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dihedral angle between the chromanone system and the norbornene six-membered-ring moiety is 54.5 (4)°, and that between the norbornene six-membered ring and the phenyl substituent is 68.0 (1)°.

Comment

The chromanone part of the title compound, (I), comprising rings *A* and *B* in Fig. 1, has useful medicinal properties. Chromanone derivatives dilate the heart

(I)
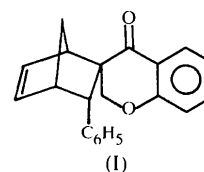
and act as remedies for angina pectoris (Hasegaida, 1967). They also show vasodilating activity on the coronary vascular bed (Nagao *et al.*, 1972). The structural analysis of the title spiro chromanone derivative was performed in order to define the conformation of the 4'-chromanone system with respect to the bicyclo-[2.2.1]heptene (norbornene) moiety.

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3-Phenylspiro[bicyclo[2.2.1]hept-5-ene-2,3'-chroman]-4'-one†

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Abstract

The title compound, $C_{21}H_{18}O_2$, resulted from a Diels–Alder reaction. The chromanone moiety consists of one benzene ring fused with a six-membered heterocyclic ring, which adopts a half-chair conformation. In the bicyclo[2.2.1]heptene (norbornene) unit, the two five-membered rings are in envelope conformations, while the six-membered ring adopts a boat conformation. The
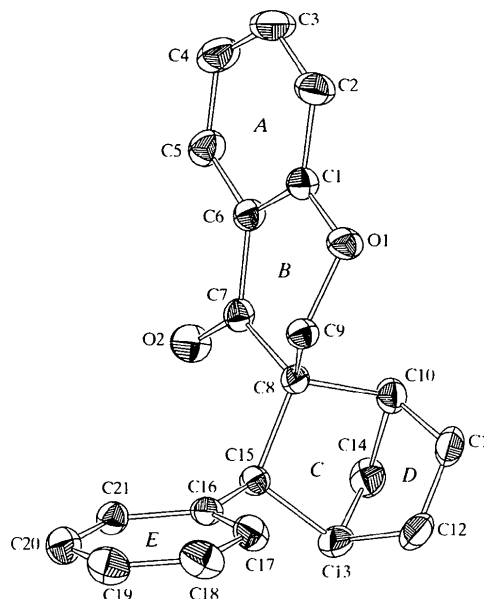
† DCB contribution No. 881.

Fig. 1. A perspective view of the title molecule showing displacement ellipsoids drawn at 50% probability and the atomic numbering scheme.

In the chromanone moiety, ring *B* has a half-chair conformation with Cremer & Pople (1975) parameters $q_2 = 0.392\,(14)$ Å, $q_3 = -0.285\,(13)$ Å, $\varphi_2 = 48.3\,(2)°$, $\theta_2 = 126.0\,(2)°$ and $Q_T = 0.484\,(13)$ Å. The O2 atom deviates by 0.162 (12) Å from the mean plane of ring *B*. The boat conformation of the norbornene six-membered

ring (C8, C10–C13, C15) is evidenced by the puckering parameters: $q_2 = 0.938\,(14)$ Å, $q_3 = 0.037\,(13)$ Å, $\varphi_2 = 56.8\,(6)°$, $\theta_2 = 87.8\,(1)°$ and $Q_T = 0.939\,(14)$ Å. In the norbornene system, the bond lengths and angles show small variations from reported values (Mackay et al., 1994). The C13—C14—C10 angle is contracted to 93.89 (11)° with respect to the regular tetrahedral value, while the endocyclic angles of the five-membered rings are in the range 98.64 (10)–100.34 (10)°, significantly less than 109.5°.

The variations of the bond angles are due to the presence of the double bond in the cyclopentene ring of the norbornene moiety. The two five-membered rings adopt envelope conformations and are orthogonal to each other [86.3 (6)°]. The orientation of the chromanone system is given by the torsion angles C7—C8—C15—C13 = 121.46 (11)° and C9—C8—C10—C11 = 51.84 (13)°. The dihedral angle between the six-membered ring of the norbornene moiety and the substituted phenyl ring is 68.0 (1)°, while the dihedral angle between the plane of the chromanone system and that of the norbornene six-membered ring is 54.5 (4)°. The molecules are held together by C—H···O hydrogen bonds.

