

Cyclopentanone and cyclobutanone

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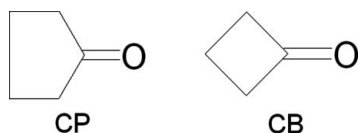
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Crystals of cyclopentanone, C_5H_8O , and cyclobutanone, C_4H_6O , have been grown *in situ* on a diffractometer. The two compounds are isostructural and contain two crystallographically independent molecules. Molecules sitting across twofold axes form antiparallel dipole–dipole dimers, while other molecules in general positions are linked together into ribbons by pairs of $C-H\cdots O$ interactions.

Comment

Over the last several years there has been a noticeable increase in single-crystal X-ray studies of compounds which are liquid or gaseous under ambient conditions. These studies nowadays include not only straightforward structural determinations of pure compounds, sometimes of new potentially important classes, such as room-temperature ionic liquids (Choudhury *et al.*, 2005), but also expand into the emerging area of low-temperature polymorphism (Kirchner *et al.*, 2009) and thus provide fascinating insights into the formation of molecular complexes (cocrystals) in liquid mixtures (Kirchner *et al.*, 2010). Despite such interest, there are still a number of chemical classes left almost unstudied. Interesting results were reported recently on polymorphism in such simple compounds as cyclohexanone (Shallard-Brown *et al.*, 2005; Ibberson, 2006; Yufit & Howard, 2008) and cyclohexanol (Ibberson *et al.*, 2008). Surprisingly, the Cambridge Structural Database (Version 5.3.1 of November 2010; Allen, 2002) contains no information on the structures of other small cyclic ketones and alcohols. In order to close the gap in the literature, we have performed a single-crystal X-ray study of two compounds of this class, namely cyclopentanone (CP) and cyclobutanone (CB), and report here the results obtained.



The crystals of the two compounds turned out to be isostructural (but not isomorphous) and, in both cases, contain two crystallographically independent molecules, one in a

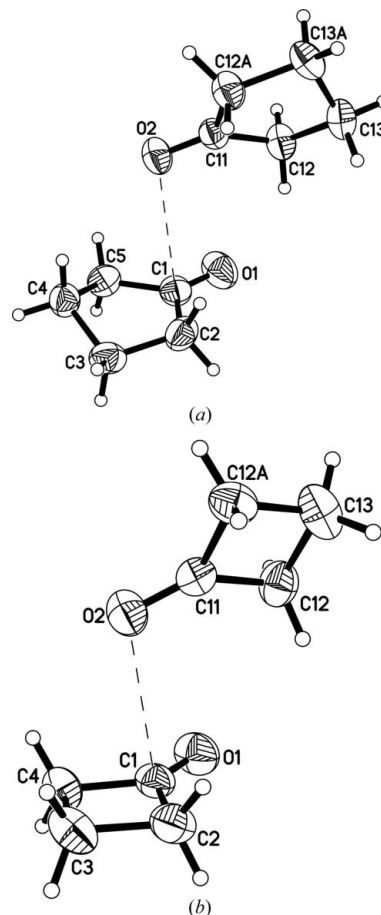


Figure 1

The molecular structure and labelling scheme for (a) CP and (b) CB. Displacement ellipsoids are shown at the 50% probability level.

general position and one sitting across a twofold axis, which passes through both atoms of the carbonyl group. The geometries of the independent molecules in each compound are identical (Fig. 1). The CP molecules adopt half-chair conformations, while the CB molecules are planar. The bond lengths and angles in CP and CB are close to calculated values (Mukhopadhyay *et al.*, 2009). A slight elongation of the carbonyl bond in CP [1.2109 (15) and 1.2148 (15) Å] in comparison with CB [1.2016 (16) and 1.2028 (14) Å] corresponds with theoretical calculations and reflects a higher polarity of that bond in CP.

As noted above, the crystals of CP and CB are isostructural; however, the difference in one methylene group between these two molecules slightly distorts the packing. As a result, similarity to the CP orientation and the position of the CB molecules in the unit cell can be achieved only by refining the CB structure using a unit cell with an acute monoclinic angle and an opposite direction of the *c* axis (Fig. 2). In order to maintain consistency of the description of intermolecular interactions in these structures and to make the comparisons more simple, the structure of CB has been refined in such a nonstandard setting of the $C2/c$ space group.

