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6-Bromo-2,2-diphenyl-2*H*-1-benzopyran

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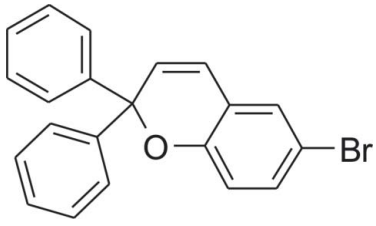
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.044; wR factor = 0.115; data-to-parameter ratio = 22.4.

2*H*-Benzopyrans (chromenes) and their analogues are the subject of considerable current interest due to their highly desirable photochromic properties. Although the benzopyran fragment in the title compound, $C_{21}H_{15}BrO$, is roughly planar, the pyran ring may be regarded as having a half-chair conformation.

Related literature

For related literature, see: Bougdid *et al.* (2007); Crano *et al.* (1996); Cremer & Pople (1975); Gemert (1999); Pozzo *et al.* (1996, 1997); Shilova *et al.* (2007).



Experimental

Crystal data

$C_{21}H_{15}BrO$
M_r = 363.24
Triclinic, $P\overline{1}$
a = 8.9633 (4) Å
b = 9.4284 (4) Å
c = 10.5524 (5) Å
α = 72.461 (3)°
β = 79.150 (3)°
γ = 75.594 (3)°
V = 817.37 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.52 mm^{-1}
T = 293 (2) K
0.20 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (Blessing & Langs, 1987)
T_{min} = 0.52, T_{max} = 0.63
(expected range = 0.566–0.686)
17241 measured reflections
4665 independent reflections
3473 reflections with $I > 2\sigma(I)$
R_{int} = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.115
S = 1.10
4665 reflections
208 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.66 e Å^{-3}

Data collection: *KappaCCD Reference Manual* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN3053).

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supplementary materials

Acta Cryst. (2007). E**63**, o3340 [**doi:10.1107/S1600536807030784**]

6-Bromo-2,2-diphenyl-2*H*-1-benzopyran

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Comment

During the last years extensive research has been directed towards the functionalization of chromenes. This interest was justified by the wide range of potential practical applications of these materials in opto-electronic and photonic technologies (Pozzo *et al.*, 1996; Pozzo *et al.*, 1997; Gemert *et al.*, 1999; Crano *et al.*, 1996). Bromine-substituted 2*H*-benzopyrans (Bougdid *et al.*, 2007) are attractive building blocks for the design of various photochromic molecules for many targets (Shilova *et al.*, 2007). Missing any thorough study of their X-ray structure has motivated us to investigate this type of compounds more detailed.

The pyrane ring in compound (I) has an half-chair conformation with puckering amplitude (Q) = 0.348 (2) Å, θ = 66.6 (5) °, φ = 31.4 (5) ° (Cremer & Pople, 1975) but the benzopyran fragment is nearly planar with the largest deviation from the plane being 0.390 (2)Å at C7 (Fig. 1).

Experimental

Diagram 1

6-Bromo-2,2-diphenyl-2*H*-1-benzopyran. 3,3-diphenylprop-1-yn-3-ol (11 mmol), 4-bromophenol (10 mmol), a catalytic amount of *p*-toluene sulfonic acid (PTSA) and dry dichloromethane (20 ml) purged with argon and stirred at room temperature for 6–10 h. The progress of the reaction was monitored by TLC (pentane/Et_2O, 1:1). After complete disappearance of the bromophenol, the reaction mixture was washed with brine (3x20 ml). The organic layer was dried with $MgSO_4$, filtered and concentrated to dryness under reduced pressure. Purification by column chromatography (SiO_2; cyclohexane/dichloromethane gradient 100:0 to 50:50) afforded the pure compound as a light yellow solid (yield 74%). Crystals appropriate for data collection were obtained by slow evaporation from acetonitrile solution at 277 K. *M*.p.125–126 ^{o}C. FT—IR (KBr): ν= 3055, 3026, 2968, 2924, 1629, 1597, 1472, 1446, 1416, 1265, 1242, 1212, 1163, 1128, 1053, 993, 945, 915, 876, 816, 767, 752, 701, 558 cm^{-1} . ^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.13 (d, J = 10.0 Hz, 1 H), 6.47 (d, J = 10.0 Hz, 1 H), 6.72 (d, J = 7.5 Hz, 1 H), 7.04 (d, J = 2.5 Hz, 1 H), 7.12 (dd, J = 2.5, 7.5 Hz, 1 H), 7.15–7.35 (m, 10 H). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ= 82.9 (OC), 113.2 (C), 118.3 (CH=), 122.4 (CH=), 123.0 (C), 127.0 (4 *x* CH=), 127.7 (2 *x* CH=), 128.2 (4 *x* CH=), 129.0 (CH=), 130.2 (CH=), 132.0 (CH=), 144.4 (2 *x* C), 151.6 (C). Anal. Calcd. for $C_{21}H_{15}BrO$: C, 69.43; H, 4.16; Br, 21.99. Found: C, 69.52; H, 4.23; Br, 22.01.

