

Acta Cryst. (1994). **C50**, 552–553

4,5:9,10-Dibenzo-1,7-dichloro-1,7-(14-chloromethanonitrilo)tetracyclo[5.5.2.-0^{2,6}.0^{8,12}]tetradec-13-ene, a 2:1 Diels–Alder Cycloaddition Product of Indene and 3,5,6-Trichloro-1,2,4-triazine

M. G. BARLOW, R. G. PRITCHARD, L. SIBOUS
AND A. E. TIPPING

*Department of Chemistry, University of Manchester
Institute of Science and Technology, PO Box 88,
Manchester M60 1QD, England*

(Received 10 May 1993; accepted 7 October 1993)

Abstract

The title molecule {alternative IUPAC names: 5,11,14-trichloro-4b,5,5a,10a,11,11a-hexahydro-10H-5,11-(methanonitrilo)indeno[2,1-*b*]fluorene or 1,11,22-trichloro-22-azahexacyclo[9.9.2.0^{2,10}.0^{3,8}.0^{12,20}.0^{14,19}]docosa-3(8),4,6,14(19),15,17,21-heptaene; C₂₁H₁₆Cl₃N} adopts a gull-wing shape and is orientated so that it is symmetric about a plane perpendicular to *c*. Both phenyl rings overlap those of neighbouring molecules *via* crystallographic inversion centres leading to π interactions, with nearest inter-ring C...C distances of 3.504 (8) and 3.795 (9) Å. As expected, the Cl—C bond to the *sp*² C atom is significantly shorter than those at the tetrahedral sites [1.729 (4) *cf* 1.809 (4) and 1.771 (4) Å].

Comment

The structure determination reported herein forms part of a more general investigation into Diels–Alder additions

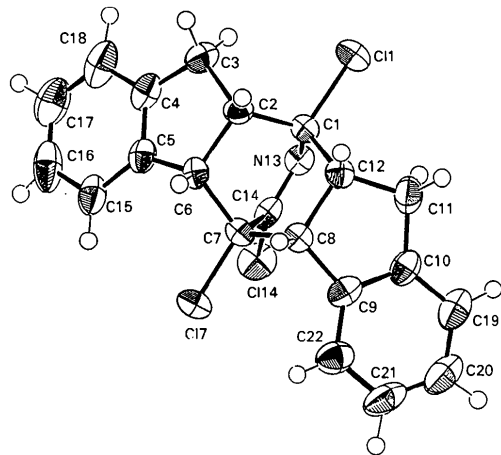
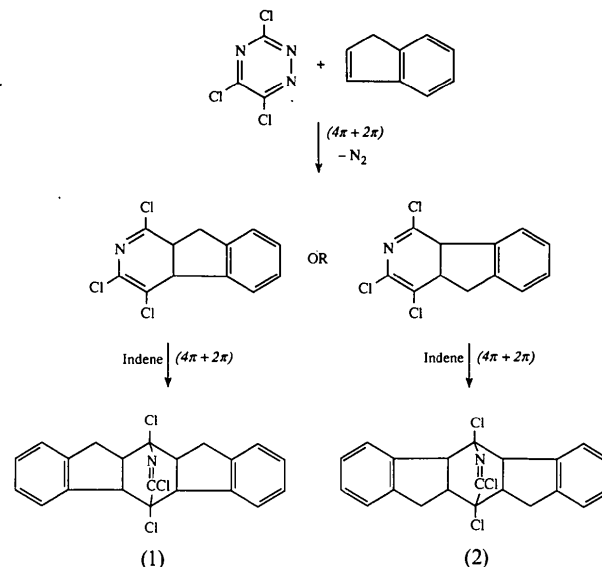


Fig. 1. The title molecule, including atomic numbering scheme, drawn using ORTEPII (Johnson, 1976).

of mono- and di-olefins to trichloro-1,2,4-triazine. In contrast to the reactions of other mono-olefins reported previously, where a second addition occurs to only a limited extent (Barlow, Haszeldine & Simpkin, 1982), the title compound (1), the only product detected, results from two regioselective additions to indene (see below). The ¹H and ¹³C NMR data showed that the product was a symmetrical 2:1 adduct, but did not allow unequivocal differentiation between the two possible structures (1) and (2).



Experimental

A mixture of 3,5,6-trichloro-1,2,4-triazine (1.40 g, 7.6 mmol) and indene (6.12 g, 52.7 mmol) was sealed *in vacuo* in a Rotaflo tube (*ca* 50 ml) and heated at 343 K for 2 d. The volatile product was identified as nitrogen (0.14 g, 5.0 mmol, 70%) and the remaining material (7.32 g) was washed from the tube with dichloromethane and the solvent was then removed *in vacuo*. The residue was treated with diethyl ether (3 × 20 ml) and filtered. Removal of the solvent from the filtrate gave material (5.10 g) which was shown (IR) to be mainly unchanged indene; recrystallization of the precipitate (2.20 g) from chloroform gave the title compound (1) (2.06 g, 5.3 mmol, 70%; analysis found C 64.6, H 4.9, N 3.6, Cl 27.7%, *M*⁺ 387/389/391/393; analysis calculated for C₂₁H₁₆NCl₃ C 64.9, H 4.1, N 3.6, Cl 27.4%, *M* 387/389/391/393) as white crystals, m.p. 523–527 K.

