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Three Polyhalogenated Tricyclo[5.1.0.0^{3,5}]-octane Compounds

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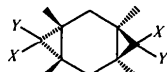
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Abstract

The structures of three new polyhalogenated tricyclo[5.1.0.0^{3,5}]octane derivatives, 4,4,8,8-tetrachloro-, 4,4,8,8-tetrabromo- and 4,8-dibromo-1,3,5,7-tetramethyl-*cis-transoid-cis*-tricyclo[5.1.0.0^{3,5}]octane, C₁₂H₁₆Cl₄, C₁₂H₁₆Br₄ and C₁₂H₁₈Br₂, respectively, are presented. The most remarkable geometric feature of these materials is the planarity of the cyclohexyl ring. The molecular conformation is similar for all three compounds with the cyclopropyl groups *anti*. All three molecules lie around crystallographic inversion centers.

Comment

The cyclohexyl rings are planar for all three compounds, 4,4,8,8-tetrachloro-, (1), 4,4,8,8-tetrabromo-, (2), and 4,8-dibromo-1,3,5,7-tetramethyl-*cis-transoid-cis*-tricyclo[5.1.0.0^{3,5}]octane, (3), with a maximum deviation from planarity of no more than 0.003 Å for any atom in the ring. The planarity of the cyclohexyl ring is accompanied by the expansion of the internal C—C—C angles, which are all close to 120°. The orientations of the cyclopropyl groups with respect to the cyclohexyl ring are similar. The dihedral angles between these groups are 105.8 (1) and 106.9 (4)° for (1) and (2), respectively. The dihedral angle is slightly larger for (3) at 108.2 (2)°.



- (1) X = Y = Cl
(2) X = Y = Br
(3) X = Br, Y = H

The structural results of this work allow an interesting comparison with those obtained for the related 4,4,8,8-tetrafluorotricyclo[5.1.0.0^{3,5}]octanes (Dolbier, Gdaniec, Gomulka, Jaskolski & Koroniak, 1984; Dolbier, Gdaniec, Jaskolski & Koroniak, 1986). In the tetrafluoro derivatives, both *syn* and *anti* structures were reported. In the *anti* structure (Dolbier *et al.*, 1984),

the cyclohexyl ring has a boat conformation with a dihedral angle of 47.3° between the planes defined by atoms C3, C2, C4 and C3' and atoms C3', C2', C4' and C3, using the numbering system employed here. Two other structures with the tricyclo[5.1.0.0^{3,5}]octane framework have been reported and both have the cyclopropyl groups *anti*. In (–)-8 α -hydroxymethyl-1 β ,4,4-trimethyltricyclo[5.1.0.0^{3,5}]octane, the cyclohexyl ring is in a shallow boat conformation with a dihedral angle of 13.8° (Cocker, Cunningham, Geraghty, Higgins & McArdle, 1984). For *anti*-8,8-dibromo-1,4,4-trimethyltricyclo[5.1.0.0^{3,5}]octane, which crystallizes with *Z'* = 3, the dihedral angles range from 0.6–

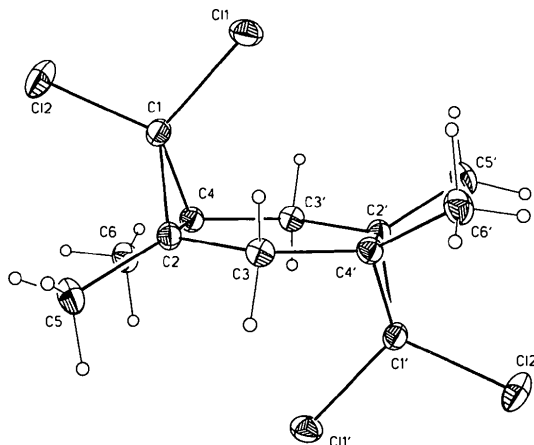


Fig. 1. Displacement-ellipsoid plot of (1) showing the atom-labelling scheme. Displacement ellipsoids are scaled to the 30% probability level. H atoms are drawn as spheres of arbitrary radii. The molecule lies around a crystallographic inversion center at $\frac{1}{2}, \frac{1}{2}, 0$. Atoms labeled with ' are related by $1 - x, 1 - y, -z$.

