



HAL
open science

Crystal structure of the monoglycidyl ether of isoeugenol

Hélène Cattey, Gilles Boni, Sylvie Pourchet, Laurent Plasseraud

► **To cite this version:**

Hélène Cattey, Gilles Boni, Sylvie Pourchet, Laurent Plasseraud. Crystal structure of the monoglycidyl ether of isoeugenol. *Acta crystallographica Section E: Crystallographic communications* [2015-..], 2022, 78 (10), pp.1052-1055. 10.1107/S2056989022009264 . hal-03795465

HAL Id: hal-03795465

<https://hal.science/hal-03795465>

Submitted on 4 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Crystal structure of the monoglycidyl ether of isoeugenol

Hélène Cattey, Gilles Boni, Sylvie Pourchet and Laurent Plasseraud

Acta Cryst. (2022). E78, 1052–1055



IUCr Journals

CRYSTALLOGRAPHY JOURNALS ONLINE

This open-access article is distributed under the terms of the Creative Commons Attribution Licence <https://creativecommons.org/licenses/by/4.0/legalcode>, which permits unrestricted use, distribution, and reproduction in any medium, provided the original authors and source are cited.





Crystal structure of the monoglycidyl ether of isoeugenol

Hélène Cattetey,* Gilles Boni, Sylvie Pourchet and Laurent Plasseraud*

ICMUB CNRS UMR 6302, Université de Bourgogne Franche-Comté, Faculté des Sciences, 9 avenue Alain Savary, 21000 Dijon, France. *Correspondence e-mail: hcattey@u-bourgogne.fr, Laurent.Plasseraud@u-bourgogne.fr

Received 27 July 2022

Accepted 19 September 2022

Edited by G. Diaz de Delgado, Universidad de Los Andes, Venezuela

Keywords: crystal structure; oxirane; phenyl-propene; bio-based molecule; isoeugenol derivative.

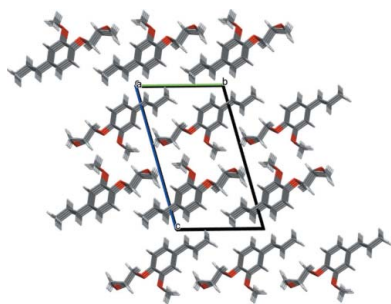
CCDC reference: 2208338

Supporting information: this article has supporting information at journals.iucr.org/e

The title compound, C₁₃H₁₆O₃ [**GE-isoEu**; systematic name: 2-([2-methoxy-4-[(*E*)-1-propen-1-yl]phenoxy)methyl)oxirane], which crystallizes in the triclinic *P*1 space group, was synthesized in one step from *iso*-eugenol, a bio-based phenylpropanoid, with an excess of epichlorohydrin. Colourless prismatic crystals suitable for X-ray diffraction were obtained from a mixture of ethyl acetate and cyclohexane, during purification by column chromatography on silica gel. **GE-isoEu**, which corresponds to the *trans* isomer of the monoglycidyl ether of *iso*-eugenol, is based on a 1,2,4-trisubstituted benzene ring by diglycidyl ether, methoxy and 1-(*E*)-propenyl groups, respectively. In the crystal, molecules are organized through offset π -stacking interactions. Chemically, **GE-isoEu** constitutes an intermediate in the synthesis protocol of 2-[3-methoxy-4-(2-oxiranylmethoxy)phenyl]-3-methyloxirane (**GEEp-isoEu**), a diepoxidized monomer used in the manufacturing of thermosetting resins and intended for the elaboration of bio-composites.

