The Acetylacetonate Ion as its *E/Z*-Isomer in 1,3-Diisopropyl-4,5-dimethylimidazolium Acetylacetonate

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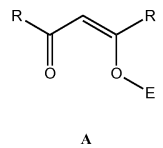
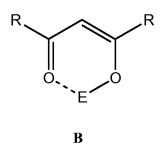
1,3-Diisopropyl-4,5-dimethylimidazolium acetylacetonate (**2**) is obtained from 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) and acetylacetone. Its crystal structure reveals the presence of ion pairs linked by C–H···O hydrogen bonds. In **2**, the acetylacetonate ion adopts the structure of its *E*/*Z*-isomer (**C**).

Key words: Heterocycles, Hydrogen Bonds, β-Diketonates, Crystal Structure

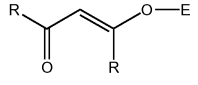
β-Diketone derivatives exist as *Z*/*Z*-, *E*/*Z*-, or *E*/*E*-isomers (**A** – **D**). While in most metal acetylacetonates the ligand commonly adopts structure **A** [1] as a consequence of the stabilizing chelate effect, with soft metal centers central C-coordination is observed [2]. In organic compounds, however, structures **C** and **D** are preferred (E = electrophile) [3]. The single crystal structure analyses of benzoylacetone [4] and acetylacetone itself [5] have revealed the presence of the type **A** tautomer including an O–H···O hydrogen bond, while in [{((*S,S,R,R*)-TangPhos)$_2$}Rh][acac] ((*S,S,R,R*)-TangPhos = **3**) the uncoordinated anion exhibits the *E*/*Z* configuration [6]. In the course of our investigation on the structural chemistry of imidazolium salts [7, 8] we became interested in the structure of the acetylacetonate ion linked to an organic cation by a hydrogen bond.



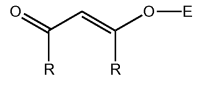
A



B



C



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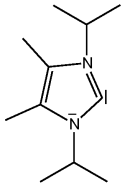
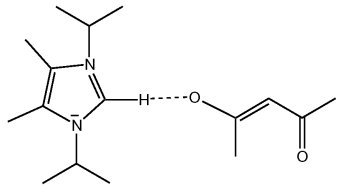
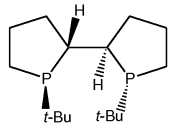


1



2



3

2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) reacts with acetylacetone to give 1,3-diisopropyl-4,5-dimethylimidazolium acetylacetonate (**2**) in good yield. Its crystal structure analysis (Table 1, Fig. 1) reveals the presence of ion pairs linked by C–H···O hydrogen bonds [C(5)–H(5A) 0.963, H(5A)···O(20) 2.132 Å; C(5)–H(5A)···O(20) 172.6°] [9]. The acetylacetonate ion in **2** adopts the structure of its *E*/*Z*-isomer, the bond lengths and angles being very close to those found in [{((*S,S,R,R*)-TangPhos)$_2$}Rh][acac] [6] (for details see Table 2). The structure of the cation parallels that of numerous salts already reported [7, 8]. The solid state ^{13}C NMR spectrum (MAS) confirms the result of the crystal structure analysis, the chemical shift values for the anion being δ = 26.0, 30.9, 101.7, and 190.3. However, in solution ^{1}H and ^{13}C NMR spectra only the signals of the cation could be detected indicating a rapid dynamic process of the

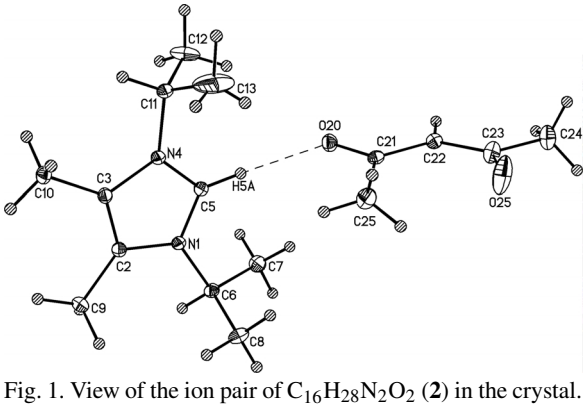


Fig. 1. View of the ion pair of $C_{16}H_{28}N_2O_2$ (**2**) in the crystal.

acetylacetonate anion in CD_2Cl_2 at ambient temperature.

