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rac-3-Benzoyl-2-methylpropionic acid and its organic salts: possibilities of Yang photocyclization in crystals

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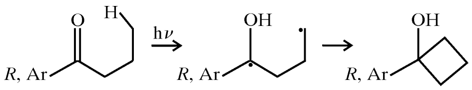
The analysis of the crystal structures of *rac*-3-benzoyl-2-methylpropionic acid, $C_{11}H_{12}O_3$, (I), morpholinium *rac*-3-benzoyl-2-methylpropionate monohydrate, $C_4H_{10}NO^+\cdot C_{11}H_{11}O_3^-\cdot H_2O$, (II), pyridinium [hydrogen bis(*rac*-3-benzoyl-2-methylpropionate)], $C_5H_6N^+\cdot(H^+\cdot 2C_{11}H_{11}O_3^-)$, (III), and pyrrolidinium *rac*-3-benzoyl-2-methylpropionate *rac*-3-benzoyl-2-methylpropionic acid, $C_4H_{10}N^+\cdot C_{11}H_{11}O_3^-\cdot C_{11}H_{12}O_3$, (IV), has enabled us to predict and understand the behaviour of these compounds in Yang photocyclization. Molecules containing the Ar—CO—C—C—CH fragment can undergo Yang photocyclization in solvents but they can be photoinert in the crystalline state. In the case of the compounds studied here, the long distances between the O atom of the carbonyl group and the γ-H atom, and between the C atom of the carbonyl group and the γ-C atom preclude Yang photocyclization in the crystals. Molecules of (I) are deprotonated in a different manner depending on the kind of organic base used. In the crystal structure of (III), strong centrosymmetric $O\cdots H\cdots O$ hydrogen bonds are observed.

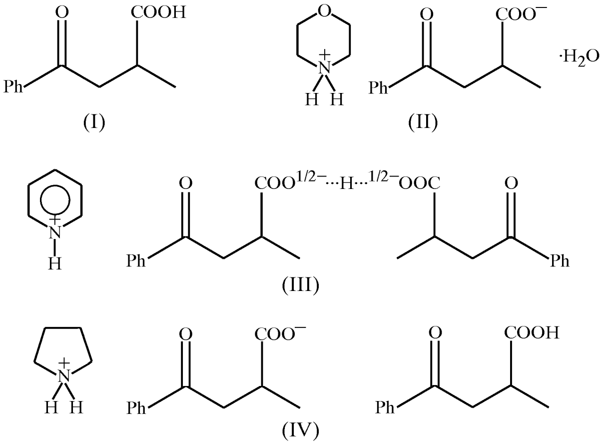
Comment

Many chemists are interested in photochemical reactions in crystals. The reasons for this are of a practical and theoretical nature (Boldyreva, 1999). Such reactions are often highly selective and can serve as a source of pure products impossible to obtain in solutions. They are environmentally friendly because they are carried out without the use of solvents (green chemistry) (Tanaka, 2003). They are also applied in modern technologies (Balzani, 2003; Dürr & Bouas-Laurent, 1990; Irie, 2000).

Photochemical reactions in crystals are also the subject of our interest. Our studies concern the step-by-step monitoring of structural changes during 'reactant crystal → product crystal' phototransformations. In particular, we study variations in the reaction centre and the positions of molecules. In the past, we have studied intermolecular photochemical reactions (Turowska-Tyrk, 2001, 2003; Turowska-Tyrk & Trzop, 2003). Our present interests are associated with intramolecular photochemical processes (Turowska-Tyrk, Bąkowicz, Scheffer & Xia, 2006; Turowska-Tyrk, Trzop, Scheffer & Chen, 2006; Turowska-Tyrk, Bąkowicz, Scheffer, 2007; Turowska-Tyrk, Łabęcka, Scheffer & Xia, 2007; Trzop & Turowska-Tyrk, 2008), mainly Yang photocyclization.