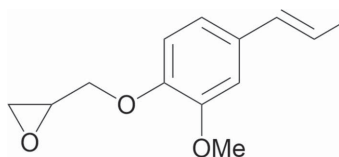
1. Chemical context

The bisphenol A diglycidyl ether molecule, also called BADGE or DGEBA, is the main building block used for the formulation of commercial epoxy resins (Mohan, 2013). Synthetically, this reagent is directly produced from 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), derived from petroleum resources (phenol) and recognized as being an endocrine disruptor (Fenichel *et al.*, 2013). With the aim of designing more sustainable synthetic routes and alternatives to fossil resources, some of the molecules derived from biomass and in particular phenylpropanoids isolated from the fragmentation of lignin, are considered as potential building blocks to replace bisphenol A and its derivatives (Auvergne *et al.*, 2014). This is particularly the case of the *iso*-eugenol molecule generally used in the composition of many perfumes and which can be also transformed into a diepoxidized monomer, 2-[3-methoxy-4-(2-oxiranylmethoxy)phenyl]-3-methyloxirane (**GEEp-isoEu**), well-suited to epoxy thermosetting applications and exhibiting comparable thermomechanical properties to DGEBA (François *et al.*, 2016, 2017). The preparation of **GEEp-isoEu** involves a two-step synthesis *via* firstly the formation of the title compound as a synthesis intermediate. We report herein the X-ray crystal structure of **GE-isoEu** [systematic name: 2-([2-methoxy-4-[(*E*)-1-propen-1-yl]phenoxy)methyl)oxirane], which crystallizes upon its purification from a mixture of cyclohexane and ethyl acetate.



OPEN ACCESS

Published under a CC BY 4.0 licence



2. Structural commentary

The title compound exhibits an asymmetrical structure, which is depicted in Fig. 1. **GE-isoEu** comprises a benzene ring substituted by two oxygenated functional groups, glycidyl ether [$-\text{OCH}_2\text{C}_2\text{H}_3\text{O}$] and methoxy [$-\text{OCH}_3$], and one 1-(*E*)-propenyl side chain [$-\text{HC}=\text{CHCH}_3$] located in *meta* and *para* positions to the methoxy and glycidyl ether functions, respectively. The aromatic ring is planar with mean bond lengths and angles of 1.392 (3) Å and 120.13 (17)°. While the $-\text{OCH}_3$ and $-\text{HC}=\text{CHCH}_3$ groups are in the plane of the benzene ring, $-\text{C}_2\text{H}_3\text{O}$ is out of the plane with an angle of 52.83 (14)°. The oxirane ring (C1/C2/O1) of the glycidyl ether group does not undergo any disorder, in contrast to what is frequently observed for diglycidyl ether derivatives (Cho *et al.*, 1999; Flippen-Anderson & Gilardi, 1981). The double-bond distance of the 1-(*E*)-propenyl side chain was determined as 1.315 (3) Å. This length is consistent with those described in the literature for similar compounds (Stomberg *et al.*, 1993; Stomberg & Lundquist, 1995).

3. Supramolecular features

The most significant supramolecular interaction observed in the crystal consists of offset π -stacking involving aromatic rings of **GE-isoEu** (Fig. 2 – red dotted lines). The interplanar and the centroid-to-centroid distances between parallel molecules are 3.456 (2) and 4.5931 (5) Å, respectively. The important difference between these two distances indicates that the benzene rings are strongly slipped. The slip angle (angle between the normal to the planes and the centroid-centroid vector) is 41.20° corresponding to a slippage distance of 3.025 (3) Å (these high values can nevertheless be consid-

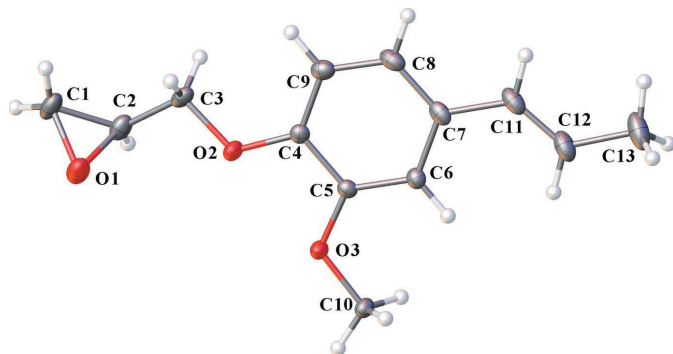


Figure 1
The molecular structure of **GE-isoEu** with displacement ellipsoids at the 30% probability level.

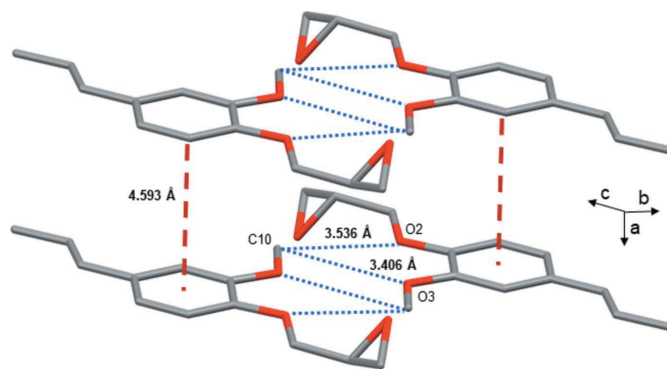


Figure 2
Mercury representation (Macrae *et al.*, 2020; colour code: C dark grey, O red; hydrogen atoms are omitted for clarity) showing intermolecular interactions in the crystal structure of the title compound with hydrogen bonding (blue dotted line, C–H...O distance) and π - π stacking (red dotted line, centroid-centroid distance).

