

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 6-Bromo-5,8-dimethyl-2,2-diphenyl-2H-1-benzopyran

Ekaterina A. Shilova, Lahoussine Bougdid, Gérard Pèpe and Corinne Moustrou\*

GCOM2 UMR-CNRS 6114, Université d'Aix-Marseille II, Campus de Luminy, Case 901, 13288 Marseille Cedex 9, France

Correspondence e-mail: pepe@luminy.univ-mrs.fr

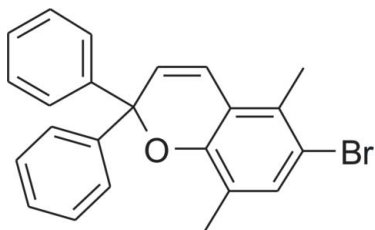
Received 21 June 2007; accepted 24 June 2007

Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.046;  $wR$  factor = 0.115; data-to-parameter ratio = 20.3.

2H-Benzopyrans (chromenes) and their analogues are the subject of considerable current interest due to their highly desirable photochromic properties. In the title compound,  $\text{C}_{23}\text{H}_{19}\text{BrO}$ , the pyran ring displays a half-chair conformation. Crystal stability is governed only by van der Waals interactions.

## Related literature

For related literature, see: Bougdid *et al.* (2007); Crano *et al.* (1996); Cremer & Pople (1975); Gemert (1999); Kodaman *et al.* (2000); Pozzo *et al.* (1996, 1997); Shilova, Bougdid *et al.* (2007); Shilova, Perevalov *et al.* (2007).



## Experimental

## Crystal data

$\text{C}_{23}\text{H}_{19}\text{BrO}$   
 $M_r = 391.29$   
 Monoclinic,  $P2_1/a$   
 $a = 8.8953$  (2) Å  
 $b = 22.4365$  (5) Å  
 $c = 9.2114$  (1) Å  
 $\beta = 93.921$  (2)°

$V = 1834.10$  (6) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 2.25$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 $0.30 \times 0.25 \times 0.25$  mm

## Data collection

Nonius KappaCCD area-detector diffractometer  
 Absorption correction: multi-scan (Blessing & Langs, 1987)  
 $T_{\min} = 0.48$ ,  $T_{\max} = 0.53$   
 (expected range = 0.516–0.570)

17209 measured reflections  
 4630 independent reflections  
 3552 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.038$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.115$   
 $S = 1.03$   
 4630 reflections

228 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.75$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.89$  e Å<sup>-3</sup>

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: DN3054).

## References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Blessing, R. H. & Langs, D. A. (1987). *J. Appl. Cryst.* **20**, 427–428.
- Bougdid, L., Heynderickx, A., Delbaere, S. & Moustrou, C. (2007). *Tetrahedron*. doi: 10.1016/j.tet.2007.05.113.
- Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
- Crano, J. C., Flood, T., Knowles, D., Kumar, A. & Van Gemert, B. (1996). *Pure Appl. Chem.* **68**, 1395–1398.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Gemert, B. V. (1999). *Organic Photochromic and Thermochromic Compounds*, Vol. 1, edited by J. C. Crano & R. Guglielmetti, pp. 111–137. New York: Plenum Press.
- Kodaman, Y., Nakabayashi, T., Segawa, K., Hattori, E., Sakuragi, M., Nishi, N. & Sakuragi, S. (2000). *J. Phys. Chem. A*, **104**, 11478–11485.
- Nonius (1998). *Kappa CCD Reference Manual*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Pozzo, J.-L., Samat, A., Guglielmetti, R., Dubest, R. & Aubard, J. (1997). *Helv. Chim. Acta*, **80**, 725–738.
- Pozzo, J.-L., Samat, A., Guglielmetti, R., Lokshin, V. & Minkin, V. (1996). *Can. J. Chem.* **74**, 1649–1659.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Shilova, E., Bougdid, L., Pèpe, G. & Moustrou, C. (2007). *Acta Cryst.* **E63**, o3340.
- Shilova, E., Perevalov, V., Samat, A. & Moustrou, C. (2007). *Tetrahedron Lett.* **48**, 4127–4130.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

**supplementary materials**

*Acta Cryst.* (2007). E63, o3341 [ doi:10.1107/S1600536807030796 ]

