

2,7-Dibromo-2,4,6-cycloheptatrien-1-one
(2,7-dibromotropone)Kanji Kubo,^{a*} Taisuke
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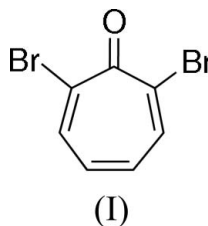
Key indicators

Single-crystal X-ray study
 $T = 123$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.019
 wR factor = 0.047
Data-to-parameter ratio = 17.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $\text{C}_7\text{H}_4\text{Br}_2\text{O}$, has mirror symmetry perpendicular to the tropone ring, and forms a head-to-head association of two nearly parallel molecules. Intermolecular π - π , halogen-halogen and $\text{C}-\text{H}\cdots\text{O}$ interactions are observed in the crystal structure.

Comment

Crystal engineering is the planning and construction of the structure and properties of crystalline materials by designing molecular building blocks (Steed & Atwood, 2000; Matsumoto *et al.*, 2002). Various interactions such as dipole-dipole, van der Waals, hydrogen-bonding, π - π , halogen-halogen, $\text{C}-\text{H}\cdots\pi$ and $\text{C}-\text{H}\cdots\text{O}$ interactions have been used in crystal engineering, and the nature of halogen-halogen interactions in crystals has long been a matter of interest and debate (Desiraju & Parthasarathy, 1989). Aryl and aliphatic halides have been studied as building blocks for constructing crystal structures with halogen-halogen interactions (Karimov *et al.*, 1998; Tanaka *et al.*, 2000; Matsumoto *et al.*, 2002), while tropenoids have been an important building block for constructing liquid crystals (Kubo *et al.*, 2002, 2004, 2005), ionophores (Mori *et al.*, 1996; Yamamoto *et al.*, 2003) and dyes (Takeshita *et al.*, 1989; Kubo & Mori, 2001; Kubo *et al.*, 2001). The tropenoid system plays an important role in generating new properties in molecular assemblies. Many crystal structures of tropenoids have a π - π interaction between intermolecular tropenes (head-to-tail) to cancel the dipole of the tropenoids (Kubo & Mori, 2001; Kubo *et al.*, 2001). We now report the structure of the title compound, (I), a new molecular building block for constructing complicated molecular assemblies, with the aim of contributing to a deeper understanding of intermolecular halogen-halogen and $\text{C}-\text{H}\cdots\text{O}$ interactions.



In (I), there is a mirror passing through the $\text{C}1-\text{O}1$ bond axis and perpendicular to the tropone ring (Fig. 1). The seven-membered ring is nearly planar; the respective deviations of each atom from the least squares plane *A* defined by atoms $\text{O}1$ and $\text{C}1-\text{C}4$ are -0.057 (1), 0.088 (2), 0.036 (1), -0.026 (1) and -0.009 (1) Å. The dihedral angle between the least-

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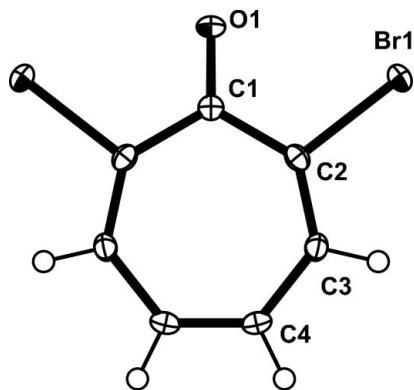


Figure 1

Molecular structure of (I), showing 50% probability displacement ellipsoids. Unlabelled atoms are related by the symmetry operation $x, -y + \frac{1}{2}, z$.

squares planes *A* and *B* [defined by atoms C2, C2ⁱ, Br1 and Br1ⁱ; symmetry code: (i) $x, -y + \frac{1}{2}, z$] is 9.9 (1)°. The C—C bond lengths of the seven-membered ring of (I) are similar to those of tropone (Barrow *et al.*, 1973).

Intermolecular π – π interaction between the tropone dimer planes (head-to-head) of (I) is observed. The C2 \cdots C3ⁱⁱ intermolecular distance between tropone planes is 3.490 (3) Å [symmetry code: (ii) $x - 1, y, z$], which is within the range associated with π – π interactions (3.3–3.8 Å; Prout *et al.*, 1973; Kubo *et al.*, 2001). The value is shorter than that [3.791 (5) Å] of the intermolecular (head-to-head) contact between the C1 atoms of 5-cyanotropone (Kubo *et al.*, 2001).