ered as limit values). Typically, for such interactions, the interplanar distance between the arene planes is found around 3.3 to 3.8 Å (Janiak, 2000). In addition, molecules of **GE-isoEu** also interact in pairs, forming dimers, *via* non-classical intermolecular hydrogen bonds involving the methyl groups of the methoxy substituents, with the oxygen atoms of the ether [C10–H10A...O2 = 3.537 (2) Å, 167°] and methoxy functions [C10–H10A...O3 = 3.405 (2) Å, 132°] (Fig. 2 – blue dotted lines). These supramolecular interactions result in a propagation of stacks of molecules oriented along the *a*-axis (Fig. 3).

4. Database survey

A search in the Cambridge Structural Database (WebCSD v1.1.2, update 2022-03-05; Groom *et al.*, 2016), highlighted that, up to now, seventeen crystal structures comprising glycidyl ether-substituted phenyl ring moieties have been

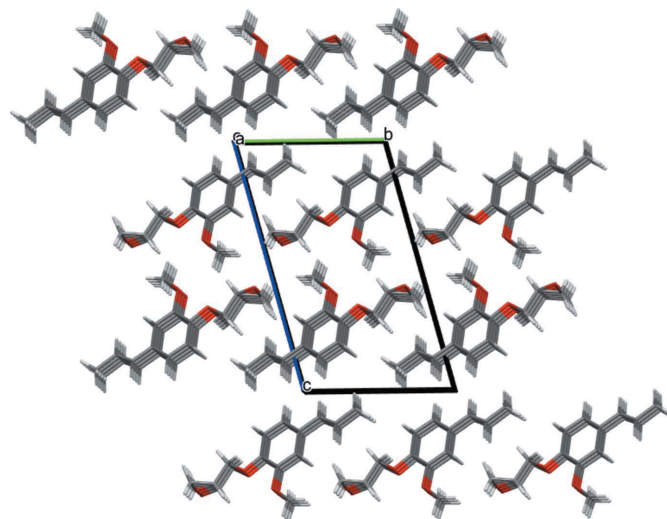


Figure 3
Stacking representation of **GE-isoEu** viewed down the *a* axis (colour code: C dark grey, O red, H white; Mercury representation; Macrae *et al.*, 2020).

reported. They include (*S*)-1-(2-chloro-5-methylphenoxy)-2,3-epoxypropane (CIKQIZ: Bredikhin *et al.*, 2018), 2,2-bis(3,5-dibromo-4-hydroxybenzene)propane diglycidyl ether (COMNEX: Saf'yanov *et al.*, 1984), 2,2-bis(4-(oxiran-2-ylmethoxy)-3,5-dibromophenyl)propane (COMNEY: Cheban *et al.*, 1985), *rac*-1,2-epoxy-3-(2-methoxyphenoxy)propane (DAXKAP: Bredikhin *et al.*, 2005), diglycidyl ether of bisphenol A (DGEBA: Flippen-Anderson & Gilardi, 1980; DGEBA01: Heinemann *et al.*, 1993; DGEBA10: Flippen-Anderson & Gilardi, 1981), *p*-di(2,3-epoxypropoxy)benzene (EOXHQE: Saf'yanov *et al.*, 1977), 2,2'-[1,3-phenylene-bis(oxyethylene)]bis(oxirane) (FITWOU: Bocelli & Grenier-Loustalot, 1987), 1,2-epoxy-3-(2-cyanophenoxy)propane (JESHOF: Bredikhin, *et al.*, 2006), 2-[(4-{3-[4-(oxiran-2-ylmethoxy)phenyl]tricyclo[3.3.1.1.3,7]decan-1-yl}phenoxy)methyl]oxirane (LANRUQ: Wang *et al.*, 2017), 2-(4-[4-(oxiran-2-ylmethoxy)phenoxy]phenyl)phenoxyethyl oxirane (LAQTII: Song *et al.*, 2012), 10-[2,5-bis(2,3-epoxy-1-propoxy)phenyl]-9-oxa-10-phosphaphenanthren-10-one (LIPSOS: Cho *et al.*, 1999), 3,7-dimethoxy-2-[4-methoxy-3-(oxiran-2-ylmethoxy)phenyl]-5-(oxiran-2-ylmethoxy)-4*H*-chromen-4-one (ORASAD: Kristufek *et al.*, 2016), 2,2'-[methylenebis[(2,1-phenylene)oxymethylene]]bis(oxirane) [PALQUS: Liu *et al.*, 2021], 2-(*N*-methoxyethanimidoyl)-5-(oxiran-2-ylmethoxy)benzimidazole (SIJZIW: Gong *et al.*, 2013); 2-[(3-methoxy-4-[(oxiran-2-yl)methoxy]phenyl)methyl]oxirane (WASCIF: Vigier *et al.*, 2017), 4-(oxiran-2-ylmethoxy)benzoic acid (ZEPYUQ: Obreza & Perdih, 2012). To the best of our knowledge, the structure of **GE-isoEu** based on a benzene ring tri-substituted by glycidyl ether, methoxy and 1-propenyl functions is new. In terms of application, several of these compounds are targeted as synthesis intermediates or precursors devoted to the formulation of thermosetting resins. The polymerization process involves the epoxy rings of molecules and occurs in the presence of hardeners (such as amines or acid anhydrides), leading to the cross-linking of infusible polymer networks.