Refinement

All H atoms were fixed geometrically and treated as riding with C—H = 0.93 Å with U_{iso}(H) = *1.2*U_{eq}(C).

Figures

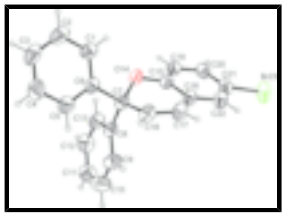


Fig. 1. Molecular view of compound (I) with the atom-labelling scheme. Ellipsoids are drawn at the 50% propability level. H atoms are represented as small sphers of arbitrary radii.

6-Bromo-2,2-diphenyl-2*H*-1-benzopyran

Crystal data

$C_{21}H_{15}BrO$	F_{000} = 368
M_r = 363.24	D_x = 1.476 Mg m^{-3}
Triclinic, $P\bar{1}$	Melting point: 399(1) K
a = 8.9633 (4) Å	Mo $K\alpha$ radiation λ = 0.71073 Å
b = 9.4284 (4) Å	Cell parameters from 17241 reflections
c = 10.5524 (5) Å	θ = 2.3–29.9º
α = 72.461 (3)º	μ = 2.52 mm^{-1}
β = 79.150 (3)º	T = 293 (2) K
γ = 75.594 (3)º	Prism, light yellow
V = 817.37 (7) Å^3	0.20 × 0.20 × 0.15 mm
Z = 2	

Data collection

Nonius KappaCCD area-detector diffractometer	4665 independent reflections
Radiation source: fine-focus sealed tube	3473 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.040
T = 293(2) K	θ_{max} = 29.9º
φ scans	θ_{min} = 2.3º
Absorption correction: multi-scan (Blessing & Langs, 1987)	h = −9→12
T_{min} = 0.52, T_{max} = 0.63	k = −13→12
17241 measured reflections	l = −14→14

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.044	H-atom parameters constrained
$wR(F^2)$ = 0.115	$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 0.5037P]$ where $P = (F_o^2 + 2F_c^2)/3$

S = 1.10	$(\Delta/\sigma)_{max} < 0.001$
4665 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
208 parameters	$\Delta\rho_{min} = -0.66$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.2030 (3)	0.5056 (3)	0.7994 (2)	0.0455 (5)
H1	−0.1481	0.4083	0.8355	0.055*
C2	−0.3641 (3)	0.5354 (4)	0.8156 (3)	0.0566 (7)
H2	−0.4161	0.4580	0.8639	0.068*
C3	−0.4478 (3)	0.6772 (4)	0.7614 (3)	0.0578 (7)
H3	−0.5557	0.6966	0.7732	0.069*
C4	−0.3699 (3)	0.7901 (4)	0.6895 (3)	0.0624 (7)
H4	−0.4254	0.8861	0.6505	0.075*
C5	−0.2086 (3)	0.7623 (3)	0.6744 (3)	0.0504 (6)
H5	−0.1574	0.8403	0.6264	0.061*
C6	−0.1237 (2)	0.6198 (3)	0.7299 (2)	0.0361 (4)
C7	0.0536 (2)	0.5925 (3)	0.7133 (2)	0.0347 (4)
C8	0.1046 (2)	0.7238 (3)	0.7401 (2)	0.0349 (4)
C9	0.1586 (3)	0.8380 (3)	0.6386 (2)	0.0481 (6)
H9	0.1703	0.8344	0.5501	0.058*
C10	0.1955 (4)	0.9587 (3)	0.6686 (3)	0.0610 (7)
H10	0.2312	1.0356	0.5998	0.073*
C11	0.1795 (4)	0.9647 (3)	0.7991 (3)	0.0604 (7)
H11	0.2049	1.0450	0.8186	0.073*
C12	0.1260 (4)	0.8525 (3)	0.8999 (3)	0.0569 (7)
H12	0.1145	0.8569	0.9882	0.068*
C13	0.0888 (3)	0.7321 (3)	0.8714 (2)	0.0444 (5)
H13	0.0529	0.6561	0.9409	0.053*
O14	0.10089 (18)	0.45443 (18)	0.81754 (15)	0.0392 (3)
C15	0.2510 (2)	0.3768 (2)	0.8033 (2)	0.0353 (4)
C16	0.3325 (3)	0.3782 (3)	0.6767 (2)	0.0378 (5)
C17	0.2525 (3)	0.4684 (3)	0.5611 (2)	0.0433 (5)

