	2.8 (5)	C10–C11–C12–C13B	25.4 (9)
C3–C8–C9–C1	–9.6 (5)	C13A–C14–C1–C10	31.2 (8)
C8–C9–C1–C2	11.9 (4)	C13B–C14–C1–C10	–14.3 (9)
C14–C1–C10–C11	–4.3 (7)		

The atom of the cyclohexene ring β to the spiro atom, C1, is disordered over two sites of equal occupancy, C13A and C13B, which results in corresponding disorder and partial occupancy for the H atoms on these C atoms and also on the neighbouring atoms, C12 and C14. During refinement, bond distances involving C13A and C13B were restrained to 1.50 (1) \AA . H atoms were placed in calculated positions, taking full account of the disorder noted above, with C–H set to 0.93 and 0.97 \AA for alkene and methylene H atoms, respectively, and refined with a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ in all cases.

Data collection: *Nicolet P3 Software* (Nicolet, 1980); cell refinement: *Nicolet P3 Software*; data reduction: *RDNIC* (Howie, 1980); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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