5. Synthesis and crystallization

The title compound was prepared in one step from a commercial source of natural isoeugenol (mixture of *cis/trans*, 99% purity, Sigma-Aldrich) according to a previously reported protocol (François *et al.*, 2016). The details of the synthesis of the title compound are summarized in Fig. 4. *iso*-Eugenol (10.0 g, 60.9 mmol) was added to an ethanolic sodium hydroxide solution (2.7 g, 66.6 mmol of NaOH in 30 mL of

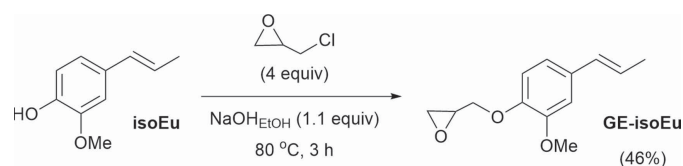


Figure 4
Synthesis protocol and reaction conditions leading to **GE-isoEu**.

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₁₃ H ₁₆ O ₃
<i>M_r</i>	220.26
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	4.5931 (5), 8.9134 (9), 15.0764 (18)
α , β , γ (°)	74.808 (3), 85.309 (4), 77.430 (3)
<i>V</i> (Å ³)	581.18 (11)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.09
Crystal size (mm)	0.5 × 0.15 × 0.15
Data collection	
Diffractometer	Bruker Kappa APEXII
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.668, 0.746
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	17290, 2647, 1865
<i>R_{int}</i>	0.038
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.650
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.049, 0.128, 1.03
No. of reflections	2647
No. of parameters	147
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.33, -0.19

Computer programs: *APEX3* (Bruker, 2020), *SAINT* (Bruker, 2016), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

EtOH), then followed by the addition of an excess of epichlorohydrin (19.1 mL, 22.5 g, 243.6 mmol). The reaction mixture was heated at 353 K over 3 h under constant stirring. 70 mL of toluene were then added at room temperature. After cannula filtration, the filtrate was washed with distilled water (3 × 20 mL) and brine (1 × 20 mL), and finally dried over anhydrous MgSO₄. After complete evaporation of the solvent under vacuum, the residue was then further purified by column chromatography using a mixture of cyclohexane/ethyl acetate (3:1, *v/v*) as eluent to give a white solid characterized as the monoglycidyl ether of *iso*-eugenol (6.2 g, yield 46%). Crystals of the *trans* isomer of **GE-isoEu** suitable for X-ray analysis were obtained during the purification by column chromatography by evaporation of the eluting solvents at room temperature. ¹H NMR (300.1 MHz, CDCl₃): 6.90–6.82 (*m*, 3H, aryl), 6.08 (*dq*, *J* = 6.6 and 15.7 Hz, 1H, *CH*-propenyl), 6.33 (*dd*, *J* = 1.6 and 15.7 Hz, 1H, *CH*-propenyl), 4.21 (*dd*, *J* = 11.4 and 3.6 Hz, 1H, CH₂O), 4.03 (*dd*, *J* = 11.4 and 5.5 Hz, 1H, CH₂O), 3.88 (*s*, 3H, OCH₃); 3.38 (*m*, 1H, *CH*-oxirane), 2.89 (*dd*, *J* = 5.1 and 4.2 Hz, 1H, CH₂-oxirane), 2.73 (*dd*, *J* = 5.0 and 2.7 Hz, 1H, CH₂-oxirane), δ 1.86 (*dd*, *J* = 1.6 and 6.6 Hz, 3H, CH₃); ¹³C{¹H} NMR (75.4 MHz, CDCl₃) δ 149.6, 147.1, 132.2, 130.5, 124.2, 118.6, 114.2, 109.1, 70.3, 55.8, 50.2, 45.0, 18.4; IR (ATR): 3023, 3000, 2957, 2937, 2913, 2878, 2842, 1601, 1582, 1509, 1464, 1450, 1419, 1259, 1226, 1195, 1158, 1135, 1024, 961, 908, 857, 805, 778, 759, 734, 621, 612, 569, 464 cm⁻¹. Analysis calculated for C₁₃H₁₆O₃: C, 69.67; H, 6.11. Found: C, 70.28; H, 7.57.

6. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms on carbon and oxygen atoms were placed at calculated positions using a riding model with C—H = 0.95 Å (aromatic) or 0.99 Å (methylene group) with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ and C—H = 0.98 Å (methyl group) with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{H})$.

Acknowledgements

The authors are also grateful for general and financial support from the Centre National de la Recherche Scientifique (CNRS-France) and the University of Bourgogne Franche-Comté. Dr Pawin Boonyaporn – Advanced Biochemical (Thailand) Co, Ltd (ABT) – is thanked for a generous donation of a sample of bio-based epichlorohydrin (Epicerol®).

Funding information

Funding for this research was provided by: Bio-Based Industries Joint Undertaking (BBI JU) under the European Union's Horizon 2020 research and innovation program (grant No. 744349).

References

- Auvergne, R., Caillol, S., David, G., Boutevin, B. & Pascual, J.-P. (2014). *Chem. Rev.* **114**, 1082–1115.
- Bocelli, G. & Grenier-Loustalot, M.-F. (1987). *Acta Cryst.* **C43**, 1221–1223.
- Bredikhin, A. A., Bredikhina, Z. A., Kurenkov, A. V., Zakharychev, D. V. & Gubaidullin, A. T. (2018). *J. Mol. Struct.* **1173**, 157–165.
- Bredikhin, A. A., Bredikhina, Z. A., Zakharychev, D. V., Akhatova, F. S., Krivolapov, D. B. & Litvinov, I. A. (2006). *Mendeleev Commun.* **16**, 245–247.
- Bredikhin, A. A., Strunskaya, E. I., Zakharychev, D. V., Krivolapov, D. B., Litvinov, I. A. & Bredikhina, Z. A. (2005). *Tetrahedron Asymmetry*, **16**, 3361–3366.
- Bruker (2016). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2020). *APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cheban, I. M., Simonov, I. A., Rotaru, V. K. & Malinovskii, T. I. (1985). *Dokl. Akad. Nauk SSSR*, **283**, 621–624.
- Cho, C.-S., Liau, W.-B. & Chen, L.-W. (1999). *Acta Cryst.* **B55**, 525–529.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Fenichel, P., Chevalier, N. & Brucker-Davis, F. (2013). *Ann. Endocrinol. (Paris)*, **74**, 211–220.
- Flippen-Anderson, J. L. & Gilardi, R. (1980). *ACA, ser. 2*, **8**, 36a.
- Flippen-Anderson, J. L. & Gilardi, R. (1981). *Acta Cryst.* **B37**, 1433–1435.
- François, C., Pourchet, S., Boni, G., Fontaine, S., Gaillard, Y., Placet, V., Galkin, M. V., Orebom, A., Samec, J. & Plasseraud, L. (2016). *RSC Adv.* **6**, 68732–68738.
- François, C., Pourchet, S., Boni, G., Rautiainen, S., Samec, S., Fournier, L., Robert, C., Thomas, C. M., Fontaine, S., Gaillard, Y., Placet, V. & Plasseraud, L. (2017). *C. R. Chim.* **20**, 1006–1016.
- Gong, T.-J., Xiao, B., Cheng, W.-M., Su, W., Xu, J., Liu, Z.-J., Liu, L. & Fu, Y. (2013). *J. Am. Chem. Soc.* **135**, 10630–10633.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Heinemann, F., Hartung, H. & Derling, S. (1993). *Z. Kristallogr.* **207**, 299–301.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Kristufek, S. L., Yang, G., Link, L. A., Rohde, B. J., Robertson, M. L. & Wooley, K. L. (2016). *ChemSusChem*, **9**, 2135–2142.
- Liu, K.-T., Chuang, J.-Y., Jeng, R.-J. & Leung, M.-K. (2021). *ACS Omega*, **6**, 27279–27287.
- Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
- Mohan, P. (2013). *Polym. Plast. Technol. Eng.* **52**, 107–125.
- Obreza, A. & Perdih, F. (2012). *Zh. Strukt. Khim.* **53**, 802–808.
- Saf'yanov, Y. N., Bochkova, T. N., Golovachev, V. P. & Kuz'min, E. A. (1977). *Zh. Struk. Khim.* **18**, 402–405.
- Saf'yanov, Y. N., Golovachev, V. P. & Kuz'min, E. A. (1984). *Zh. Struk. Khim.* **25**, 156–157.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Song, T., Liu, J.-G. & Yang, S.-Y. (2012). *Acta Cryst.* **E68**, o719.
- Stomberg, R. & Lundquist, K. (1995). *Z. Kristallogr.* **210**, 66–67.
- Stomberg, R., Lundquist, K. & Wallis, A. F. A. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 317–331.
- Vigier, J., François, C., Pourchet, S., Boni, G., Plasseraud, L., Placet, V., Fontaine, S. & Cattley, H. (2017). *Acta Cryst.* **E73**, 694–697.
- Wang, S.-J., Jing, X.-L., Meng, Y.-D. & Jia, Q.-X. (2017). *Chin. J. Struct. Chem.* **36**, 396–400.