H17	0.2933	0.4561	0.4764	0.052*
C18	0.1215 (3)	0.5682 (3)	0.5767 (2)	0.0404 (5)
H18	0.0706	0.6242	0.5026	0.049*
C19	0.3154 (3)	0.2885 (3)	0.9189 (2)	0.0406 (5)
H19	0.2586	0.2864	1.0026	0.049*
C20	0.4657 (3)	0.2032 (3)	0.9082 (2)	0.0438 (5)
H20	0.5105	0.1436	0.9847	0.053*
C21	0.5477 (3)	0.2079 (3)	0.7829 (3)	0.0443 (5)
C22	0.4828 (3)	0.2917 (3)	0.6675 (2)	0.0449 (5)
H22	0.5390	0.2904	0.5841	0.054*
Br23	0.75853 (3)	0.10283 (4)	0.77031 (3)	0.06376 (13)

Atomic displacement parameters (Å^2)

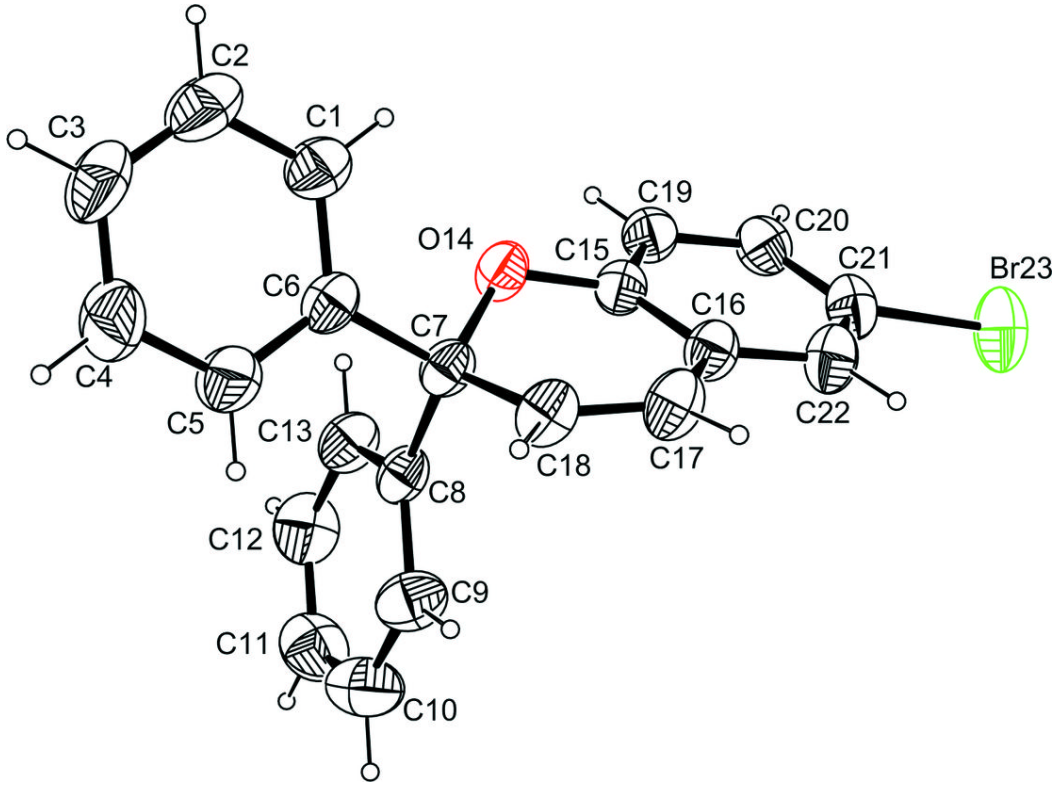
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0412 (12)	0.0520 (14)	0.0471 (13)	−0.0164 (10)	−0.0043 (10)	−0.0143 (11)
C2	0.0449 (14)	0.0749 (19)	0.0608 (16)	−0.0297 (14)	0.0021 (12)	−0.0251 (14)
C3	0.0302 (12)	0.082 (2)	0.0717 (18)	−0.0139 (12)	−0.0017 (11)	−0.0365 (16)
C4	0.0355 (13)	0.0635 (17)	0.088 (2)	−0.0017 (12)	−0.0165 (13)	−0.0215 (16)
C5	0.0341 (12)	0.0518 (14)	0.0621 (16)	−0.0093 (10)	−0.0091 (10)	−0.0081 (12)
C6	0.0306 (10)	0.0476 (12)	0.0343 (10)	−0.0106 (9)	−0.0034 (8)	−0.0154 (9)
C7	0.0314 (10)	0.0431 (11)	0.0278 (9)	−0.0074 (8)	−0.0027 (7)	−0.0076 (8)
C8	0.0255 (9)	0.0455 (12)	0.0332 (10)	−0.0059 (8)	−0.0048 (7)	−0.0100 (9)