Apparently, only minor differences in energy exist for the acetylacetone tautomers as concluded from neutron scattering experiments [10]. The configuration of β-diketone derivatives may be interpreted in terms of conflicting effects. The Z/Z-configuration is favored in metal complexes as a consequence of the stabilizing chelate effect and is present even in alkali metal complexes [11]. On the other hand, the close approach of negative charges at the oxygen atoms in the Z/Z-configuration favors the E/Z configuration in compounds containing un-coordinated or η^1-coordinated acetylacetonates. The different conformations of the acetylacetonate fragment in acetylacetone itself and in **2** may be influenced by the tendency to avoid bifurcated hydrogen bridges.

Experimental Section

All experiments were performed in purified solvents under argon. 2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (**1**) was obtained by a published procedure [12].

CCDC 698829 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

$C_{16}H_{28}N_2O_2$ (2)

To a solution of 2,3-dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (0.300 g, 1.67 mmol) in THF (25 mL) acetylacetone (0.334 g, 3.33 mmol) was added at −30 °C. After stirring for 2 h at r. t., the precipitate was filtered off, washed with diethyl ether and dried *in vacuo*. Yield after recrystallization from acetone/diethyl ether: 0.326 g (70 %). – ^{1}H NMR (CD_2Cl_2): δ = 1.53 (d, 12 H, 1,3-CH*Me*$_2$, ^3J = 7 Hz), 2.17 (s, 6 H, 4,5-Me), 4.39 (sept, 2 H, 1,3-C*H*Me$_2$), acac not observed. – ^{13}C NMR (CD_2Cl_2): δ = 8.8 (4,5-Me), 29.4 (1,3-CH*Me*$_2$), 51.2 (1,3-*C*HMe$_2$), 126.1 (C^2), 134.4 (C^{4,5}), acac not observed. – ^{13}C NMR (MAS): 9.8, 10.6 (4,5-Me$_{Im}$), 23.6 (1,3-CH*Me*$_{Im}$), 26.0, 30.9 (Me$_{acac}$), 51.7 (1,3-*C*HMe$_{Im}$), 101.7 (CH$_{acac}$), 129.0 (C^2$_{Im}$), 135.0 (C^{4,5}$_{Im}$), 190.3 (CO$_{acac}$). – IR (KBr): ν(CO) = 1631 (s), 1585 (s) cm^{-1}. – Elemental analysis for $C_{16}H_{28}N_2O_2$ (280.41): calcd. C 68.53, H 10.06, N 9.99; found C 68.43, H 10.73, N 10.02.

Table 1. Crystal data and structure refinement for $C_{16}H_{28}N_2O_2$ (**2**).

Empirical formula	$C_{16}H_{28}N_2O_2$
Formula weight, g mol^{-1}	280.40
Temperature, K	173(2)
Wavelength, Å	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	11.928(2)
b, Å	10.379(2)
c, Å	13.615(3)
β, deg	102.87(3)
V, Å^3	1643.2(6)
Z	4
Density, g·cm^{-3}	1.133
μ(MoK_α), mm^{-1}	0.074
F(000), e	616
θ range for data collection, deg	3.07 – 26.37
hkl ranges	±14, ±12, ±17
Reflections collected/independent	23116/3348
R_{int}	0.094
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3348 / 0 / 294
Goodness-of-fit on F^2	1.063
$R1$	0.051
$wR2$ (all data)	0.119
$\Delta\rho$ (max/min), e Å^{-3}	0.33/–0.31

Table 2. Selected bond lengths (Å) and angles (deg) for $C_{16}H_{28}N_2O_2$ (**2**).

N(1)–C(5)	1.330(2)	C(5)–N(1)–C(2)	109.3(1)
N(1)–C(2)	1.393(2)	C(5)–N(4)–C(3)	109.1(1)
N(4)–C(5)	1.334(2)	C(3)–C(2)–N(1)	106.6(1)
N(4)–C(3)	1.392(2)	C(2)–C(3)–N(4)	106.7(1)
O(20)–C(21)	1.263(2)	N(1)–C(5)–N(4)	108.3(1)
O(25)–C(23)	1.245(2)	O(20)–C(21)–C(22)	122.9(1)
C(2)–C(3)	1.361(2)	O(20)–C(21)–C(25)	116.6(2)
C(21)–C(22)	1.402(2)	C(22)–C(21)–C(25)	120.5(2)
C(21)–C(25)	1.515(2)	C(21)–C(22)–C(23)	127.2(2)
C(22)–C(23)	1.415(2)	O(25)–C(23)–C(22)	126.4(2)
C(23)–C(24)	1.521(3)	O(25)–C(23)–C(24)	116.6(2)
		C(22)–C(23)–C(24)	117.1(2)

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