supporting information

Acta Cryst. (2022). E78, 1052-1055 [https://doi.org/10.1107/S2056989022009264]

Crystal structure of the monoglycidyl ether of isoeugenol

Hélène Cattey, Gilles Boni, Sylvie Pouchet and Laurent Plasseraud

Computing details

Data collection: *APEX3* (Bruker, 2020); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

2-[2-Methoxy-4-(prop-1-en-1-yl)phenoxyethyl]oxirane

Crystal data

$C_{13}H_{16}O_3$	$Z = 2$
$M_r = 220.26$	$F(000) = 236$
Triclinic, $P\bar{1}$	$D_x = 1.259 \text{ Mg m}^{-3}$
$a = 4.5931 (5) \text{ \AA}$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$b = 8.9134 (9) \text{ \AA}$	Cell parameters from 5145 reflections
$c = 15.0764 (18) \text{ \AA}$	$\theta = 2.5\text{--}26.6^\circ$
$\alpha = 74.808 (3)^\circ$	$\mu = 0.09 \text{ mm}^{-1}$
$\beta = 85.309 (4)^\circ$	$T = 150 \text{ K}$
$\gamma = 77.430 (3)^\circ$	PRISM, colourless
$V = 581.18 (11) \text{ \AA}^3$	$0.5 \times 0.15 \times 0.15 \text{ mm}$