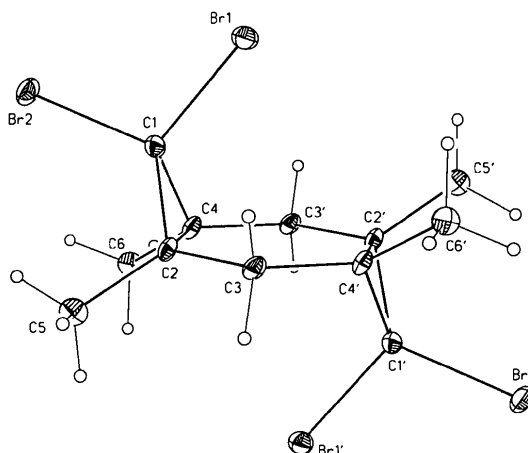


Fig. 2. Displacement-ellipsoid plot of (2) showing the atom-labelling scheme. Displacement ellipsoids are scaled to the 30% probability level. H atoms are drawn as spheres of arbitrary radii. The molecule lies around a crystallographic inversion center at $\frac{1}{2}, 0, \frac{1}{2}$. Atoms labeled with ' are related by $1 - x, -y, 1 - z$.

6.1° (Reck, 1970). The geometry of the cyclopropyl group was shown to be distorted upon fluoro substitution. The C—C bonds of the *gem*-difluoro C atom were substantially shorter than that of the remaining C—C bond of the three-membered ring [averages 1.450 (3) and 1.546 (4) Å, respectively]. The differences in this study are less dramatic. The largest difference (0.031 Å) is found in the tetrachloro derivative, (1).

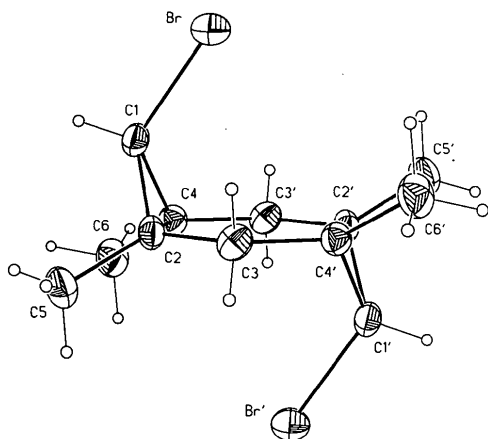


Fig. 3. Displacement-ellipsoid plot of (3) showing the atom-labelling scheme. Displacement ellipsoids are scaled to the 30% probability level. H atoms are drawn as spheres of arbitrary radii. The molecule lies around a crystallographic inversion center at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Atom labeled with ' are related by $1-x, 1-y, 1-z$.

Experimental

Compounds (1) and (2) were prepared by the simultaneous addition of two dihalocarbenes to 1,2,4,5-tetramethyl-1,4-cyclohexadiene using a phase-transfer catalyst (Adogen 464) (Banwell & Halton, 1979*a,b,c*). Compound (3) was prepared by selective reduction of the analogous tetrabromo compound using tri(*n*-butyl)SnH in hexane at 313 K. Previous attempts to partially reduce similar materials resulted in either mixed isomers or the completely reduced species along with starting materials (Banwell & Halton, 1979*a,b,c*). Colorless crystals were grown by slow evaporation from CHCl₃ for all samples.

Compound (1)

Crystal data

C₁₂H₁₆Cl₄
M_r = 302.07
 Monoclinic
*P*2₁/*c*
a = 6.436 (4) Å
b = 6.954 (3) Å
c = 14.850 (9) Å
 β = 100.33 (5)°
V = 653.9 (6) Å³
Z = 2
D_x = 1.53 Mg m⁻³

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 16 reflections
 θ = 6.3–10.1°
 μ = 0.8806 mm⁻¹
T = 193 K
 Plate
 0.38 × 0.38 × 0.15 mm
 Colorless

Data collection

Nicolet R3 diffractometer
 ω scans (width 1.2°; rate 5–10° min⁻¹)
 Absorption correction: refined from ΔF (XABS; Sheldrick, 1991)
 T_{\min} = 0.81, T_{\max} = 1.37
 2446 measured reflections
 1164 independent reflections
 1058 observed reflections
 $[F > 4.0\sigma(F)]$