Crystal data

C₂₁H₁₆Cl₃N
*M*_r = 388.72
Monoclinic
*P*2₁/*n*
a = 8.637 (2) Å
b = 14.976 (3) Å
c = 13.714 (3) Å
 β = 94.39 (2)°
V = 1768 (1) Å³
Z = 4

*D*_x = 1.460 Mg m⁻³
Mo K α radiation
 λ = 0.71069 Å
Cell parameters from 23 reflections
 θ = 20.53–34.77°
 μ = 0.5220 mm⁻¹
T = 296 K
Fragment
0.35 × 0.25 × 0.20 mm
Colourless

Data collection

AFC-6S diffractometer	$\theta_{\max} = 24.97^\circ$
$\omega/2\theta$ scans	$h = 0 \rightarrow 10$
Absorption correction:	$k = 0 \rightarrow 17$
not applied	$l = -16 \rightarrow 16$
3649 measured reflections	3 standard reflections
3649 independent reflections	monitored every 150
1786 observed reflections	reflections
$[I > 3\sigma(I)]$	intensity variation: none

Refinement

Refinement on F	$(\Delta/\sigma)_{\max} = 0.0003$
$R = 0.0443$	$\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$
$wR = 0.0494$	$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
$S = 1.627$	Extinction correction: not applied
1786 reflections	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
291 parameters	
All H-atom parameters refined	
Weighting scheme based on measured e.s.d.'s	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U_{eq}
C11	1.0108 (1)	0.47234 (10)	0.28143 (10)	0.0589
C17	0.3397 (1)	0.35103 (9)	0.21595 (9)	0.0500
C114	0.6096 (2)	0.20949 (7)	0.23810 (9)	0.0539
N13	0.7972 (4)	0.3454 (2)	0.2547 (2)	0.0360
C1	0.8075 (5)	0.4431 (3)	0.2621 (3)	0.0365
C2	0.7390 (5)	0.4873 (3)	0.1681 (3)	0.0355
C3	0.8260 (6)	0.4707 (4)	0.0758 (4)	0.0547
C4	0.7207 (6)	0.4149 (3)	0.0115 (3)	0.0466
C5	0.5796 (5)	0.4009 (3)	0.0499 (3)	0.0388
C6	0.5716 (5)	0.4498 (3)	0.1463 (3)	0.0308
C7	0.5320 (5)	0.3919 (3)	0.2352 (3)	0.0334
C8	0.5512 (5)	0.4479 (3)	0.3320 (3)	0.0318
C9	0.5184 (6)	0.3960 (3)	0.4227 (3)	0.0401
C10	0.6513 (6)	0.3866 (3)	0.4854 (3)	0.0432
C11	0.7873 (7)	0.4331 (4)	0.4481 (3)	0.0483
C12	0.7256 (5)	0.4745 (3)	0.3490 (3)	0.0349
C14	0.6566 (5)	0.3217 (3)	0.2439 (3)	0.0324
C15	0.4664 (7)	0.3501 (3)	-0.0020 (4)	0.0526
C16	0.503 (1)	0.3127 (4)	-0.0914 (4)	0.0692
C17	0.6441 (9)	0.3290 (4)	-0.1280 (4)	0.0697
C18	0.7529 (8)	0.3793 (4)	-0.0776 (4)	0.0664
C19	0.6473 (8)	0.3392 (4)	0.5724 (4)	0.0615
C20	0.5093 (9)	0.3030 (4)	0.5955 (4)	0.0683
C21	0.3763 (9)	0.3146 (4)	0.5364 (4)	0.0674
C22	0.3787 (7)	0.3624 (4)	0.4493 (4)	0.0533

Table 2. Selected geometric parameters (\AA , $^\circ$)

C11—C1	1.809 (4)	C1—C12	1.507 (6)
C17—C7	1.771 (4)	C2—C6	1.559 (6)
C114—C14	1.729 (4)	C6—C7	1.557 (6)
N13—C1	1.468 (6)	C7—C8	1.568 (6)
N13—C14	1.263 (6)	C7—C14	1.503 (6)
C1—C2	1.528 (6)	C8—C12	1.558 (6)
N13—C1—C2	110.9 (3)	C6—C7—C14	104.6 (3)
N13—C1—C12	109.6 (4)	C8—C7—C14	106.2 (3)
C2—C1—C12	110.9 (4)	C114—C14—N13	120.0 (3)
C6—C7—C8	110.5 (3)	C114—C14—C7	120.8 (3)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduc-

tion: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN, MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *CSSR* (1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71722 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1062]

References

- Barlow, M. G., Haszeldine, R. N. & Simpkin, D. J. (1982). *J. Chem. Soc. Perkin Trans. 1*, pp. 1245–1249.
- CSSR (1984). *Crystal Structure Search and Retrieval Instruction Manual*. SERC Daresbury Laboratory, Warrington, England.
- Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Acta Cryst. (1994). **C50**, 553–556

exo,exo-4,4,12,12,16,16-Hexakis(trifluoromethyl)-17-(3,3,3-trifluoro-2-trifluoromethyl-1-azapropenyl)-3,11,17-triazaheptacyclo[12.4.1.1^{6,9}.0^{2,13}.0^{3,11}.0^{5,10}.0^{15,18}]-icos-7-ene Formed via Novel 1,3-Dipolar Cycloaddition to Quadricyclane

M. G. BARLOW, R. G. PRITCHARD, N. S. SULIMAN AND A. E. TIPPING

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

(Received 30 April 1993; accepted 24 August 1993)

Abstract

The title compound, $\text{C}_{26}\text{H}_{16}\text{F}_{24}\text{N}_4$, crystallizes as a racemic mixture with two crystallographically independent molecules in the asymmetric unit, which differ only slightly in conformation. In both cases, the central diazo region bears a close resemblance to the struc-