C9	0.0506 (14)	0.0567 (15)	0.0373 (12)	−0.0187 (12)	−0.0073 (10)	−0.0054 (11)
C10	0.0639 (18)	0.0525 (16)	0.0650 (18)	−0.0227 (14)	−0.0153 (14)	−0.0004 (13)
C11	0.0584 (17)	0.0527 (15)	0.080 (2)	−0.0148 (13)	−0.0191 (14)	−0.0225 (14)
C12	0.0592 (17)	0.0668 (17)	0.0536 (15)	−0.0121 (14)	−0.0115 (12)	−0.0271 (14)
C13	0.0437 (13)	0.0562 (14)	0.0361 (11)	−0.0141 (11)	−0.0015 (9)	−0.0152 (10)
O14	0.0324 (8)	0.0455 (8)	0.0334 (7)	−0.0038 (6)	−0.0009 (6)	−0.0067 (6)
C15	0.0331 (10)	0.0375 (11)	0.0365 (11)	−0.0068 (8)	−0.0030 (8)	−0.0125 (9)
C16	0.0358 (11)	0.0452 (12)	0.0350 (11)	−0.0078 (9)	−0.0027 (8)	−0.0159 (9)
C17	0.0413 (12)	0.0607 (14)	0.0309 (11)	−0.0088 (10)	−0.0023 (8)	−0.0190 (10)
C18	0.0381 (11)	0.0554 (13)	0.0285 (10)	−0.0089 (10)	−0.0063 (8)	−0.0114 (9)
C19	0.0427 (12)	0.0406 (11)	0.0361 (11)	−0.0078 (9)	−0.0028 (9)	−0.0083 (9)
C20	0.0439 (13)	0.0404 (12)	0.0458 (13)	−0.0034 (10)	−0.0108 (10)	−0.0108 (10)
C21	0.0376 (12)	0.0436 (12)	0.0541 (14)	0.0005 (9)	−0.0091 (10)	−0.0217 (11)
C22	0.0395 (12)	0.0549 (14)	0.0433 (12)	−0.0039 (10)	−0.0024 (9)	−0.0237 (11)
Br23	0.04440 (17)	0.0739 (2)	0.0716 (2)	0.01358 (13)	−0.01355 (13)	−0.03444 (16)

Geometric parameters (Å, °)