There is an intermolecular Br \cdots Br interaction (Table 2). The Br1 \cdots Br1ⁱⁱⁱ distance is 3.4115 (3) Å [symmetry code: (iii) $-x, -y, 2 - z$], which is shorter than the sum (3.72 Å) of the van der Waals radii of Br atoms (Desiraju & Parthasarathy, 1989), and shorter than the Br \cdots Br distances in hexabromobenzene [3.564 (1) and 3.696 (1) Å; Baharie & Pawley, 1979]. There is also an intermolecular C—H \cdots O hydrogen bond (Table 2). The H \cdots O distance is similar to those of [Hg(NO₃)₂ (18-crown-6)] (2.48 Å; Calleja & Steed, 2003) and 7,16-bis(1-pyrenylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (2.58 Å; Kubo *et al.*, 1997; Meadows *et al.*, 2000). Thus, the crystal structure of (I) has intermolecular π – π , halogen–halogen and C—H \cdots O interactions.

Experimental

Compound (I) was synthesized by bromination of tropone (Takeshita *et al.*, 1993). Crystals of (I) were grown from a chloroform solution by slow evaporation.

Crystal data

C ₇ H ₄ Br ₂ O	$D_x = 2.416 \text{ Mg m}^{-3}$
$M_r = 263.92$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/m$	Cell parameters from 1084 reflections
$a = 4.010$ (1) Å	$\theta = 3.3$ – 27.5°
$b = 14.829$ (5) Å	$\mu = 11.12 \text{ mm}^{-1}$
$c = 6.111$ (2) Å	$T = 123.1 \text{ K}$
$\beta = 93.274$ (2)°	Needle, yellow
$V = 362.8$ (2) Å ³	$0.13 \times 0.03 \times 0.02 \text{ mm}$
$Z = 2$	

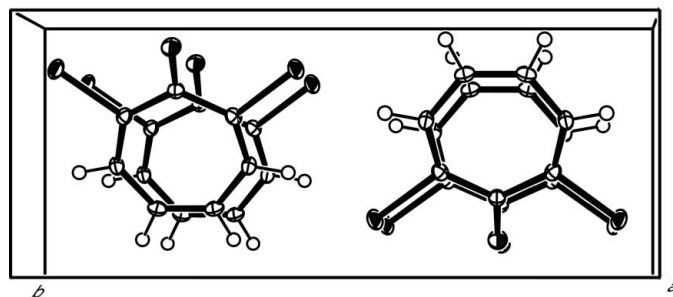


Figure 2

Packing diagram of (I), viewed down the *a* axis.

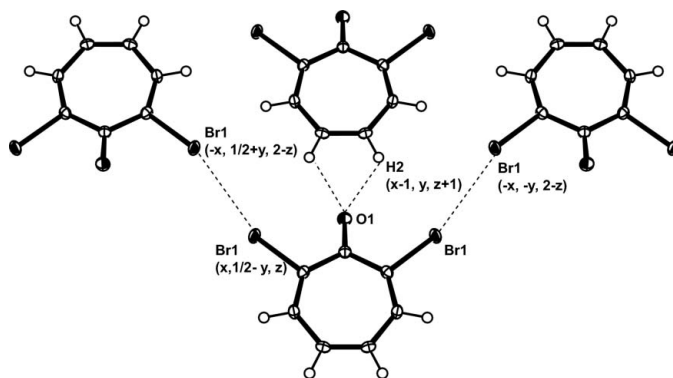


Figure 3

Bromine–bromine and C—H \cdots O interactions (indicated by broken lines) in (I).

Data collection

Rigaku Saturn diffractometer	684 reflections with $F^2 > 2\sigma(F^2)$
ω scans	$R_{\text{int}} = 0.031$
Absorption correction: multi-scan (Jacobson, 1998)	$\theta_{\text{max}} = 27.5^\circ$
$T_{\text{min}} = 0.606, T_{\text{max}} = 0.801$	$h = -5 \rightarrow 5$
4008 measured reflections	$k = -19 \rightarrow 19$
859 independent reflections	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 0.107P]$
$R(F) = 0.019$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.047$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.64 \text{ e \AA}^{-3}$
859 reflections	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
50 parameters	
H-atom parameters constrained	

Table 2

Selected geometric parameters (Å, °).

Br1—C2	1.903 (2)	C2—C3	1.350 (3)
O1—C1	1.223 (4)	C3—C4	1.425 (3)
C1—C2	1.474 (3)	C4—C4 ⁱ	1.352 (3)
Br1—C2—C1	111.8 (2)	C2 ⁱ —C1—C2	118.8 (2)
Br1—C2—C3	115.9 (2)	C2—C3—C4	129.9 (2)
O1—C1—C2	120.6 (1)	C3—C4—C4 ⁱ	127.9 (2)
C1—C2—C3	132.2 (2)		
O1—C1—C2—Br1	−9.0 (4)	C1—C2—C3—C4	2.8 (4)
O1—C1—C2—C3	169.1 (3)	C3—C2—C1—C2 ⁱ	−11.8 (5)
Br1—C2—C3—C4	−179.2 (2)	C2—C3—C4—C4 ⁱ	4.0 (4)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

Table 2

π - π , halogen-halogen and C-H...O interactions (\AA , $^\circ$) in (I).

