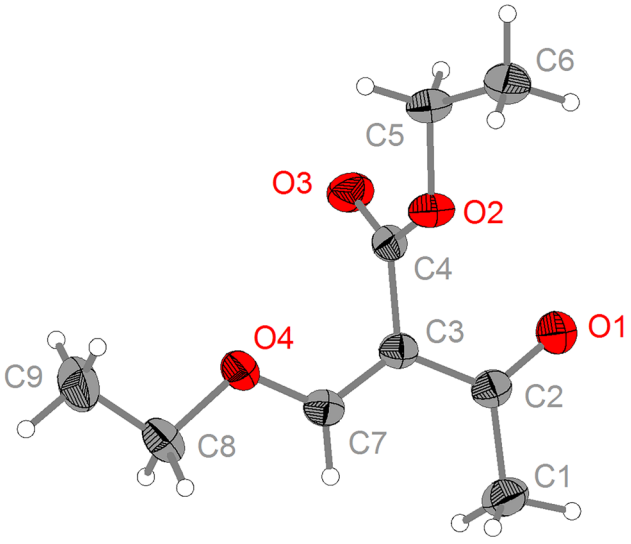
Andreas Hentsch and Kurt Merzweiler*

# The crystal structure of ethyl (*Z*)-2-(ethoxymethylene)-3-oxobutanoate, $C_9H_{14}O_4$




https://doi.org/10.1515/ncrs-2024-0230
Received May 27, 2024; accepted July 11, 2024;
published online August 13, 2024

**Abstract**

$C_9H_{14}O_4$, monoclinic, $P2_1/n$ (no. 14), $a$ = 8.9332(5) Å, $b$ = 6.8170(2) Å, $c$ = 17.0530(9) Å, $\beta$ = 102.816(4)°, $V$ = 1,012.62(8) Å$^3$, $Z$ = 4, $R[F^2 > 2\sigma(F^2)]$ = 0.0363, $wR(F^2)$ = 0.1046, T = 170 K.

**CCDC no.:** 2369843

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

## 1 Source of material

Ethyl (*Z*)-2-(ethoxymethylene)-3-oxobutanoate (**1**) was prepared from acetyl acetoacetate and triethyl orthoformate according to Claisen.[6] Due to its moisture sensitivity all manipulations were carried out under argon atmosphere. **1** is a liquid at room temperature. In order to prepare single crystals the product was purified by distillation and then stored at 247 K to give a solid. The polycrystalline mass was cooled with dry ice. A single crystal was separated mechanically, mounted on a goniometer head and quickly placed under the cold air flow (170 K) of the diffractometer.

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Colourless block |
| Size: | 0.40 × 0.40 × 0.35 mm |
| Wavelength: | Mo *K*α radiation (0.71073 Å) |
| μ: | 0.10 mm$^{-1}$ |
| Diffractometer, scan mode: | Stoe IPDS 2, rotation |
| $\theta_{max}$, completeness: | 29.1°, >99 % |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 15,668, 2,732, 0.050 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\sigma(I_{obs})$, 2,065 |
| $N(param)_{refined}$: | 121 |
| Programs: | X-Area[1], SHELX[2,3], Diamond[4], Olex2[5] |

## 2 Experimental details

H atoms were geometrically placed and refined as riding atoms with $U_{iso}$(H) = 1.5 $U_{eq}$(C) for $CH_3$ groups and $U_{iso}$(H) = 1.2 $U_{eq}$(C) for CH and $CH_2$ groups.

## 3 Comment

Ethyl (*Z*)-2-(ethoxymethylene)-3-oxobutanoate (**1**) is a valuable reagent in organic synthesis. In coordination chemistry **1** found application as starting material for the synthesis of various Schiff Base ligands. This was first reported by Jäger et al.[7] and up to now these ligands are of vivid interest, particularly due to the special magnetic properties of the corresponding iron(II) complexes.[8] **1** crystallizes in the monoclinic system, space group $P2_1/n$ with four formula units per unit cell. The crystal structure consists of discrete molecules without any unusual short intermolecular contacts. **1** contains a central C–C double bond (C3–C7) with the OEt and $CO_2$Et groups in Z-arrangement. The distance C3–C7 (1.342(1) Å) is typical for a C–C double bond that is involved in $\pi$-conjugation with a carbonyl group. The formal

***Corresponding author: Kurt Merzweiler**, Martin-Luther-Universität Halle-Wittenberg, Naturwissenschaftliche Fakultät II, Institut für Chemie, D-06099 Halle, Germany, E-mail: kurt.merzweiler@chemie.uni-halle.de. https://orcid.org/0000-0001-6349-347X
**Andreas Hentsch**, Martin-Luther-Universität Halle-Wittenberg, Naturwissenschaftliche Fakultät II, Institut für Chemie, D-06099 Halle, Germany