C1—C6	1.382 (3)	C11—C12	1.365 (4)
C1—C2	1.389 (4)	C11—H11	0.9300
C1—H1	0.9300	C12—C13	1.386 (4)
C2—C3	1.371 (5)	C12—H12	0.9300
C2—H2	0.9300	C13—H13	0.9300
C3—C4	1.370 (4)	O14—C15	1.367 (3)
C3—H3	0.9300	C15—C19	1.388 (3)
C4—C5	1.391 (4)	C15—C16	1.395 (3)

C4—H4	0.9300	C16—C22	1.394 (3)
C5—C6	1.383 (3)	C16—C17	1.458 (3)
C5—H5	0.9300	C17—C18	1.327 (3)
C6—C7	1.530 (3)	C17—H17	0.9300
C7—O14	1.456 (3)	C18—H18	0.9300
C7—C18	1.517 (3)	C19—C20	1.390 (3)
C7—C8	1.537 (3)	C19—H19	0.9300
C8—C9	1.382 (3)	C20—C21	1.381 (4)
C8—C13	1.390 (3)	C20—H20	0.9300
C9—C10	1.396 (4)	C21—C22	1.379 (4)
C9—H9	0.9300	C21—Br23	1.903 (2)
C10—C11	1.374 (4)	C22—H22	0.9300
C10—H10	0.9300		
C6—C1—C2	120.4 (3)	C12—C11—H11	120.1
C6—C1—H1	119.8	C10—C11—H11	120.1
C2—C1—H1	119.8	C11—C12—C13	120.4 (3)
C3—C2—C1	121.0 (3)	C11—C12—H12	119.8
C3—C2—H2	119.5	C13—C12—H12	119.8
C1—C2—H2	119.5	C12—C13—C8	120.7 (2)
C4—C3—C2	119.0 (3)	C12—C13—H13	119.6
C4—C3—H3	120.5	C8—C13—H13	119.6
C2—C3—H3	120.5	C15—O14—C7	117.79 (16)
C3—C4—C5	120.6 (3)	O14—C15—C19	117.65 (19)
C3—C4—H4	119.7	O14—C15—C16	120.90 (19)
C5—C4—H4	119.7	C19—C15—C16	121.3 (2)
C6—C5—C4	120.7 (3)	C22—C16—C15	118.7 (2)
C6—C5—H5	119.6	C22—C16—C17	123.9 (2)
C4—C5—H5	119.6	C15—C16—C17	117.4 (2)
C1—C6—C5	118.3 (2)	C18—C17—C16	120.0 (2)
C1—C6—C7	121.9 (2)	C18—C17—H17	120.0
C5—C6—C7	119.8 (2)	C16—C17—H17	120.0
O14—C7—C18	109.85 (18)	C17—C18—C7	121.2 (2)
O14—C7—C6	104.92 (16)	C17—C18—H18	119.4
C18—C7—C6	110.74 (17)	C7—C18—H18	119.4
O14—C7—C8	108.43 (16)	C15—C19—C20	119.3 (2)
C18—C7—C8	112.69 (18)	C15—C19—H19	120.3
C6—C7—C8	109.90 (18)	C20—C19—H19	120.3
C9—C8—C13	118.5 (2)	C21—C20—C19	119.3 (2)
C9—C8—C7	122.7 (2)	C21—C20—H20	120.3
C13—C8—C7	118.66 (19)	C19—C20—H20	120.3
C8—C9—C10	120.2 (2)	C22—C21—C20	121.7 (2)
C8—C9—H9	119.9	C22—C21—Br23	119.49 (18)
C10—C9—H9	119.9	C20—C21—Br23	118.78 (18)
C11—C10—C9	120.4 (3)	C21—C22—C16	119.6 (2)
C11—C10—H10	119.8	C21—C22—H22	120.2
C9—C10—H10	119.8	C16—C22—H22	120.2
C12—C11—C10	119.8 (3)		
O14—C7—C8—C9	142.9 (2)	O14—C7—C6—C5	161.2 (2)

Fig. 1


C2
C3
C1
C19
C20
O14
C15
C21
Br23
C6
C16
C7
C4
C22
C5
C13
C18
C17
C8
C12
C9
C11
C10