## 6-Bromo-5,8-dimethyl-2,2-diphenyl-2H-1-benzopyran

E. A. Shilova, L. Bougdid, G. Pèpe and C. Moustrou

### Comment

This type of compounds (Gemert *et al.*, 1999; Vol. 1, Chapter 3.) has many useful applications in the marketplace (Pozzo *et al.*, 1996; Pozzo *et al.*, 1997; Crano *et al.*, 1996), for example they are used to construct ophthalmic glasses (Crano *et al.*, 1996). Functionalization of chromenes with halogen units greatly enlarges their field of applications. Bromine-substituted 2H-benzopyrans are very convenient starting material for the synthesis of a wide range of modified chromenes (Shilova, Perevalov *et al.*, 2007). The structure of this class of compounds has been well documented by UV and NMR spectroscopy (Kodaman *et al.*, 2000; Bougdid *et al.*, 2007). However no X-ray crystallographic analysis for halogen-substituted 2H-benzopyrans were presented to date. The aim of the current study is to identify more exactly the structure of these key chromenes.

As observed in compound (I) (Shilova, Bougdid *et al.*, 2007) the pyran ring displays half-chair conformation with puckering amplitude (Q) = 0.446 (2) Å,  $\theta = 112.1$  (4)°,  $\varphi = 214.7$  (4)° (Cremer & Pople, 1975) (Fig. 1). Except for the C7 atom which is out of the mean plane defined by the benzopyran ring, by 0.492 Å, this fragment is roughly planar. The crystal stability is only assumed by van der Waals interactions.

Figure 2, where the pyran rings have been superimposed, shows light geometry differences at the benzene rings level. They correspond to rotations around the bonds linking these rings to the pyran one, as it appears in the values of the torsion angles O14—C7—C8—C9; O14—C7—C6—C5, respectively 142.9 (2); 161.2 (2) for compound (I) and 134.5 (2); 171.6 (2) for compound (II). These rotations around  $\sigma$  bonds are not significative in terms of strain energy.

### Experimental

6-Bromo-5,8-dimethyl-2,2-diphenyl-2H-1-benzopyran. 3,3-diphenylprop-1-yn-3-ol (11 mmol), 4-bromo-2,5-dimethylphenol (Bougdid *et al.*, 2007) (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<sub>2</sub>O, 1:1). After complete disappearance of the bromophenol, the reaction mixture was washed with brine (3x20 ml). The organic layer was dried with MgSO<sub>4</sub>, filtered and concentrated to dryness under reduced pressure. Purification by column chromatography (SiO<sub>2</sub>; cyclohexane/dichloromethane gradient 100:0 to 50:50) afforded pure compound as a white solid (yield 85%). Light yellow crystals appropriate for data collection were obtained by slow evaporation from acetonitrile solution at 277 K. *M.p.* 153–154 °C. FT—IR (KBr):  $\nu = 3060, 3024, 2952, 2921, 2853, 1625, 1593, 1493, 1450, 1380, 1364, 1236, 1230, 1203, 1168, 1095, 1062, 1031, 970, 907, 864, 770, 754, 700, 573$  cm<sup>-1</sup>. <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>):  $\delta = 2.25$  (s, 3 H), 2.35 (s, 3 H), 6.21 (d, *J* = 10.0 Hz, 1 H), 6.84 (d, *J* = 10.0 Hz, 1 H), 7.18 (br s, 1 H), 7.21–7.46 (m, 10 H). <sup>13</sup>C NMR (62.5 MHz, CDCl<sub>3</sub>):  $\delta = 15.5$  (CH<sub>3</sub>), 18.1 (CH<sub>3</sub>), 81.6 (OC), 116.2 (C), 120.9 (C), 121.4 (CH=), 125.2 (C), 126.7 (4 x CH=), 127.5 (2 x CH=), 128.1 (4 x CH=), 129.3 (CH=), 130.8 (C), 133.7 (CH=), 144.9 (2 x C), 149.8 (C). Anal. Calcd. for C<sub>23</sub>H<sub>19</sub>BrO: C, 70.59; H, 4.89; Br, 20.42. Found: C, 70.56; H, 4.79; Br, 20.48.