Data collection

Bruker kappa APEXII diffractometer	$T_{\min} = 0.668$, $T_{\max} = 0.746$
Radiation source: X-ray tube, Siemens KFF Mo 2K-180	17290 measured reflections
Graphite monochromator	2647 independent reflections
Detector resolution: $8.3 \text{ pixels mm}^{-1}$	1865 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.038$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.4^\circ$
	$h = -5 \rightarrow 5$
	$k = -11 \rightarrow 11$
	$l = -19 \rightarrow 19$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.049$	H-atom parameters constrained
$wR(F^2) = 0.128$	$w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.3763P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
2647 reflections	$(\Delta/\sigma)_{\max} < 0.001$
147 parameters	$\Delta\rho_{\max} = 0.33 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\min} = -0.19 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O3	0.5215 (3)	0.37762 (14)	0.60436 (8)	0.0300 (3)
O2	0.8022 (3)	0.53432 (15)	0.67363 (9)	0.0327 (3)
O1	0.7925 (3)	0.88375 (17)	0.59690 (12)	0.0498 (4)
C5	0.6121 (4)	0.3053 (2)	0.69197 (11)	0.0234 (4)
C6	0.5628 (4)	0.1597 (2)	0.74236 (12)	0.0262 (4)
H6	0.457467	0.102195	0.715929	0.031*
C4	0.7670 (4)	0.3919 (2)	0.73067 (12)	0.0247 (4)
C7	0.6660 (4)	0.0952 (2)	0.83221 (12)	0.0307 (4)
C9	0.8683 (4)	0.3293 (2)	0.81886 (13)	0.0322 (4)
H9	0.973015	0.386713	0.845569	0.039*
C3	0.9823 (4)	0.6233 (2)	0.70261 (14)	0.0319 (4)
H3A	1.174343	0.554383	0.725793	0.038*
H3B	0.878503	0.670214	0.752225	0.038*
C8	0.8175 (4)	0.1822 (2)	0.86875 (13)	0.0356 (5)
H8	0.888622	0.140217	0.929532	0.043*
C10	0.3618 (4)	0.2968 (2)	0.56109 (12)	0.0288 (4)
H10A	0.312228	0.360518	0.498608	0.043*
H10B	0.177676	0.280713	0.596581	0.043*
H10C	0.485826	0.193544	0.558386	0.043*
C11	0.6167 (5)	−0.0610 (2)	0.88692 (13)	0.0393 (5)
H11	0.697432	−0.096779	0.946634	0.047*
C2	1.0334 (4)	0.7498 (2)	0.62068 (15)	0.0376 (5)
H2	1.143379	0.712477	0.567846	0.045*
C12	0.4742 (5)	−0.1566 (2)	0.86288 (15)	0.0462 (6)
H12	0.392242	−0.122483	0.803335	0.055*
C1	1.0655 (5)	0.9043 (2)	0.62760 (18)	0.0450 (5)
H1A	1.065235	0.921634	0.689846	0.054*
H1B	1.195933	0.961206	0.581395	0.054*
C13	0.4301 (6)	−0.3142 (3)	0.92108 (17)	0.0583 (7)
H13A	0.509844	−0.396339	0.888173	0.087*
H13B	0.216596	−0.310609	0.934385	0.087*
H13C	0.534885	−0.338975	0.978846	0.087*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0366 (7)	0.0279 (7)	0.0274 (6)	−0.0150 (5)	−0.0068 (5)	−0.0015 (5)
O2	0.0337 (7)	0.0320 (7)	0.0361 (7)	−0.0159 (5)	−0.0066 (6)	−0.0057 (6)
O1	0.0354 (8)	0.0392 (9)	0.0766 (11)	−0.0119 (7)	−0.0132 (7)	−0.0106 (8)

C5	0.0197 (8)	0.0257 (9)	0.0231 (8)	-0.0015 (7)	0.0001 (6)	-0.0060 (7)
C6	0.0266 (9)	0.0240 (9)	0.0268 (9)	-0.0029 (7)	0.0019 (7)	-0.0068 (7)
C4	0.0185 (8)	0.0255 (9)	0.0290 (9)	-0.0020 (7)	0.0002 (7)	-0.0071 (7)
C7	0.0323 (10)	0.0251 (9)	0.0276 (9)	0.0058 (7)	0.0037 (7)	-0.0052 (7)
C9	0.0275 (9)	0.0362 (11)	0.0331 (10)	-0.0001 (8)	-0.0045 (8)	-0.0130 (8)
C3	0.0215 (9)	0.0350 (10)	0.0444 (11)	-0.0065 (7)	-0.0044 (8)	-0.0175 (9)
C8	0.0390 (11)	0.0352 (11)	0.0259 (9)	0.0063 (8)	-0.0046 (8)	-0.0064 (8)
C10	0.0315 (9)	0.0293 (10)	0.0288 (9)	-0.0132 (7)	-0.0015 (7)	-0.0070 (7)
C11	0.0492 (12)	0.0295 (11)	0.0281 (10)	0.0056 (9)	0.0039 (9)	-0.0005 (8)
C2	0.0257 (10)	0.0380 (11)	0.0545 (13)	-0.0114 (8)	0.0037 (9)	-0.0188 (10)
C12	0.0630 (15)	0.0281 (11)	0.0378 (12)	-0.0021 (10)	0.0079 (10)	-0.0001 (9)
C1	0.0323 (11)	0.0379 (12)	0.0731 (16)	-0.0144 (9)	-0.0054 (10)	-0.0211 (11)
C13	0.0827 (18)	0.0276 (12)	0.0526 (14)	-0.0028 (11)	0.0208 (13)	-0.0029 (10)

Geometric parameters (Å, °)