A molecule containing a carbonyl group and a γ-H atom can create a 1,4-hydroxy biradical in a Norrish type II photoreaction (see scheme above) (Braslavsky, 2007). In the next step, named Yang photocyclization, a cyclobutane ring can be formed from such a biradical (Braslavsky, 2007; Chen *et al.*, 2004; Yang *et al.*, 2005). For instance, Ph–CO–CH_2–CH_2–CH_2–CH_3, Ph–CO–CH_2–CH_2–$CH(CH_3)$–CH_2–CH_3 and other compounds of similar formulae undergo Yang photocyclization in solvents (Wagner, 1971). Compounds which are photoactive in solvents can be photoinert in the crystalline state. In this paper, we analyse the crystal structures of *rac*-3-benzoyl-2-methylpropionic acid, (I), morpholinium *rac*-3-benzoyl-2-methylpropionate monohydrate, (II), pyridinium [hydrogen bis(*rac*-3-benzoyl-2-methylpropionate)], (III), and pyrrolidinium *rac*-3-benzoyl-2-methylpropionate *rac*-3-benzoyl-2-methylpropionic acid, (IV), in order to predict and understand the behaviour of these compounds in Yang photocyclization in crystals and to check the influence of organic cations on this reaction. As can be seen in the scheme below, the compounds may be presented by the general formula given in the first scheme; potentially, they can form 1,4-hydroxy biradicals and can undergo Yang photocyclization (Braga *et al.*, 2004; Chen *et al.*, 2004; Wagner, 1971).



Figs. 1–4 present views of the crystal lattice fragments and strong hydrogen bonds for compounds (I)–(IV), respectively. In the case of compound (I), molecules of the 3-benzoyl-2-methylpropionic acid form centrosymmetric dimers. The step between the planes of two carboxylic acid groups in the dimer is very small, *viz.* 0.12 and 0.03 Å for symmetrically independent molecules *A* and *B*, respectively. In the crystal structure of compound (II), all molecules of the acid are deprotonated. Anions, cations and water molecules are involved in strong

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N—H···O and O—H···O hydrogen bonds, forming ribbons along the *b* crystal axis. Cations are located inside these ribbons. A very interesting situation takes place in the crystal of compound (III), namely two symmetrically dependent anions have contacts with the same H atom located on an inversion centre and a cationic species lies on a twofold axis. The distances between this H atom and two neighbouring O atoms are both 1.236 (2) Å. This short O···O distance and the linear O···H···O geometry indicate the existence of a strong hydrogen bond. Symmetric hydrogen bonds have also been observed in the crystal structures of several other carboxylic acids and pyridines (Bhogala *et al.*, 2005; Wilson, 2001; Wilson *et al.*, 2003). O···H···O and N—H···O hydrogen bonds form zigzags along the *c* crystal axis. In the crystal structure of compound (IV), only half of the molecules of the acid are dissociated (molecules *A*) but all molecules of the amine are protonated. N—H···O and O—H···O hydrogen bonds form ribbons along the *c* crystal axis. The geometry of the hydrogen bonds in compounds (I)–(IV) is presented in Table 1.

Fig. 5 shows a superposition of the molecules and anions of compounds (I)–(IV). As can be seen, the presence of organic cations in the crystal structures of compounds (II)–(IV) does not cause significant changes in the overall shape of the anions. The methyl group containing the γ-H atoms and the carbonyl group are situated on different sides of the chain. This arrangement has an impact on the reactivity of the compounds in a Norrish–Yang photoreaction. In general, the reactivity of compounds in a Norrish–Yang photoreaction in the crystalline state is influenced by several geometric parameters (Ihmels & Scheffer, 1999; Natarajan *et al.*, 2005). Fig. 6 presents a definition of these parameters, and Table 2 gives their ideal and average literature values for compounds undergoing this photoreaction (Natarajan *et al.*, 2005; Xia *et al.*, 2005), and additionally the values for compounds (I)–(IV). These data indicate that compounds (I)–(IV) will not undergo Yang photocyclization in the crystalline state. The distance between