## Refinement

All H atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic) or 0.96 Å (methyl) with  $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$  where  $x = 1.2$  for H aromatic and 1.5 for H methyl.

## Figures

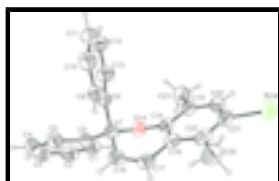


Fig. 1. Molecular view of compound (I) with the atom-labelling scheme. Ellipsoids are drawn at the 50% probability level. H atoms are represented as small spheres of arbitrary radii.

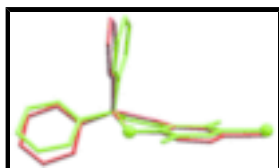


Fig. 2. Compounds (I) and compound (II) with the pyran rings superimposed.

## 6-Bromo-5,8-dimethyl-2,2-diphenyl-2H-1-benzopyran

### Crystal data

$\text{C}_{23}\text{H}_{19}\text{BrO}$

$M_r = 391.29$

Monoclinic,  $P2_1/a$

$a = 8.8953$  (2) Å

$b = 22.4365$  (5) Å

$c = 9.2114$  (1) Å

$\beta = 93.921$  (2)°

$V = 1834.10$  (6) Å<sup>3</sup>

$Z = 4$

$F_{000} = 800$

$D_x = 1.417$  Mg m<sup>-3</sup>

Melting point: 427(1) K

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 17209 reflections

$\theta = 0.9\text{--}28.7^\circ$

$\mu = 2.25$  mm<sup>-1</sup>

$T = 293$  (2) K

Cube, light yellow

$0.30 \times 0.25 \times 0.25$  mm

### Data collection

Nonius KappaCCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 293$ (2) K

$\varphi$  scans

Absorption correction: multi-scan (Blessing & Langs, 1987)

$T_{\text{min}} = 0.48$ ,  $T_{\text{max}} = 0.53$

17209 measured reflections

4630 independent reflections

3552 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\text{max}} = 28.7^\circ$

$\theta_{\text{min}} = 3.2^\circ$

$h = -11 \rightarrow 9$

$k = -30 \rightarrow 27$

$l = -10 \rightarrow 12$

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.046$	H-atom parameters constrained
$wR(F^2) = 0.115$	$w = 1/[\sigma^2(F_o^2) + (0.0381P)^2 + 1.5124P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
4630 reflections	$(\Delta/\sigma)_{\max} = 0.014$
228 parameters	$\Delta\rho_{\max} = 0.75 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.89 \text{ e } \text{\AA}^{-3}$
	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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1988 (3)	0.46171 (12)	0.1181 (3)	0.0500 (6)
H1	0.1956	0.4588	0.0172	0.060*
C2	0.1233 (3)	0.50778 (13)	0.1826 (4)	0.0607 (7)
H2	0.0706	0.5357	0.1244	0.073*
C3	0.1255 (3)	0.51266 (14)	0.3307 (4)	0.0655 (8)
H3	0.0749	0.5437	0.3731	0.079*
C4	0.2032 (4)	0.47115 (16)	0.4163 (4)	0.0692 (8)
H4	0.2048	0.4741	0.5171	0.083*
C5	0.2789 (3)	0.42512 (14)	0.3535 (3)	0.0578 (7)
H5	0.3306	0.3972	0.4124	0.069*
C6	0.2786 (3)	0.42021 (11)	0.2033 (3)	0.0421 (5)
C7	0.3662 (3)	0.36977 (10)	0.1367 (2)	0.0384 (5)
C8	0.5311 (3)	0.37212 (10)	0.1974 (2)	0.0385 (5)
C9	0.5947 (3)	0.32934 (11)	0.2914 (3)	0.0456 (5)
H9	0.5374	0.2969	0.3177	0.055*
C10	0.7431 (3)	0.33457 (14)	0.3465 (3)	0.0551 (7)
H10	0.7845	0.3059	0.4103	0.066*
C11	0.8296 (3)	0.38209 (15)	0.3073 (3)	0.0605 (7)