Refinement

Refinement on *F*
R = 0.0243
wR = 0.0333
S = 1.361
 1058 reflections
 106 parameters
 All H-atom parameters refined
 $w = 1/[\sigma^2(F) + 0.0004F^2]$
 $(\Delta/\sigma)_{\max}$ = 0.002
 $\Delta\rho_{\max}$ = 0.33 e Å⁻³
 $\Delta\rho_{\min}$ = -0.17 e Å⁻³

Compound (2)

Crystal data

C₁₂H₁₆Br₄
M_r = 479.87
 Monoclinic
*C*2/*c*
a = 17.177 (9) Å
b = 6.426 (2) Å
c = 14.516 (4) Å
 β = 120.74 (3)°
V = 1377.1 (10) Å³
Z = 4
D_x = 2.31 Mg m⁻³

Data collection

Nicolet R3 diffractometer
 ω scans (width 1.2°; rate 6–12° min⁻¹)
 Absorption correction: analytical
 T_{\min} = 0.082, T_{\max} = 0.210
 3477 measured reflections
 1600 independent reflections
 1132 observed reflections
 $[F > 4.0\sigma(F)]$

Refinement

Refinement on *F*
R = 0.0387
wR = 0.0391
S = 1.126
 1132 reflections
 83 parameters

R_{int} = 0.011
 θ_{\max} = 25°
 $h = 0 \rightarrow 7$
 $k = -8 \rightarrow 8$
 $l = -17 \rightarrow 17$
 2 standard reflections monitored every 98 reflections
 intensity variation: 1.3%

Extinction correction: modified Larson (1982); SHELXTL-Plus (Sheldrick, 1991)
 Extinction coefficient: $6.2(2) \times 10^{-5}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Mo *K*α radiation
 λ = 0.71073 Å
 Cell parameters from 37 reflections
 θ = 8.2–11.6°
 μ = 11.55 mm⁻¹
T = 173 K
 Block
 0.17 × 0.27 × 0.30 mm
 Colorless

R_{int} = 0.026
 θ_{\max} = 27.5°
 $h = -22 \rightarrow 22$
 $k = 0 \rightarrow 8$
 $l = -18 \rightarrow 18$
 4 standard reflections monitored every 96 reflections
 intensity variation: 1%

Extinction correction: modified Larson (1982); SHELXTL-Plus (Sheldrick, 1991)
 Extinction coefficient: $3.8(6) \times 10^{-7}$

H-atom parameters not refined
 $w = 1/[\sigma^2(F) + 0.0004F^2]$
 $(\Delta/\sigma)_{\max} = 0.07$
 $\Delta\rho_{\max} = 1.50 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.69 \text{ e } \text{Å}^{-3}$

Compound (3)*Crystal data*C₁₂H₁₈Br₂M_r = 322.08

Monoclinic

P2₁/c

a = 6.430 (2) Å

b = 13.437 (4) Å

c = 7.804 (2) Å

β = 113.55 (2)°

V = 618.2 (3) Å³

Z = 2

D_x = 1.73 Mg m⁻³*Data collection*

Nicolet R3 diffractometer

ω scans (width 1.2°; rate 5–10° min⁻¹)

Absorption correction: analytical

T_{min} = 0.152, T_{max} = 0.231

3124 measured reflections

1431 independent reflections

874 observed reflections

[F > 4.0σ(F)]

Refinement

Refinement on F

R = 0.0346

wR = 0.0346

S = 1.025

874 reflections

100 parameters

All H-atom parameters refined

 $w = 1/[\sigma^2(F) + 0.0004F^2]$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 20 reflections

θ = 4.1–11.6°

μ = 6.457 mm⁻¹

T = 298 K

Block

0.44 × 0.31 × 0.27 mm

Colorless

R_{int} = 0.041θ_{max} = 27.5°

h = -8 → 7

k = 0 → 17

l = 0 → 10

4 standard reflections monitored every 96 reflections

intensity variation: 6%

 $(\Delta/\sigma)_{\max} = 0.003$ $\Delta\rho_{\max} = 0.36 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.66 \text{ e } \text{Å}^{-3}$