The packing of molecules in CP and CB is of note: molecules in general positions form dimers with an antiparallel arrangement of the carbonyl groups and with corresponding

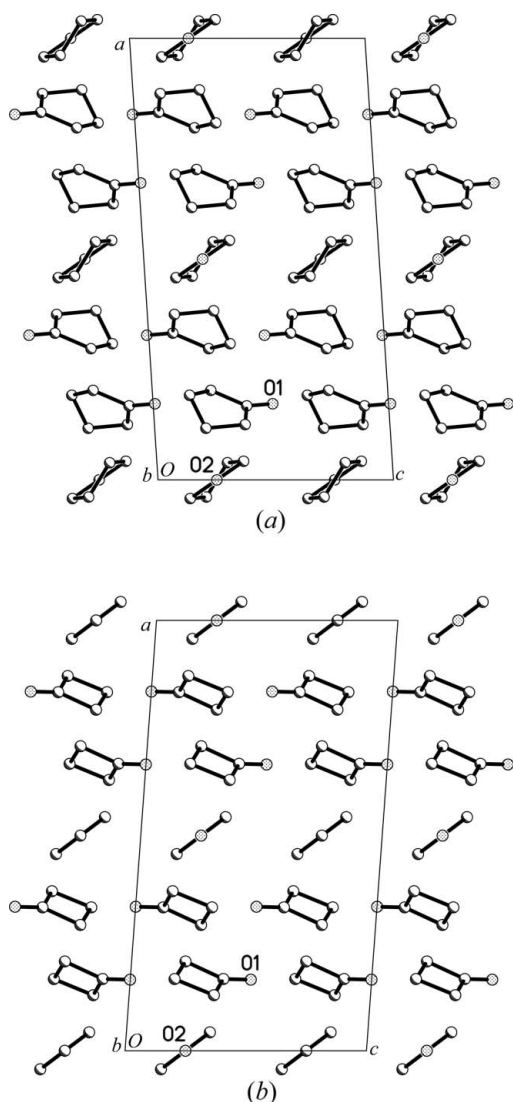


Figure 2
The packing of molecules in the structures of (a) CP and (b) CB. The view is along the *b* axis and H atoms have been omitted for clarity.

$\text{O1} \cdots \text{C1}(-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1)$ distances of 3.1915 (15) and 3.2295 (13) Å in CP and CB, respectively (Fig. 3). Such an arrangement indicates the presence of strong dipole–dipole interactions between these molecules. The geometrical parameters of these and other intermolecular contacts are given in Table 1. In contrast, the molecules sitting across twofold axes are linked together into ribbons, parallel to the *c* direction, by pairs of $\text{C}—\text{H} \cdots \text{O}$ interactions. There are short $\text{O} \cdots \text{C}(\text{carbonyl})$ contacts [3.2425 (12) and 3.0924 (11) Å in CP and CB, respectively] between molecules in ribbons and in dimers, but in these contacts the carbonyl groups are nonparallel and form $\text{O1}—\text{C1} \cdots \text{O2}—\text{C11}$ torsion angles of -46.90 (8) and -47.91 (8)° in CP and CB, respectively, and therefore they cannot be regarded as dipole–dipole interactions. The $\text{C}—\text{C}(=\text{O})—\text{C}$ planes of the molecules involved in these $\text{O} \cdots \text{C}$ interactions are inclined at 57.29 (7) (in CP) and 62.58 (8)° (in CB) to each other, so one of the lone pairs of electrons of the O atom is directed towards the carbonyl C atom of one of the dimer molecules.

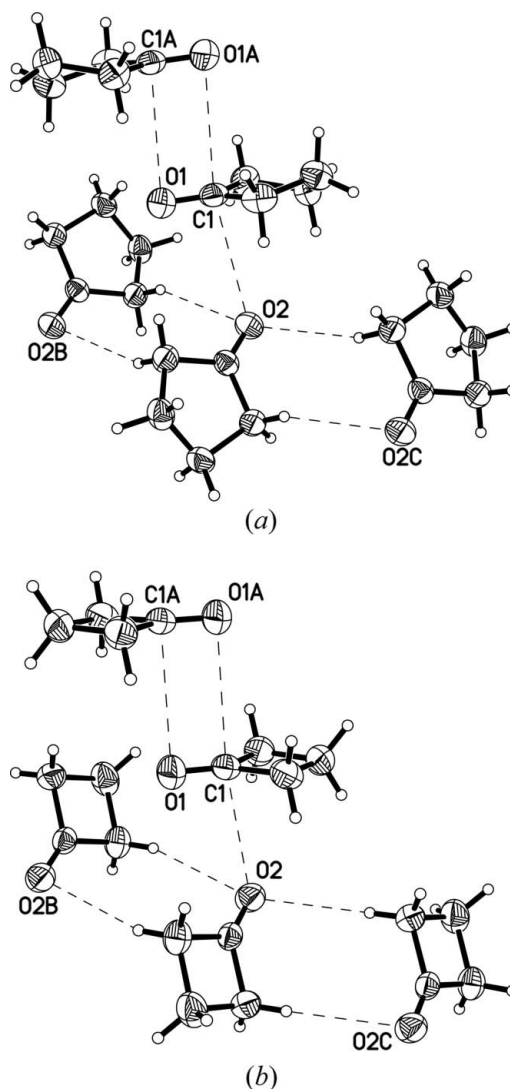


Figure 3
Fragments of the structures of (a) CP and (b) CB, showing the intermolecular contacts. [Symmetry codes: (A) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (B) $-x, -y + 1, -z + 1$; (C) $x, -y + 1, z - \frac{1}{2}$.]