## supplementary materials

H11	0.9292	0.3855	0.3440	0.073*
C12	0.7673 (3)	0.42461 (15)	0.2131 (3)	0.0636 (8)
H12	0.8256	0.4565	0.1855	0.076*
C13	0.6186 (3)	0.42003 (12)	0.1595 (3)	0.0530 (6)
H13	0.5771	0.4493	0.0975	0.064*
O14	0.36250 (18)	0.38213 (7)	-0.01785 (16)	0.0401 (4)
C15	0.4191 (2)	0.33737 (10)	-0.1008 (2)	0.0383 (5)
C16	0.3976 (3)	0.27765 (11)	-0.0641 (3)	0.0416 (5)
C17	0.3108 (3)	0.26690 (11)	0.0623 (3)	0.0469 (6)
H17	0.2682	0.2296	0.0759	0.056*
C18	0.2926 (3)	0.30986 (11)	0.1574 (3)	0.0460 (5)
H18	0.2349	0.3034	0.2365	0.055*
C19	0.4881 (3)	0.35455 (11)	-0.2249 (3)	0.0439 (5)
C20	0.5425 (3)	0.30952 (12)	-0.3095 (3)	0.0503 (6)
H20	0.5911	0.3192	-0.3926	0.060*
C21	0.5256 (3)	0.25056 (12)	-0.2724 (3)	0.0499 (6)
C22	0.4524 (3)	0.23218 (11)	-0.1512 (3)	0.0472 (6)
C23	0.5019 (4)	0.41928 (13)	-0.2651 (3)	0.0616 (7)
H23A	0.5482	0.4225	-0.3560	0.092*
H23B	0.5627	0.4396	-0.1906	0.092*
H23C	0.4035	0.4370	-0.2745	0.092*
Br24	0.60679 (4)	0.192806 (16)	-0.39843 (4)	0.07243 (14)
C25	0.4343 (4)	0.16768 (13)	-0.1121 (4)	0.0683 (8)
H25A	0.3649	0.1490	-0.1824	0.102*
H25B	0.3963	0.1648	-0.0173	0.102*
H25C	0.5303	0.1481	-0.1116	0.102*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0454 (14)	0.0468 (14)	0.0574 (15)	0.0011 (11)	0.0006 (11)	-0.0021 (11)
C2	0.0478 (15)	0.0481 (15)	0.086 (2)	0.0045 (12)	0.0019 (14)	-0.0048 (14)
C3	0.0476 (16)	0.0611 (18)	0.089 (2)	0.0034 (13)	0.0184 (15)	-0.0213 (16)
C4	0.0638 (19)	0.085 (2)	0.0607 (18)	0.0075 (17)	0.0183 (14)	-0.0171 (16)
C5	0.0547 (16)	0.0704 (18)	0.0491 (15)	0.0091 (14)	0.0096 (12)	-0.0023 (13)
C6	0.0344 (11)	0.0439 (12)	0.0484 (13)	-0.0035 (10)	0.0049 (9)	-0.0023 (10)
C7	0.0397 (11)	0.0400 (12)	0.0357 (11)	-0.0021 (9)	0.0033 (8)	0.0023 (8)
C8	0.0408 (12)	0.0410 (12)	0.0340 (11)	0.0014 (9)	0.0049 (8)	-0.0027 (8)
C9	0.0468 (13)	0.0483 (13)	0.0419 (13)	0.0031 (11)	0.0039 (10)	0.0013 (10)
C10	0.0487 (15)	0.0694 (18)	0.0464 (14)	0.0136 (13)	-0.0024 (11)	0.0011 (12)
C11	0.0398 (14)	0.083 (2)	0.0573 (16)	0.0015 (14)	-0.0031 (11)	-0.0092 (14)
C12	0.0490 (16)	0.0716 (19)	0.0696 (19)	-0.0171 (14)	-0.0012 (13)	0.0048 (15)
C13	0.0495 (15)	0.0527 (15)	0.0562 (15)	-0.0075 (12)	-0.0019 (11)	0.0081 (12)
O14	0.0463 (9)	0.0382 (8)	0.0359 (8)	0.0003 (7)	0.0021 (6)	0.0026 (6)
C15	0.0357 (11)	0.0401 (12)	0.0382 (11)	-0.0025 (9)	-0.0038 (8)	-0.0027 (9)
C16	0.0406 (12)	0.0404 (12)	0.0430 (12)	-0.0065 (10)	-0.0027 (9)	0.0005 (9)
C17	0.0483 (14)	0.0391 (13)	0.0531 (14)	-0.0122 (11)	0.0013 (10)	0.0057 (10)
C18	0.0457 (13)	0.0470 (14)	0.0458 (13)	-0.0086 (11)	0.0071 (10)	0.0070 (10)

