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

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1,3-Diisopropyl-4,5-dimethylimidazolium acetylacetone (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 acetylacetone 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\textsubscript{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 acetylacetone ion linked to an organic cation by a hydrogen bond.

2,3-Dihydro-1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (1) reacts with acetylacetone to give 1,3-diisopropyl-4,5-dimethylimidazolium acetylacetone (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. In 2, the acetylacetone ion adopts the structure of its E/Z-isomer (C).

The structure of the cation parallels that of numerous salts already reported [7, 8]. The solid state \textsuperscript{13}C NMR spectrum (MAS) confirms the result of the crystal structure analysis, the chemical shift values for the anion being \( \delta = 26.0, 30.9, 101.7, \) and 190.3. However, in solution \textsuperscript{1}H and \textsuperscript{13}C NMR spectra only the signals of the cation could be detected indicating a rapid dynamic process of the
acetylacetonate anion in CD$_2$Cl$_2$ 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 acetylacetones. 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 (I) 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$_2$Cl$_2$): $\delta = 1.53$ (d, 12 H, 1,3-CHMe$_2$,$^3$J = 7 Hz), 2.17 (s, 6 H, 4,5-Me), 4.39 (sept, 2 H, 1,3-CHMe$_2$), acac not observed. – $^{13}$C NMR (CD$_2$Cl$_2$): $\delta = 8.8$ (4,5-Me), 29.4 (1,3-CHMe$_2$), 51.2 (1,3-CHMe$_2$), 126.1 (C$^2$), 134.4 (C$^4$-$^5$), acac not observed. – $^{13}$C NMR (MAS): 9.8, 10.6 (4,5-Me$^1$), 23.6 (1,3-CHMe$_2$), 26.0, 30.9 (Me$^1$acac), 51.7 (1,3-CHMe$_2$), 101.7 (CH$^1$acac), 129.0 (C$^2$-Im$^1$), 135.0 (C$^4$-$^5$-Im$^1$), 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.

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