Experimental

BF$_3$.OEt$_2$ (10 mmol) was added to a solution of 3-benzylidene-4-chromanone (10 mmol) and cyclopentadiene (10 mmol) in dry methylene chloride under a nitrogen atmosphere, and the reaction mixture was stirred at room temperature for 24 h. After adding water, the product was extracted with methylene chloride, washed with aqueous sodium bicarbonate, dried (Na$_2$SO$_4$) and concentrated under vacuum. The resulting crude product was purified by column chromatography (hexane–EtOAc, 9:1) and crystallized from chloroform (Shanmuga Sundaram & Raghunathan, 1997).

Crystal data

$C_{21}H_{18}O_2$	Mo $K\alpha$ radiation
$M_r = 302.35$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 44
$P\bar{1}$	reflections
$a = 6.739\,(1)$ Å	$\theta = 5.45–10.58°$
$b = 10.731\,(1)$ Å	$\mu = 0.082$ mm^{-1}
$c = 11.606\,(1)$ Å	$T = 293\,(2)$ K
$\alpha = 100.960\,(1)°$	Rectangular block
$\beta = 98.010\,(1)°$	$0.68 \times 0.48 \times 0.38$ mm
$\gamma = 105.11\,(1)°$	Colourless
$V = 779.54\,(10)$ Å^3	
$Z = 2$	
$D_x = 1.288$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.017$
$\theta/2\theta$ scans	$\theta_{max} = 27.51°$
Absorption correction:	$h = -1 \rightarrow 8$
CYLABS (Nardelli, 1997)	$k = -13 \rightarrow 13$
$T_{min} = 0.947$, $T_{max} = 0.970$	$l = -15 \rightarrow 15$
4467 measured reflections	3 standard reflections
3567 independent reflections	every 97 reflections
2640 reflections with	intensity decay: <3%
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.238$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.042$	$\Delta\rho_{min} = -0.166$ e Å^{-3}
$wR(F^2) = 0.130$	Extinction correction:
$S = 1.054$	SHELXL97 (Sheldrick,
3567 reflections	1997)
209 parameters	Extinction coefficient:
H atoms riding	0.018 (5)
$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2]$	Scattering factors from
where $P = (F_o^2 + 2F_c^2)/3$	International Tables for
$(\Delta/\sigma)_{max} < 0.001$	Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C1	1.3631 (16)	C8—C10	1.5929 (17)
O1—C9	1.4416 (15)	C10—C11	1.512 (2)
C1—C6	1.3926 (19)	C10—C14	1.5375 (19)
C6—C7	1.4780 (17)	C11—C12	1.321 (2)
C7—C8	1.5251 (16)	C12—C13	1.510 (2)
C8—C9	1.5211 (16)	C13—C14	1.536 (2)
C8—C15	1.5712 (16)	C13—C15	1.5662 (18)
C1—O1—C9	113.77 (9)	C11—C10—C14	99.68 (11)
O1—C1—C6	122.04 (11)	C11—C10—C8	106.38 (11)
C6—C7—C8	115.73 (10)	C14—C10—C8	100.34 (10)
C9—C8—C7	107.35 (10)	C12—C11—C10	107.59 (12)
C9—C8—C15	113.95 (10)	C11—C12—C13	108.05 (13)
C7—C8—C15	112.03 (9)	C12—C13—C14	99.78 (12)
C9—C8—C10	113.13 (10)	C12—C13—C15	109.97 (11)
C7—C8—C10	108.42 (10)	C14—C13—C15	98.64 (10)
C15—C8—C10	101.87 (9)	C13—C14—C10	93.89 (11)
O1—C9—C8	112.24 (10)		
C1—C6—C7—C8	−3.91 (18)	C8—C10—C14—C13	−58.27 (12)
C1—O1—C9—C8	56.02 (14)	C14—C13—C15—C8	−42.15 (12)
C9—C8—C10—C11	51.84 (13)	C7—C8—C15—C16	−106.85 (12)
C12—C13—C14—C10	−50.15 (12)	C9—C8—C15—C13	−116.41 (11)
C11—C10—C14—C13	50.50 (12)		

H atoms were positioned geometrically and refined using a riding model.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: ZORTEP (Zsolnai, 1997). Software used to prepare material for publication: SHELXL97 and PARST (Nardelli, 1995).