Extinction correction: none

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

C2	0.4487 (3)	0.1695 (9)	0.5191 (4)	0.015 (2)
C3	0.5489 (3)	0.2024 (10)	0.5581 (4)	0.016 (2)
C4	0.4000 (3)	-0.0317 (9)	0.4607 (4)	0.015 (2)
C5	0.4219 (4)	0.2739 (10)	0.5919 (4)	0.021 (2)
C6	0.3266 (4)	-0.1212 (10)	0.4780 (5)	0.019 (2)
(3)				
Br	0.13627 (7)	0.59033 (3)	0.18891 (5)	0.0523 (2)
C1	0.3094 (7)	0.6329 (3)	0.4412 (5)	0.0390 (15)
C2	0.5584 (6)	0.6094 (2)	0.5370 (5)	0.0350 (14)
C3	0.6687 (7)	0.5480 (3)	0.4342 (6)	0.039 (2)
C4	0.3883 (6)	0.5607 (3)	0.6024 (5)	0.0348 (14)
C5	0.7090 (10)	0.6927 (4)	0.6490 (8)	0.053 (2)
C6	0.3723 (9)	0.5970 (4)	0.7806 (6)	0.053 (2)

Table 2. Geometric parameters (Å, °)

X = C11 and Y = C12 for (1), X = Br1 and Y = Br2 for (2), and X = Br and Y = H for (3).

	(1)	(2)	(3)
C1—X	1.763 (2)	1.932 (7)	1.921 (3)
C1—Y	1.763 (2)	1.925 (6)	—
C2—C1	1.506 (2)	1.515 (7)	1.505 (5)
C4—C1	1.511 (2)	1.517 (8)	1.507 (5)
C3—C2	1.519 (2)	1.527 (8)	1.511 (7)
C4—C2	1.539 (2)	1.537 (8)	1.526 (6)
C5—C2	1.513 (3)	1.508 (10)	1.509 (6)
C6—C4	1.513 (2)	1.519 (10)	1.516 (7)
C4 ¹ —C3	1.517 (2)	1.515 (9)	1.506 (5)
C2—C1—X	119.01 (11)	120.2 (4)	120.8 (3)
C2—C1—Y	120.57 (12)	121.0 (5)	—
C4—C1—X	119.42 (11)	118.7 (5)	121.9 (3)
C4—C1—Y	120.13 (10)	121.3 (5)	—
X—C1—Y	109.44 (9)	108.4 (3)	—
C3—C2—C4	120.27 (13)	120.8 (5)	119.7 (3)
C3—C2—C5	111.88 (14)	111.6 (4)	112.5 (4)
C3—C2—C1	117.19 (13)	118.1 (6)	118.9 (3)
C4—C2—C5	119.85 (13)	119.1 (6)	120.3 (4)
C2—C1—C4	61.36 (10)	60.9 (4)	60.9 (2)
C4—C2—C1	59.49 (10)	59.6 (4)	59.6 (3)
C1—C4—C2	59.14 (10)	59.4 (3)	59.5 (2)
C5—C2—C1	118.90 (13)	118.7 (5)	116.2 (3)
C6—C4—C1	118.78 (12)	119.0 (5)	115.8 (3)
C6—C4—C2	119.28 (14)	119.4 (6)	119.3 (3)
C4 ¹ —C3—C2	119.11 (13)	118.7 (5)	120.0 (4)
C3 ¹ —C4—C6	112.00 (13)	111.2 (5)	112.7 (4)
C3 ¹ —C4—C1	117.59 (13)	118.6 (6)	119.4 (3)
C3 ¹ —C4—C2	120.62 (12)	120.4 (5)	120.3 (4)

Symmetry code (i) is 1 - x, 1 - y, -z for (1), 1 - x, -y, 1 - z for (2) and 1 - x, 1 - y, 1 - z for (3).

Data collection and cell refinement: Siemens P3/V Data Collection Software, version 4.1 (Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA). Data reduction, structure solution, structure refinement and molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *FUER* (Larson, 1982); *MPLN* (Cordes, 1982).