C19	0.0420 (12)	0.0495 (13)	0.0396 (12)	-0.0082 (10)	-0.0013 (9)	0.0006 (10)
C20	0.0472 (14)	0.0657 (17)	0.0379 (12)	-0.0065 (12)	0.0017 (10)	-0.0054 (11)
C21	0.0426 (13)	0.0581 (15)	0.0478 (14)	0.0030 (11)	-0.0063 (10)	-0.0148 (11)
C22	0.0450 (13)	0.0417 (13)	0.0531 (14)	-0.0021 (10)	-0.0092 (10)	-0.0059 (10)
C23	0.079 (2)	0.0568 (17)	0.0496 (15)	-0.0152 (15)	0.0081 (13)	0.0084 (12)
Br24	0.0667 (2)	0.0817 (3)	0.0678 (2)	0.01434 (16)	-0.00321 (14)	-0.03119 (16)
C25	0.081 (2)	0.0399 (15)	0.083 (2)	-0.0024 (14)	-0.0017 (17)	-0.0063 (14)

*Geometric parameters (Å, °)*

C1—C6	1.383 (4)	C12—H12	0.9300
C1—C2	1.388 (4)	C13—H13	0.9300
C1—H1	0.9300	O14—C15	1.378 (3)
C2—C3	1.367 (5)	C15—C19	1.389 (3)
C2—H2	0.9300	C15—C16	1.398 (3)
C3—C4	1.376 (5)	C16—C22	1.406 (3)
C3—H3	0.9300	C16—C17	1.460 (3)
C4—C5	1.381 (4)	C17—C18	1.320 (4)
C4—H4	0.9300	C17—H17	0.9300
C5—C6	1.388 (4)	C18—H18	0.9300
C5—H5	0.9300	C19—C20	1.383 (4)
C6—C7	1.526 (3)	C19—C23	1.506 (4)
C7—O14	1.449 (3)	C20—C21	1.377 (4)
C7—C18	1.513 (3)	C20—H20	0.9300
C7—C8	1.534 (3)	C21—C22	1.393 (4)
C8—C13	1.386 (3)	C21—Br24	1.914 (3)
C8—C9	1.388 (3)	C22—C25	1.503 (4)
C9—C10	1.387 (4)	C23—H23A	0.9600
C9—H9	0.9300	C23—H23B	0.9600
C10—C11	1.377 (4)	C23—H23C	0.9600
C10—H10	0.9300	C25—H25A	0.9600
C11—C12	1.380 (4)	C25—H25B	0.9600
C11—H11	0.9300	C25—H25C	0.9600
C12—C13	1.384 (4)		
C6—C1—C2	120.2 (3)	C12—C13—H13	119.7
C6—C1—H1	119.9	C8—C13—H13	119.7
C2—C1—H1	119.9	C15—O14—C7	114.90 (17)
C3—C2—C1	120.8 (3)	O14—C15—C19	117.0 (2)
C3—C2—H2	119.6	O14—C15—C16	120.2 (2)
C1—C2—H2	119.6	C19—C15—C16	122.7 (2)
C2—C3—C4	119.3 (3)	C15—C16—C22	119.9 (2)
C2—C3—H3	120.3	C15—C16—C17	116.1 (2)
C4—C3—H3	120.3	C22—C16—C17	123.9 (2)
C3—C4—C5	120.4 (3)	C18—C17—C16	120.3 (2)
C3—C4—H4	119.8	C18—C17—H17	119.9
C5—C4—H4	119.8	C16—C17—H17	119.9
C4—C5—C6	120.6 (3)	C17—C18—C7	119.4 (2)
C4—C5—H5	119.7	C17—C18—H18	120.3
C6—C5—H5	119.7	C7—C18—H18	120.3