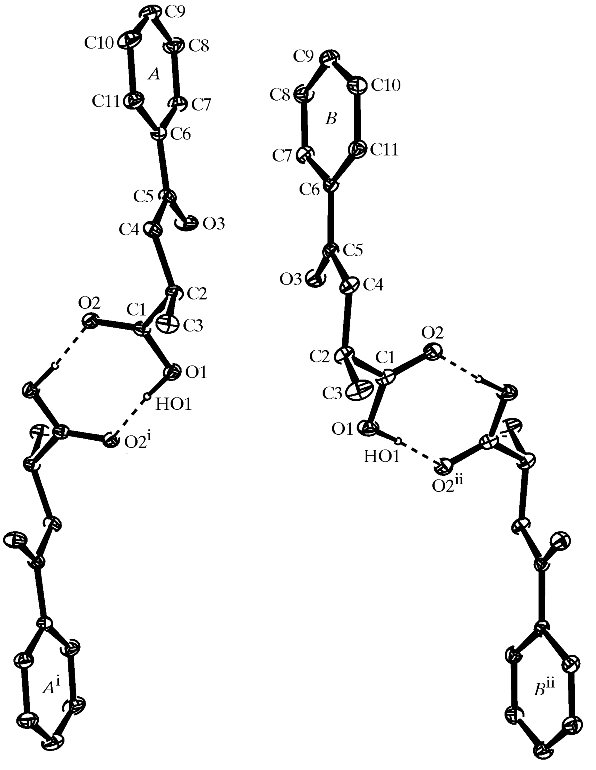


Figure 1
A view of the hydrogen-bonded dimers for compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 10% probability level. H atoms not taking part in hydrogen bonds have been omitted for clarity. See Table 1 for symmetry codes.

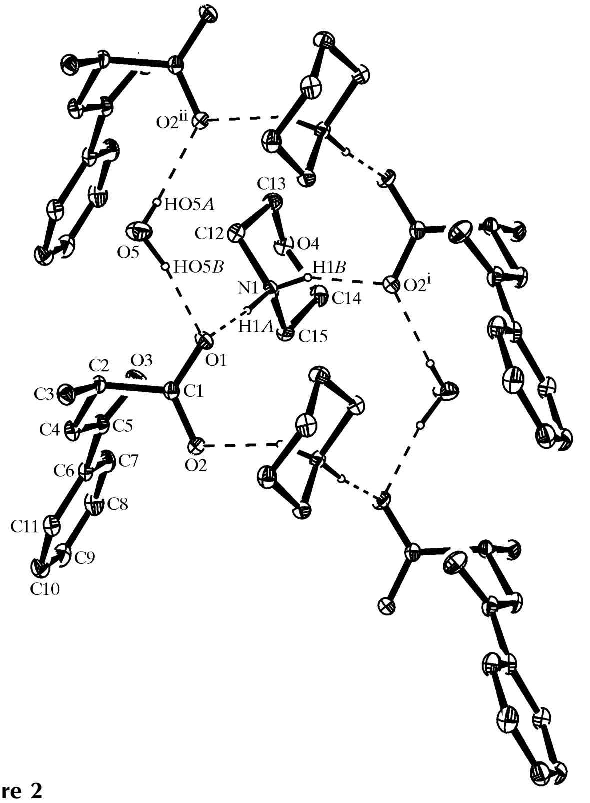


Figure 2
A view of the crystal lattice fragment for compound (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 10% probability level. H atoms not taking part in hydrogen bonds have been omitted for clarity. See Table 1 for symmetry codes.

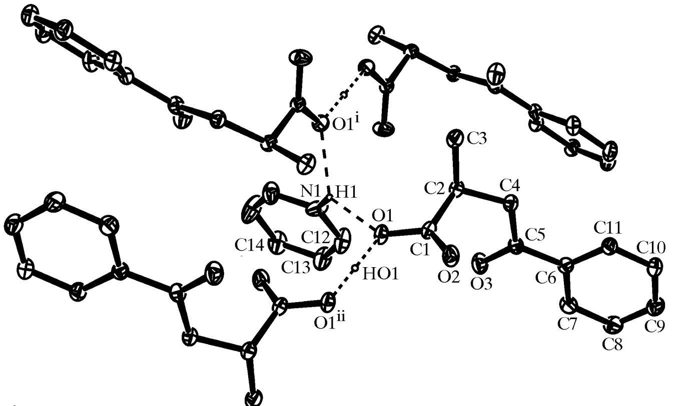


Figure 3
A view of the crystal lattice fragment for compound (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 10% probability level. H atoms not taking part in hydrogen bonds have been omitted for clarity. See Table 1 for symmetry codes.

the carbonyl C atom and the γ-C atom, parameter D, is too large (*ca* 3.9 Å) in comparison with the average literature value (3.0 Å). Yang photocyclization was not observed in crystals where D was larger than 3.2 Å (Xia *et al.*, 2005). The carbonyl O and γ-H atoms are also too far from each other; parameter d is larger than 4.5 Å (average literature value is *ca* 2.6 Å). The values of these two parameters preclude the possibility of Yang photocyclization of compounds (I)–(IV) in the crystalline state.