C1...C4 ⁱⁱ	3.540 (3)	C2...C4 ⁱⁱ	3.499 (3)
C2...C3 ⁱⁱ	3.490 (3)	Br1...Br1 ⁱⁱⁱ	3.4115 (3)
<i>D</i> -H... <i>A</i>	<i>D</i> -H	H... <i>A</i>	<i>D</i> ... <i>A</i>
C4-H2...O1 ^{iv}	0.93	2.5132	3.170 (3)
			128

Symmetry codes: (ii) $x - 1, y, z$; (iii) $-x, -y, 2 - z$; (iv) $1 + x, y, z - 1$.

All H atoms were located at ideal positions (C-H = 0.93 \AA) and constrained with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MS & Rigaku, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP III* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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.
 Baharie, E. & Pawley, G. S. (1979). *Acta Cryst.* **A35**, 233–235.
 Barrow, M. J., Mills, O. S. & Filippini, G. (1973). *J. Chem. Soc. Chem. Commun.* pp. 66–67.
 Burnett, M. N. & Johnson, C. K. (1996). *ORTEP III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Calleja, M. & Steed, J. W. (2003). *J. Chem. Crystallogr.* **33**, 609–612.
 Desiraju, G. R. & Parthasarathy, R. (1989). *J. Am. Chem. Soc.* **111**, 8725–8726.
 Jacobson, R. (1998). *REQAB*. Private communication to Rigaku Corporation.
 Karimov, Z., Talipov, S. A., Ibragimov, B. T., Tashmukhamedona, A. K., Stempnevskaya, I. A. & Aripov, T. F. (1998). *Kristallografiya*, **43**, 478–481.
 Kubo, K., Kato, N. & Sakurai, T. (1997). *Acta Cryst.* **C53**, 132–134.
 Kubo, K. & Mori, A. (2001). *Acta Cryst.* **E57**, o328–o329.
 Kubo, K., Mori, A., Ujiie, S. & Tschierske, C. (2004). *J. Oleo Sci.* **53**, 575–579.
 Kubo, K., Mori, A., Ujiie, S. & Tschierske, C. (2005). *J. Oleo Sci.* **54**, 179–183.
 Kubo, K., Sutoh, T., Mori, A. & Ujiie, S. (2002). *Bull. Chem. Soc. Jpn*, **75**, 1353–1358.
 Kubo, K., Tsujimoto, T. & Mori, A. (2001). *Acta Cryst.* **E57**, o225–o227.
 Kubo, K., Tsuruta, T. & Mori, A. (2001). *Acta Cryst.* **E57**, o326–o327.
 Kubo, K., Yamamoto, E. & Mori, A. (2001). *Acta Cryst.* **C57**, 611–613.
 Matsumoto, A., Tanaka, T., Tsubouchi, T., Tashiro, K., Saragai, S. & Nakamoto, S. (2002). *J. Am. Chem. Soc.* **124**, 8891–8902.
 Meadows, E. S., De Wall, S. L., Barbour, L. J., Fronczek, F. R., Kim, M.-S. & Gokel, G. W. (2000). *J. Am. Chem. Soc.* **122**, 3325–3335.
 Mori, A., Kubo, K. & Takeshita, H. (1996). *Coord. Chem. Rev.* **148**, 71–96.
 Prout, C. K., Orley, T. M., Tickle, I. J. & Wright, J. D. (1973). *J. Chem. Soc. Perkin Trans. 2*, pp. 523–527.
 Rigaku (1999). *CrystalClear*. Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
 Rigaku/MS & Rigaku (2004). *CrystalStructure*. Version 3.6.0. Rigaku/MS, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, 3-9-12 Akishima, Tokyo 196-8666, Japan.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Steed, J. W. & Atwood, J. L. (2000). *Supramol. Chem.* pp. 389–462.
 Takeshita, H., Mori, A., Nagao, T. & Nagamura, T. (1989). *Chem. Lett.* **10**, 1719–1722.
 Takeshita, H., Yin, B. Z., Kubo, K. & Mori, A. (1993). *Bull. Chem. Soc. Jpn*, **66**, 3451–3455.
 Tanaka, K., Fujimoto, D. & Toda, F. (2000). *Tetrahedron Lett.* **41**, 6095–6099.
 Yamamoto, E., Kubo, K. & Mori, A. (2003). *Bull. Chem. Soc. Jpn*, **76**, 627–634.