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Structure of a Cyclopropachromene

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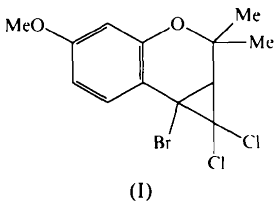
Abstract

The tricyclic molecule 3a-bromo-3,3-dichloro-2a,3a-dihydro-6-methoxy-2,2-dimethyl-2*H*,3*H*-cyclopropa[2,3-*c*]chromene, $C_{13}H_{13}BrCl_2O_2$, has a pyran ring fused to both a benzene ring and a cyclopropane ring, constraining the degree of puckering so that only two C atoms lie markedly out of the mean plane of the other atoms. The cyclopropane ring is positioned pseudo-axially relative to the pyran ring.

Comment

The title compound (I) was prepared in order to compare its ease of Ag-ion-assisted solvolysis with that of the corresponding trichloro compound (which has a Cl in place of the Br atom). The comparison of the two reactions served to demonstrate the probable mechanism of solvolysis (Brown & Islam, 1987; Brown, Clegg, Islam & Steele, 1990).



(I)

Although the chroman and chromene ring systems are constituents of the molecules of many natural products and pharmaceutical substances, whose crystal structures have been reported widely, cyclopropa[*c*]chromene derivatives have not been documented previously.

The conformation of the pyran ring is constrained by the fused benzene and cyclopropane rings, imposing small ring torsion angles about the C4a—C8a and C3—C4 bonds (−3.3 and −6.7°, respectively). Thus, with reference to the mean plane of the atoms O1, C8a, C4a and C4 (r.m.s. Δ = 0.010 Å), C3 lies only 0.246 Å out of the plane, compared with 0.602 Å for C2. The cyclopropane ring is positioned pseudo-axially, with the Br atom and the H atom attached to C3 occupying pseudo-equatorial sites on the pyran ring (Fig. 1).

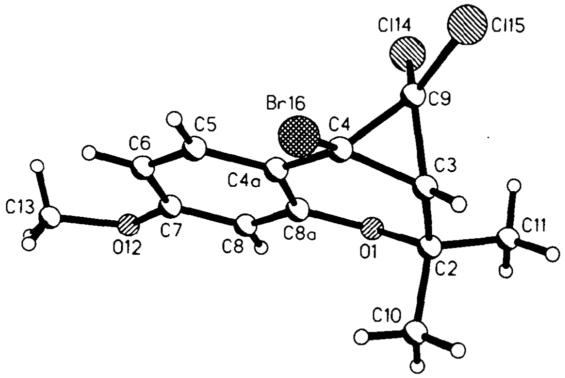


Fig. 1. Molecular structure of the cyclopropachromene illustrating the ring conformations.

The C atom of the methoxy substituent lies almost in the plane of the benzene ring, allowing some involvement of oxygen in the delocalized π-bonding system. There are no unusual intramolecular or intermolecular interactions.

Experimental

The compound was prepared as described previously (Brown, Clegg, Islam & Steele, 1990) and crystallized from light petroleum.

Crystal data

$C_{13}H_{13}BrCl_2O_2$
M_r = 352.04
Monoclinic
$P2_1/c$
a = 12.434 (2) Å
b = 10.244 (2) Å
c = 11.134 (2) Å
β = 100.851 (14)°
V = 1392.8 (4) Å^3
Z = 4
D_x = 1.679 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 32 reflections
θ = 24.14-27.68°
μ = 7.486 mm^{-1}
T = 295 (2) K
Block
0.56 × 0.48 × 0.44 mm
Colourless

Data collection

Stoe Siemens diffractometer
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: empirical
$T_{\min}$ = 0.016, $T_{\max}$ = 0.107
9281 measured reflections
2336 independent reflections
2224 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0774
$\theta_{\max}$ = 64.99°
$h = -14 \rightarrow 14$
$k = -12 \rightarrow 12$
$l = -12 \rightarrow 12$
3 standard reflections
frequency: 60 min
intensity variation: 3%