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The geometry of the protonated 3,4-dimethylpyridine molecule is as expected. The Br^- ion is bound *via* a hydrogen bond to the protonated N atom [H1$\cdots$Br1 2.37 (9) Å and N1—H1$\cdots$Br1 163 (8)°] and three further contacts less than 3 Å from the Br^- ion to an aromatic H atom can be found [Br1$\cdots$H2^i 2.96 (2) Å and Br1$\cdots$H2^i—C2^i 123 (2)°; Br1$\cdots$H5^{ii} 2.83 (2) Å and Br1$\cdots$H5^{ii}—C5^{ii} 162 (2)°; Br1$\cdots$H6^{iii} 2.67 (2) Å and Br1$\cdots$H6^{iii}—C6^{iii} 163 (2)°; symmetry codes: (i) $-x$, $-y + 1$, $-z + 2$; (ii) x, y, $z + 1$; (iii) $-x$, $-y$, $-z + 2$].

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The Twinned Crystal Structure of 3,4-Dimethylpyridine Hydrobromide at 157 K

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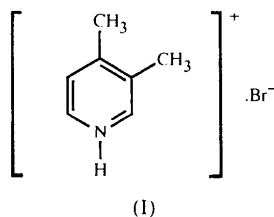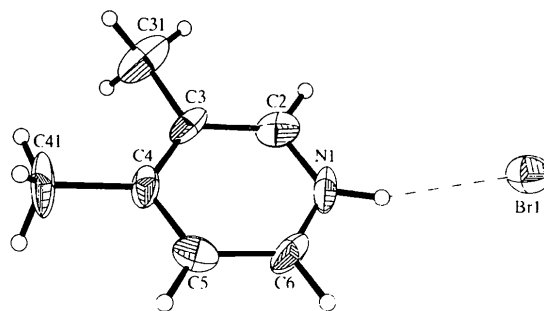
Fig. 1. Perspective view of the title compound with the atom numbering; displacement ellipsoids are at the 50% probability level.

Abstract

Crystals of the title salt, 3,4-dimethylpyridinium bromide, $C_7H_{10}N^+.Br^-$, the structure of which has been determined by single-crystal X-ray diffraction at 157 K, appeared to be twinned. Transformation to a monoclinic *C*-centred cell was necessary in order to derive the twin law. But since the structure is in fact triclinic primitive, cell parameters, reflection indices, coordinates and the twin law have to be transformed back to carry out a proper refinement. The protonated N atom forms a hydrogen bond to the Br^- ion, and three further contacts shorter than 3 Å from the Br^- ion to aromatic H atoms can be found.

Comment

The reaction of 3,4-dimethylpyridine with HBr, accidentally present in another reagent, led to the title compound, (I).

(I)

Experimental

Phenyldibromosilane was dissolved in acetonitrile under an atmosphere of dry argon. The phenyldibromosilane was prepared according to the procedure of Rühlmann & Mansfield (1964) and appears to have been contaminated with HBr. 3,4-Dimethylpyridine was added dropwise at room temperature with stirring. Single crystals of the title compound were obtained after slow evaporation.

Crystal data

$C_7H_{10}N^+.Br^-$	Mo $K\alpha$ radiation
$M_r = 188.07$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 2247
$P\bar{1}$	reflections
$a = 7.3367 (7)$ Å	$\theta = 1–25°$
$b = 7.7985 (8)$ Å	$\mu = 5.055$ mm^{-1}
$c = 8.3960 (9)$ Å	$T = 157$ K
$\alpha = 69.989 (1)°$	Plate
$\beta = 64.152 (1)°$	$0.25 \times 0.20 \times 0.05$ mm
$\gamma = 89.997 (2)°$	Colourless
$V = 399.85 (7)$ Å^3	
$Z = 2$	
$D_x = 1.562$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens CCD three-circle diffractometer	1243 reflections with $I > 2\sigma(I)$