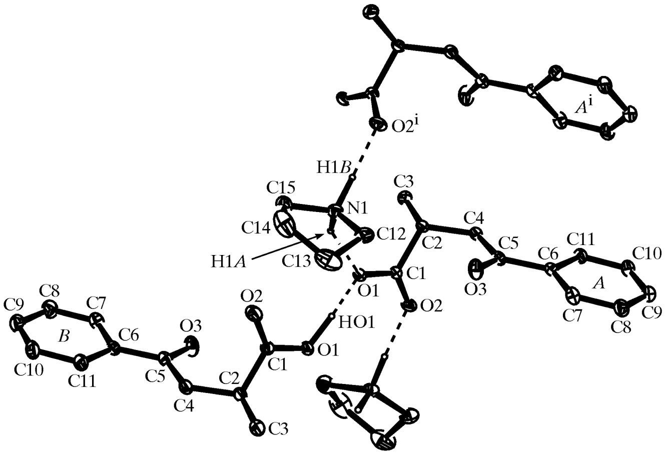


Figure 4
A view of the crystal lattice fragment for compound (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 10% probability level. H atoms not taking part in hydrogen bonds have been omitted for clarity. See Table 1 for symmetry code.

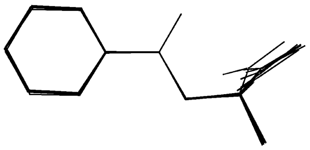
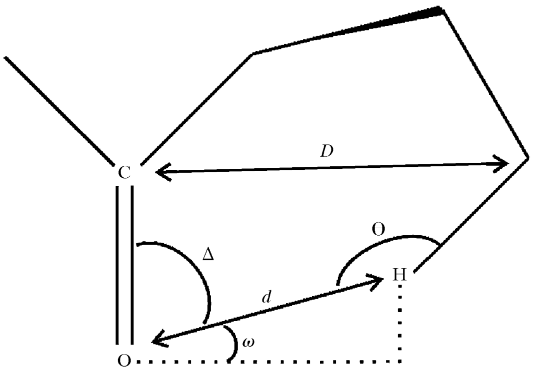


Figure 5
Superposition of the molecules and anions of compounds (I)–(IV).



d C=O···γ-H distance
D O=C···γ-C distance
ω deviation of γ-H from the mean plane of the carbonyl group
Δ CO···H angle
Θ CH···O angle

Figure 6
Definition of the parameters influencing the reactivity of compounds in a Norrish–Yang photoreaction in the crystalline state.

Experimental

Compound (I) was purchased from Sigma–Aldrich. Organic salts (II)–(IV) were prepared by us. Morpholine (0.1 ml, 0.0011 mol) was added to compound (I) (0.192 g, 0.0010 mol) dissolved in toluene (10 ml). The mixture was left for evaporation at room temperature. After 1 d, colourless crystals of (II) were collected. Pyridine (0.0435 g, 0.00055 mol) and pyrrolidine (0.03912 g, 0.00055 mol) were added to compound (I) (0.100 g, 0.0005 mol) dissolved in toluene (10 ml). After several days, colourless crystalline products, (III) and (IV), were collected and recrystallized from toluene.

Compound (I)

Crystal data

$C_{11}H_{12}O_3$
M_r = 192.21
Monoclinic, $P2_1/c$
a = 14.951 (3) Å
b = 6.0452 (9) Å
c = 22.935 (4) Å
β = 101.201 (17)°
V = 2033.4 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 299 (2) K
0.40 × 0.20 × 0.20 mm

Data collection

Kuma KM-4-CCD diffractometer
10560 measured reflections
3550 independent reflections
1715 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.056

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.139
S = 0.95
3550 reflections
261 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.16 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.15 e Å^{-3}

Compound (II)

Crystal data

$C_4H_{10}NO^+\cdot C_{11}H_{11}O_3^-\cdot H_2O$
M_r = 297.34
Monoclinic, $P2_1/n$
a = 15.010 (5) Å
b = 6.697 (2) Å
c = 16.017 (5) Å
β = 99.21 (3)°
V = 1589.3 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 299 (2) K
0.50 × 0.20 × 0.10 mm

Data collection

Kuma KM-4-CCD diffractometer
8314 measured reflections
2746 independent reflections
1366 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.128
S = 0.96
2746 reflections
198 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max}$ = 0.12 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.17 e Å^{-3}

Compound (III)