## supplementary materials

---

C1—C6—C5	118.6 (2)	C20—C19—C15	116.9 (2)
C1—C6—C7	121.9 (2)	C20—C19—C23	121.9 (2)
C5—C6—C7	119.6 (2)	C15—C19—C23	121.2 (2)
O14—C7—C18	108.25 (18)	C21—C20—C19	120.9 (2)
O14—C7—C6	105.95 (18)	C21—C20—H20	119.6
C18—C7—C6	111.76 (19)	C19—C20—H20	119.6
O14—C7—C8	107.96 (17)	C20—C21—C22	123.3 (2)
C18—C7—C8	113.33 (19)	C20—C21—Br24	116.6 (2)
C6—C7—C8	109.25 (18)	C22—C21—Br24	120.2 (2)
C13—C8—C9	118.8 (2)	C21—C22—C16	116.3 (2)
C13—C8—C7	118.3 (2)	C21—C22—C25	122.7 (3)
C9—C8—C7	122.9 (2)	C16—C22—C25	121.0 (3)
C10—C9—C8	120.5 (2)	C19—C23—H23A	109.5
C10—C9—H9	119.7	C19—C23—H23B	109.5
C8—C9—H9	119.7	H23A—C23—H23B	109.5
C11—C10—C9	120.3 (3)	C19—C23—H23C	109.5
C11—C10—H10	119.9	H23A—C23—H23C	109.5
C9—C10—H10	119.9	H23B—C23—H23C	109.5
C10—C11—C12	119.5 (3)	C22—C25—H25A	109.5
C10—C11—H11	120.2	C22—C25—H25B	109.5
C12—C11—H11	120.2	H25A—C25—H25B	109.5
C11—C12—C13	120.4 (3)	C22—C25—H25C	109.5
C11—C12—H12	119.8	H25A—C25—H25C	109.5
C13—C12—H12	119.8	H25B—C25—H25C	109.5
C12—C13—C8	120.5 (3)		
O14—C7—C8—C9	-134.5 (2)	O14—C7—C6—C5	-171.6 (2)



Fig. 1

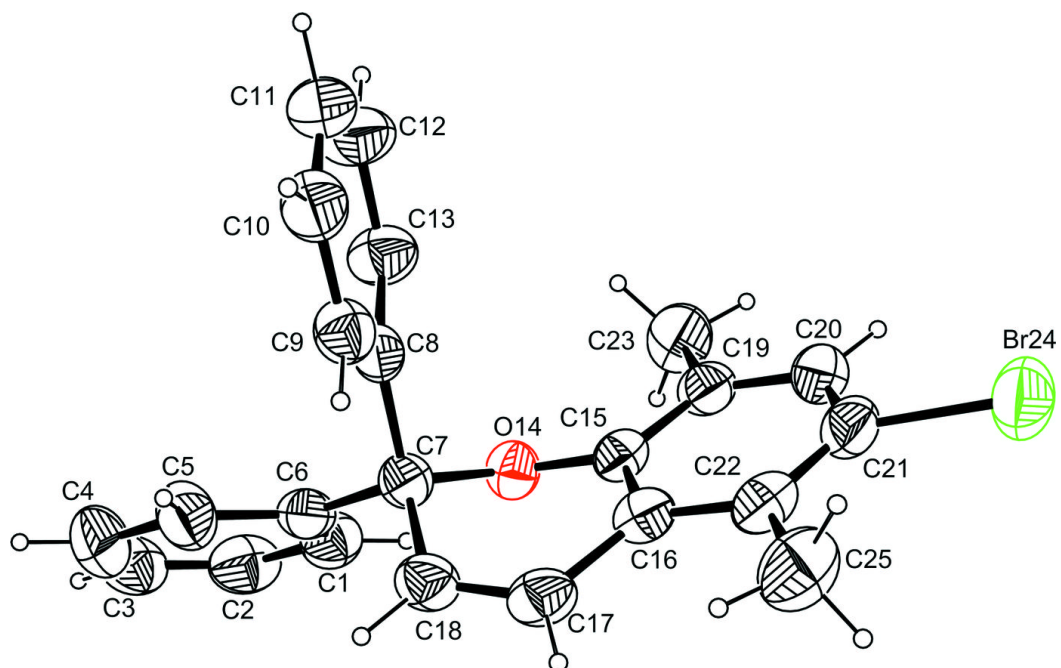


Fig. 2