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Refinement

Refinement on F^2
$R(F) = 0.0414$
$wR(F^2) = 0.1213$
$S = 1.105$
2335 reflections
166 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 0.3353P]$, where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max} = 0.495$ e Å^{-3}
$\Delta\rho_{min} = -0.381$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	0.3983 (2)	0.5726 (2)	0.2975 (2)	0.0724 (6)
C2	0.3885 (2)	0.6856 (3)	0.2155 (3)	0.0689 (7)
C3	0.2765 (2)	0.6910 (3)	0.1319 (3)	0.0635 (7)
C4	0.1795 (2)	0.6364 (3)	0.1783 (3)	0.0615 (6)
C4a	0.2029 (2)	0.5680 (3)	0.2968 (3)	0.0591 (6)
C5	0.1217 (2)	0.5262 (3)	0.3588 (3)	0.0659 (7)
C6	0.1451 (2)	0.4631 (3)	0.4688 (3)	0.0651 (7)
C7	0.2535 (2)	0.4388 (3)	0.5229 (3)	0.0610 (6)
C8	0.3362 (2)	0.4778 (3)	0.4624 (3)	0.0635 (7)
C8a	0.3117 (2)	0.5423 (3)	0.3522 (3)	0.0614 (6)
C9	0.2155 (3)	0.5773 (3)	0.0671 (3)	0.0671 (7)
C10	0.4055 (3)	0.8081 (4)	0.2918 (4)	0.0863 (10)
C11	0.4779 (3)	0.6652 (5)	0.1418 (3)	0.0839 (10)
O12	0.2861 (2)	0.3780 (2)	0.6317 (2)	0.0697 (5)
C13	0.2051 (3)	0.3546 (4)	0.7053 (3)	0.0847 (10)
Cl14	0.26943 (8)	0.41981 (8)	0.07565 (9)	0.0867 (3)
Cl15	0.13757 (8)	0.60868 (10)	−0.07848 (8)	0.0845 (3)
Br16	0.04460 (3)	0.73515 (4)	0.14835 (3)	0.0753 (2)

Table 2. *Selected geometric parameters* (Å, °)

O1—C8a	1.370 (3)	C4a—C5	1.393 (4)
O1—C2	1.465 (4)	C4a—C8a	1.402 (4)
C2—C10	1.507 (5)	C5—C6	1.367 (4)
C2—C11	1.516 (4)	C6—C7	1.392 (4)
C2—C3	1.524 (4)	C7—O12	1.355 (4)
C3—C9	1.499 (4)	C7—C8	1.389 (4)
C3—C4	1.507 (4)	C8—C8a	1.376 (4)
C4—C4a	1.473 (4)	C9—Cl14	1.743 (3)
C4—C9	1.520 (4)	C9—Cl15	1.754 (3)
C4—Br16	1.933 (3)	O12—C13	1.433 (4)
C8a—O1—C2	118.4 (2)	C8a—C4a—C4	119.7 (3)
O1—C2—C10	108.7 (3)	C6—C5—C4a	122.6 (3)
O1—C2—C11	104.2 (3)	C5—C6—C7	119.8 (3)
C10—C2—C11	112.4 (3)	O12—C7—C8	116.3 (2)
O1—C2—C3	111.7 (2)	O12—C7—C6	124.8 (3)
C10—C2—C3	109.2 (3)	C8—C7—C6	118.9 (3)
C11—C2—C3	110.7 (3)	C8a—C8—C7	120.7 (3)
C9—C3—C4	60.7 (2)	O1—C8a—C8	116.4 (2)
C9—C3—C2	126.0 (3)	O1—C8a—C4a	122.4 (3)
C4—C3—C2	118.4 (3)	C8—C8a—C4a	121.0 (3)
C4a—C4—C3	116.6 (2)	C3—C9—C4	59.9 (2)
C4a—C4—C9	120.1 (2)	C3—C9—Cl14	122.6 (2)
C3—C4—C9	59.4 (2)	C4—C9—Cl14	119.6 (2)
C4a—C4—Br16	115.0 (2)	C3—C9—Cl15	116.3 (2)
C3—C4—Br16	118.1 (2)	C4—C9—Cl15	118.9 (2)
C9—C4—Br16	116.5 (2)	Cl14—C9—Cl15	111.1 (2)
C5—C4a—C8a	116.9 (3)	C7—O12—C13	117.7 (2)
C5—C4a—C4	123.4 (2)		

Refinement was on F^2 for all reflections except for one with very negative F_o^2. Isotropic H atoms were constrained to give C—H 0.93 Å (aromatic, on ring-angle external bisectors) or 0.97 Å (aliphatic, with H—C—H 109.5°) and U(H) = 1.2U_{eq}(C). All e.s.d.'s are estimated using the full covariance matrix. Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, in preparation). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93 and local programs.

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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 71614 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1073]

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(4a*R*,8*R*,*SR*)-8-(*p*-Tolylsulfinyl)-2,3,4,4a,5,6,7,8-octahydro-4a-quinolinol

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Abstract

The title compound, $C_{16}H_{21}NO_2S$, isolated from the reaction of lithiated racemic 2,3,4,4a,5,6,7,8-octahydroquinoline with 0.5 equivalents of (−)-(1*R*,2*S*,5*R*)-menthyl (*SS*)-*p*-toluenesulfinate, possesses the unusual conformation in which the OH and bulky *p*-toluenesulfinyl groups are in axial positions. The S=O bond distance of 1.519 (3) Å is longer than expected because of intramolecular hydrogen bonding between the hydroxyl group and the sulfinyl O atom.