Crystal data

$C_5H_6N^+\cdot H^+\cdot 2C_{11}H_{11}O_3^-$
M_r = 463.51
Monoclinic, $C2/c$
a = 25.759 (6) Å
b = 10.172 (2) Å
c = 9.776 (2) Å
β = 96.34 (2)°
V = 2545.8 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 299 (2) K
0.60 × 0.30 × 0.15 mm

Data collection

Kuma KM-4-CCD diffractometer
6670 measured reflections
2199 independent reflections
1454 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.210$
$S = 1.11$
2199 reflections
156 parameters
7 restraints
H-atom parameters constrained
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

Compound (IV)

Crystal data

$C_4H_{10}N^+ \cdot C_{11}H_{11}O_3^- \cdot C_{11}H_{12}O_3$
$M_r = 455.53$
Monoclinic, $P2_1/c$
$a = 26.249$ (9) Å
$b = 9.556$ (3) Å
$c = 9.869$ (3) Å
$\beta = 95.32$ (3)°
$V = 2464.8$ (14) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 299$ (2) K
0.35 × 0.25 × 0.20 mm

Data collection

Kuma KM-4-CCD diffractometer
12988 measured reflections
4295 independent reflections
1733 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.199$
$S = 0.96$
4295 reflections
310 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 1
Geometry of strong hydrogen bonds in the crystal structures of compounds (I)–(IV) (Å, °).

	D—H	H···A	D···A	D—H···A
(I)				
O1A—HO1A···O2A^{i}	0.94 (4)	1.70 (4)	2.634 (3)	172 (4)
O1B—HO1B···O2B^{ii}	1.02 (5)	1.65 (5)	2.667 (3)	176 (4)
(II)				
N1—H1A···O1	0.90	1.85	2.732 (3)	167
N1—H1B···O2$^{\text{i}}$	0.90	1.86	2.717 (3)	158
O5—HO5B···O1	0.93 (4)	1.89 (4)	2.810 (4)	170 (4)
O5—HO5A···O2$^{\text{ii}}$	0.77 (4)	2.06 (4)	2.823 (4)	176 (4)
(III)				
N1—H1···O1	0.86	2.18	2.806 (3)	130
N1—H1···O1$^{\text{i}}$	0.86	2.18	2.806 (3)	130
O1···HO1···O1$^{\text{ii}}$	1.24	1.24	2.473 (4)	180
(IV)				
N1—H1A···O1A	0.97 (4)	1.91 (4)	2.769 (4)	146 (3)
N1—H1B···O2A^{i}	1.08 (5)	1.63 (5)	2.683 (4)	166 (4)
O1B—HO1B···O1A	1.13 (5)	1.39 (5)	2.521 (3)	176 (4)

Symmetry codes for (I): (i) $-x, -y+2, -z$; (ii) $-x+1, -y+1, -z$. Symmetry codes for (II): (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, y+1, z$. Symmetry codes for (III): (i) $-x, y, -z+\frac{1}{2}$; (ii) $-x, -y+1, -z$. Symmetry code for (IV): (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$.

H atoms were positioned geometrically and treated as riding, with C—H = 0.93–0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl groups or $1.2U_{\text{eq}}(\text{C})$ for the remaining groups. H atoms of carboxyl groups, the water molecule and on the N atom of the pyrrolidinium cation were located in difference Fourier maps and refined without constraints. Several geometric restraints for bond lengths and angles were applied for the pyridinium cation owing to features of disorder.

Table 2
Values of geometric parameters influencing Yang photocyclization.

	d (Å)	D (Å)	ω (°)	Δ (°)	Θ (°)
Ideal value	<2.7		0	90–120	180
Average literature value†	2.64 (8)	3.00 (9)	54 (10)	82 (8)	116 (3)
(IA)	4.58	3.87	−17.8	56.9	64.3
(IB)	4.59	3.86	14.1	57.4	63.9
(II)	4.60	3.85	−9.5	58.0	63.6
(III)	5.31	3.85	14.3	57.7	68.0
(IVA)	4.58	3.86	13.3	56.9	65.8
(IVB)	4.57	3.86	13.2	57.7	65.7

† The mean values of d, ω, Δ and Θ are given for 54 aromatic ketones undergoing Yang photocyclization (Natarajan *et al.*, 2005) and that of D for 53 structures (Xia *et al.*, 2005).

For all four compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3242). Services for accessing these data are described at the back of the journal.

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