Thus, these small cyclic ketones show several different types of intermolecular interactions within the same structure. The observed packing pattern is quite different from those found in several polymorphs of cyclohexanone, where the molecules are linked by various $\text{C}—\text{H} \cdots \text{O}$ interactions but not by dipole–dipole interactions (Shallard-Brown *et al.*, 2005; Ibberson, 2006; Yufit & Howard, 2008). Interestingly, cyclopentanone solvent molecules in other crystals either do not interact with each other (Toda *et al.*, 2000) or form $\text{C}—\text{H} \cdots \text{O}$ -linked dimers or chains (Bock *et al.*, 1998; Liu *et al.*, 2006), similar to those found in CP, but no dipole–dipole-linked dimers were observed. To the best of our knowledge, no cocrystals containing cyclobutanone molecules have been reported so far.

Experimental

The liquid samples were sealed in 0.3 mm borosilicate glass capillaries which were mounted on a diffractometer using a special attachment

Table 1

Parameters of intermolecular contacts in CP and CB (Å, °).

	$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
CP	$C12-H122\cdots O2^i$	0.985 (15)	2.655 (15)	3.5384 (13)	149.4 (11)
CB	$C12-H121\cdots O2^i$	0.931 (16)	2.659 (16)	3.5625 (13)	163.7 (12)
CP	$O2\cdots C1$			3.1915 (15)	
CB	$O2\cdots C1$			3.0924 (11)	
CP	$O1\cdots C1^{ii}$			3.2425 (12)	
CB	$O1\cdots C1^{ii}$			3.2295 (13)	

Symmetry codes: (i) $-x, -y + 1, -z + 1$ and $x, -y + 1, z - \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.

(Yufit & Howard, 2005). The crystals of both compounds were grown *in situ* on a diffractometer by flash-freezing of the overcooled liquid at 220 K, followed by partial melting of the resulting polycrystalline material and slow growing of the crystals at 200.5 K. The cylindrical crystals which formed were cooled to 200 K and data were collected at this temperature. In both cases, the data were collected using two 180° ω scans with a step size of -0.3° . Between the scans the crystals were manually rotated by 180° around the ω axis. This data collection mode does not cover the whole sphere of data and the coverage up to $\sin\theta/\lambda = 0.65$ was 88 and 98% for CP and CB, respectively. The difference in coverage is caused by different orientations of the crystals inside the capillaries.

CP

Crystal data

C_5H_8O	$V = 1454.7 (2) \text{ \AA}^3$
$M_r = 84.11$	$Z = 12$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 16.7421 (16) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$b = 9.7941 (8) \text{ \AA}$	$T = 200 \text{ K}$
$c = 8.8898 (7) \text{ \AA}$	$0.5 \times 0.3 \times 0.3 \text{ mm}$
$\beta = 93.69 (2)^\circ$	

Data collection

Bruker SMART CCD 6000 area-detector diffractometer	1660 independent reflections
6027 measured reflections	1336 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	132 parameters
$wR(F^2) = 0.099$	All H-atom parameters refined
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
1660 reflections	$\Delta\rho_{\text{min}} = -0.14 \text{ e \AA}^{-3}$

CB

Crystal data

C_4H_6O	$V = 1212.9 (2) \text{ \AA}^3$
$M_r = 70.09$	$Z = 12$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 15.5022 (16) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$b = 9.0662 (9) \text{ \AA}$	$T = 200 \text{ K}$
$c = 8.6531 (7) \text{ \AA}$	$0.5 \times 0.35 \times 0.35 \text{ mm}$
$\beta = 85.83 (3)^\circ$	

Data collection

Bruker SMART CCD 6000 area-detector diffractometer	1440 independent reflections
5379 measured reflections	1127 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	106 parameters
$wR(F^2) = 0.121$	All H-atom parameters refined
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.23 \text{ e \AA}^{-3}$
1440 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$

As mentioned in the *Comment*, in order to maintain consistency in the description of the structures of CP and CB, the CB structure was refined in a nonstandard setting of the $C2/c$ space group with an acute β angle. The data were collected in a standard setting and then the cell parameters in the input file were changed manually. Also, the signs of the L indices in the hkl file were changed to the opposite ones with the help of a locally written service program.

For both compounds, data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3210). Services for accessing these data are described at the back of the journal.

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