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U _{eq}
(1)				
C11	0.32561 (6)	0.19240 (6)	0.06276 (3)	0.0294 (2)
C12	0.14379 (7)	0.11237 (6)	-0.12506 (3)	0.0366 (2)
C1	0.3062 (2)	0.2716 (2)	-0.05125 (10)	0.0223 (4)
C2	0.4956 (2)	0.3634 (2)	-0.08022 (10)	0.0205 (4)
C3	0.6954 (2)	0.3786 (2)	-0.00859 (11)	0.0212 (5)
C4	0.3002 (2)	0.4847 (2)	-0.07138 (10)	0.0201 (4)
C5	0.5435 (3)	0.3178 (3)	-0.17398 (12)	0.0303 (6)
C6	0.1584 (3)	0.5568 (3)	-0.15708 (11)	0.0279 (5)
(2)				
Br1	0.42507 (4)	0.20030 (11)	0.30040 (4)	0.0207 (3)
Br2	0.26750 (4)	0.31189 (11)	0.34034 (4)	0.0226 (3)
C1	0.3821 (3)	0.1710 (10)	0.3995 (4)	0.016 (2)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Methoxy-3-methyl-4'-nitrostilbene, C₁₆H₁₅NO₃

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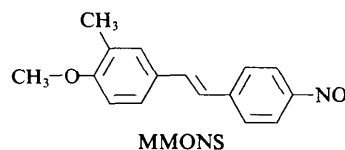
Abstract

The molecule is planar to within 0.2 Å with a C(4)—C(7)—C(8)—C(9) torsion angle of $-179(2)^\circ$. The charge-transfer axis lies along the line joining the N atom at one end of the molecule to the O atom at the other. The final crystal structure is the result of complicated interplay between the short-range van der Waals interactions and the long-range dipole–

dipole interactions, making the crystal highly polarized.

Comment

The considerable potential of organic non-linear optical materials for optical-device applications is now well established (Chemla & Zyss, 1987). 4-Methoxy-3-methyl-4'-nitrostilbene (MMONS) shows one of the largest powder second harmonic generation (SHG) signals ($1250 \times$ urea) (Tam, Guerin, Calabrese & Stevenson, 1989; Bierlein, Cheng, Wang & Tam, 1990). It is a typical organic material in which van der Waals interactions and permanent dipole–dipole interactions are responsible for the intermolecular binding. This results in relatively low melting points and high vapour pressure. In order to understand the basic non-linear optical, thermal and mechanical properties, we carried out the X-ray structure analysis of MMONS.



MMONS was synthesized by the Wittig reaction of diethyl *p*-nitrobenzylphosphonate and 3-methyl-*p*-anisaldehyde. The product was checked and confirmed by ¹H NMR and high-resolution mass spectra. The material was recrystallized from methyl ethyl ketone (MEK) solution and was purified further using liquid column chromatography. The sample crystal was grown by slow evaporation of MEK at room temperature.

Fig. 1 is an ORTEP (Johnson, 1971) view of the molecule showing the atom-numbering scheme. The bond lengths O(3)—C(12) [1.351 (7) Å], O(3)—C(16) [1.413 (9) Å] and C(11)—C(15) [1.513 (10) Å] are in good agreement with the comparable bonds in 9-methoxy-11-dimethylellipticine [1.366 (4), 1.427 (7) and 1.505 (5) Å (Gansser, Viel, Mauguen & Tsoucaris, 1988)]. The mean N—O bond length of 1.22 Å for the nitro groups shows that their bond order is 1.5.

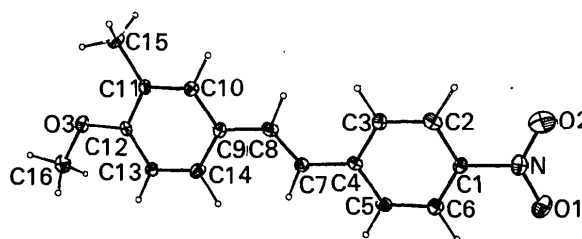


Fig. 1. Molecular structure of MMONS showing atom-numbering scheme. H atoms are drawn as circles of arbitrary radii.