**Table 2:** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$).

| Atom | *x* | *y* | *z* | $U_{iso}^*/U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.08774 (13) | 0.31974 (18) | 0.86079 (8) | 0.0395 (3) |
| H1A | 0.040648 | 0.200913 | 0.833696 | 0.059* |
| H1B | 0.042623 | 0.435493 | 0.830437 | 0.059* |
| H1C | 0.069152 | 0.325269 | 0.915262 | 0.059* |
| C2 | 0.25853 (12) | 0.31598 (15) | 0.86536 (6) | 0.0299 (2) |
| C3 | 0.31391 (11) | 0.31826 (14) | 0.79080 (6) | 0.0270 (2) |
| C4 | 0.48430 (11) | 0.31499 (14) | 0.79912 (6) | 0.0271 (2) |
| C5 | 0.70987 (11) | 0.51322 (17) | 0.82727 (7) | 0.0351 (2) |
| H5A | 0.738114 | 0.519622 | 0.774374 | 0.042* |
| H5B | 0.762820 | 0.399571 | 0.857390 | 0.042* |
| C6 | 0.75509 (13) | 0.69883 (19) | 0.87331 (8) | 0.0432 (3) |
| H6A | 0.700490 | 0.809749 | 0.843330 | 0.065* |
| H6B | 0.866018 | 0.718748 | 0.880855 | 0.065* |
| H6C | 0.728371 | 0.689542 | 0.925910 | 0.065* |
| C7 | 0.21969 (11) | 0.32019 (14) | 0.71758 (6) | 0.0289 (2) |
| H7 | 0.111771 | 0.321437 | 0.713057 | 0.035* |
| C8 | 0.16007 (13) | 0.31787 (17) | 0.57531 (7) | 0.0379 (3) |
| H8A | 0.090455 | 0.431985 | 0.572201 | 0.046* |
| H8B | 0.098031 | 0.196406 | 0.570952 | 0.046* |
| C9 | 0.24506 (18) | 0.3266 (2) | 0.50957 (8) | 0.0542 (4) |
| H9A | 0.171707 | 0.330092 | 0.457496 | 0.081* |
| H9B | 0.310630 | 0.210473 | 0.512171 | 0.081* |
| H9C | 0.308806 | 0.445025 | 0.515755 | 0.081* |
| O1 | 0.35033 (9) | 0.30890 (12) | 0.93017 (5) | 0.0388 (2) |
| O2 | 0.54406 (8) | 0.49323 (10) | 0.81655 (5) | 0.03274 (19) |
| O3 | 0.55801 (9) | 0.17170 (11) | 0.79152 (5) | 0.0405 (2) |
| O4 | 0.27490 (8) | 0.32037 (11) | 0.65108 (4) | 0.03439 (19) |

single bond C2–C3 (1.463(1) Å) that is also part of the $\pi$-conjugation is slightly shorter than the C3–C4 bond to the ester group (1.497(1) Å). Regarding the conformational aspects it is worth mentioning, that the atoms of the ethoxymethylene and the acetyl group are nearly coplanar with the central C3–C2–C4–C7 unit. Contrary to this the ester group fragment O2–C4–O4 is rotated by nearly 80° with respect to mean plane C3–C2–C4–C7.

## References


1. Stoe & Cie. *X–AREA* (Version 1.90); Stoe & Cie GmbH: Darmstadt, Germany, 2020.
2. Sheldrick, G. M. SHELXT – Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr.* **2015**, *A71*, 3–8.
3. Sheldrick, G. M. Crystal Structure Refinement with *SHELXL*. *Acta Crystallogr.* **2015**, *C71*, 3–8.
4. Brandenburg, K. *DIAMOND* Ver. 4.6.8; Crystal Impact GbR: Bonn, Germany, 2022.
5. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
6. Claisen, L. R. Ueber die Oxymethylenderivate des Acetessigäthers, des Acetylacetons und des Malonsäureäthers. *Chem. Ber.* **1893**, *26*, 2729–2735.
7. Wolf, L.; Jäger, E.-G. α-(Aminomethylen)-β-dicarbonylverbindungen als Komplexliganden. I. Kupfer- und Nickelchelate von Diaminderivaten. *Z. Anorg. Allg. Chem.* **1966**, *346*, 76–91.
8. For a Review, see: Weber, B. Spin Crossover Complexes with $N_4O_2$ Coordination Sphere – The Influence of Covalent Linkers on Cooperative Interactions. *Coord. Chem. Rev.* **2009**, *253*, 2432–2449.