O3—C5	1.364 (2)	C3—C2	1.479 (3)
O3—C10	1.427 (2)	C8—H8	0.9500
O2—C4	1.368 (2)	C10—H10A	0.9800
O2—C3	1.425 (2)	C10—H10B	0.9800
O1—C2	1.430 (2)	C10—H10C	0.9800
O1—C1	1.435 (2)	C11—H11	0.9500
C5—C6	1.377 (2)	C11—C12	1.315 (3)
C5—C4	1.408 (2)	C2—H2	1.0000
C6—H6	0.9500	C2—C1	1.448 (3)
C6—C7	1.403 (2)	C12—H12	0.9500
C4—C9	1.377 (2)	C12—C13	1.495 (3)
C7—C8	1.382 (3)	C1—H1A	0.9900
C7—C11	1.474 (3)	C1—H1B	0.9900
C9—H9	0.9500	C13—H13A	0.9800
C9—C8	1.388 (3)	C13—H13B	0.9800
C3—H3A	0.9900	C13—H13C	0.9800
C3—H3B	0.9900		
C5—O3—C10	117.72 (13)	O3—C10—H10C	109.5
C4—O2—C3	118.70 (14)	H10A—C10—H10B	109.5
C2—O1—C1	60.72 (12)	H10A—C10—H10C	109.5
O3—C5—C6	125.24 (15)	H10B—C10—H10C	109.5
O3—C5—C4	114.77 (15)	C7—C11—H11	116.1
C6—C5—C4	119.99 (16)	C12—C11—C7	127.7 (2)
C5—C6—H6	119.5	C12—C11—H11	116.1
C5—C6—C7	120.90 (17)	O1—C2—C3	116.11 (16)
C7—C6—H6	119.5	O1—C2—H2	115.7
O2—C4—C5	114.35 (15)	O1—C2—C1	59.82 (12)
O2—C4—C9	126.27 (16)	C3—C2—H2	115.7
C9—C4—C5	119.38 (16)	C1—C2—C3	122.05 (19)
C6—C7—C11	121.60 (18)	C1—C2—H2	115.7
C8—C7—C6	118.10 (17)	C11—C12—H12	117.2

C8—C7—C11	120.29 (17)	C11—C12—C13	125.7 (2)
C4—C9—H9	120.0	C13—C12—H12	117.2
C4—C9—C8	119.97 (18)	O1—C1—C2	59.46 (12)
C8—C9—H9	120.0	O1—C1—H1A	117.8
O2—C3—H3A	110.5	O1—C1—H1B	117.8
O2—C3—H3B	110.5	C2—C1—H1A	117.8
O2—C3—C2	106.23 (15)	C2—C1—H1B	117.8
H3A—C3—H3B	108.7	H1A—C1—H1B	115.0
C2—C3—H3A	110.5	C12—C13—H13A	109.5
C2—C3—H3B	110.5	C12—C13—H13B	109.5
C7—C8—C9	121.65 (17)	C12—C13—H13C	109.5
C7—C8—H8	119.2	H13A—C13—H13B	109.5
C9—C8—H8	119.2	H13A—C13—H13C	109.5
O3—C10—H10A	109.5	H13B—C13—H13C	109.5
O3—C10—H10B	109.5		
O3—C5—C6—C7	179.86 (15)	C4—O2—C3—C2	167.73 (14)
O3—C5—C4—O2	-0.3 (2)	C4—C5—C6—C7	-0.3 (2)
O3—C5—C4—C9	-179.96 (15)	C4—C9—C8—C7	0.0 (3)
O2—C4—C9—C8	-179.64 (16)	C7—C11—C12—C13	-179.97 (19)
O2—C3—C2—O1	78.43 (19)	C3—O2—C4—C5	-173.56 (14)
O2—C3—C2—C1	147.72 (17)	C3—O2—C4—C9	6.1 (2)
C5—C6—C7—C8	0.2 (2)	C3—C2—C1—O1	-103.7 (2)
C5—C6—C7—C11	-179.63 (16)	C8—C7—C11—C12	178.9 (2)
C5—C4—C9—C8	0.0 (3)	C10—O3—C5—C6	0.2 (2)
C6—C5—C4—O2	179.83 (14)	C10—O3—C5—C4	-179.68 (14)
C6—C5—C4—C9	0.2 (2)	C11—C7—C8—C9	179.78 (17)
C6—C7—C8—C9	-0.1 (3)	C1—O1—C2—C3	113.5 (2)
C6—C7—C11—C12	-1.2 (3)		
