Synthesis and Solid-state Structure of 2,2,2′,2′ -(Tetrahydroxymethyl)-dibutylether (Di-TMP), an Environmentally Benign Polymer Crosslinker and High-potential Additive for Lubricants

Guido D. Frey[a], Rian D. Dewhurst[b], and Eberhardt Herdtweck[c]

[a] Oxea GmbH, Otto-Roelen-Straße 3, 46147 Oberhausen, Germany
[b] Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany
[c] Department für Chemie, Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

Reprint requests to Dr. Guido D. Frey.
Tel.: +49(0)208 693 2340.
E-mail: guido.frey@oxea-chemicals.com

Z. Naturforsch. **2012**, *67b,* 181 – 184;
received November 5, 2011

Dedicated to Dr. Karl Öfele on the occasion of his 80th birthday

The crystal structure of the industrially relevant tetrahydroxy ether 2,2,2′,2′-(tetrahydroxymethyl)-dibutylether (technically known as di(trimethylol)propane, Di-TMP; $C_{12}H_{26}O_5$) was determined from single-crystal X-ray data at 123 K: monoclinic, space group $C2/c$ (no. 15), a = 20.1202(13), b = 5.8169(4), c = 13.0323(8) Å, β = 114.296(3)°, V = 1390.17(16) Å^3 and Z = 4. The adjacent molecules assemble into a two-dimensional framework in the solid state, linked by two intermolecular O–H···O hydrogen bonds. The compound is characterized *via* spectroscopic methods and mass spectrometry.

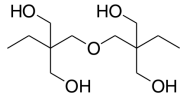
Key words: Crystal Structure, Di-TMP, Polyol, Symmetric Ether

Introduction

High-boiling polyols play an important role in the modern lubricant industry. Accordingly, trimethylolpropane (TMP) has been known since the 1960s for its effectiveness as an additive for lubricants in order to improve high-pressure resistance, inhibit corrosion or promote heat transfer. Polyols have also made a dramatic impact as environmentally benign alternatives to halocarbons for use as refrigerants [1]. Due to their cross-linking abilities, the polyols TMP and Di-TMP {2,2′-[oxybis(methylene)]bis[2-ethylpropane-1,3-diol]} have also been widely used in paints [2] and polymers [3]. Moreover, the use of polyols with anhydridic or epoxy reagents in paints accelerates the drying process [4]. Di-TMP is often used as the alcohol component in esterification reactions with long-chain acids [5 – 7], producing semisolid waxes for use in cosmetics [8], as well as certain sunscreen ingredients [9].

Results and Discussion

We report here the crystal structure of Di-TMP (**1**), which is used as a high-value paint additive and lubricant with a low vapor pressure and high boiling point.



1

The industrial synthesis of Di-TMP [10] is generally accomplished concurrent to the production of TMP [11]. In most cases, a side stream of TMP production and work-up is used for the purification of Di-TMP. Normally the residue (high boiler) from the final TMP distillation is used for this purpose [12]. It is also possible to increase the yield of Di-TMP in the reaction mixture during the production of TMP by addition of methylidenebutanal (ethylacrolein) to the TMP-formalin-butanal mixture [13]. The purification of the residue is accomplished for example by recrystallization from ethyl acetate [14] or water [15]. A patented method from Wada and Ishihara describes the purification of Di-TMP *via* steam distillation [16]. This process is only possible on a commercial scale and was not suitable for our laboratory scale. The direct formation of Di-TMP starting from TMP by etherification was accomplished by the reaction of TMP at 200 °C with removal of the formed water under acidic conditions, using *p*-toluenesulfonic acid or an acidic resin (Nafion) [17].

We prepared Di-TMP (**1**) according to the procedure by Ninomiya *et al.* [18] *via* an Aldol/Cross-Cannizzaro reaction, in which butanal is treated with formalin under strongly alkaline conditions. The reaction mixture

Table 1. Selected bond lengths (Å) and bond angles (deg) for compound **1**[a].

O1–C1	1.426(2)	C1–O1–C1^{i}	111.95(11)
O2–C3	1.435(2)	O1–C1–C2	109.05(10)
O3–C4	1.428(2)	C1–C2–C3	107.94(12)
C1–C2	1.532(2)	C1–C2–C4	108.62(10)
C2–C3	1.537(2)	C1–C2–C5	111.48(12)
C2–C4	1.537(2)	C3–C2–C4	109.94(12)
C2–C5	1.544(2)	C3–C2–C5	109.22(10)
C5–C6	1.521(2)	C4–C2–C5	109.62(12)
		O2–C3–C2	113.02(13)
		O3–C4–C2	113.55(12)
		C2–C5–C6	116.12(11)

[a] Symmetry operation for equivalent atoms: (i) $-x$, y, $0.5-z$.

Table 2. Hydrogen bond geometry (Å, deg) for compound **1**[a].

D-H·*A*	*D*-H	H·*A*	*D*·*A*	*D*-H·*A*
O2–H2·O3^{ii}	0.83(2)	1.87(2)	2.689(2)	166(2)
O3–H3·O2^{iii}	0.85(2)	1.93(2)	2.753(2)	164(2)

Symmetry operations for equivalent atoms (ii): x, $1+y$, z; (iii): $0.5-x$, $1.5+y$, $1-z$.

was worked up by distillation (removal of water and formalin) and extraction (with ethyl acetate), in order to remove the sodium formate. Afterwards TMP was separated from Di-TMP by distillation. Following this, we attempted to recrystallize Di-TMP from the distillation residue. Due to the low solubility in non-hydrogen bonding solvents, recrystallization of Di-TMP was successful only with the use of polar solvents. To this end, solvents such as acetone, ethyl acetate, *n*-butyl acetate and methylisobutyl ketone were all found to be effective. In this manner, analytically pure Di-TMP (**1**) was obtained and characterized by ^{1}H, ^{13}C{^{1}H} NMR spectroscopy and high-resolution mass spectrometry, confirming its formulation.

Suitable single crystals for X-ray diffraction studies were grown from a r. t.-saturated methylisobutyl ketone solution by slow evaporation of the solvent and cooling to 15 °C. A view of the low-temperature (123 K) molecular structure of compound **1** is given in Fig. 1. Selected geometric and structural parameters are listed in Table 1 and 2.

The packing of the molecules in the crystal is dominated by two intermolecular O–H···O hydrogen bond interactions (see Table 2), which are present twice in the structure due to the symmetry requirements of the space group. As expected, the hydroxyl functions are linked to each other *via* hydrogen bonding to build up a two-dimensional structure, in contrast to the studies on the related polyol TMP, in which a three-dimensional framework was observed [20, 21]. This reduced dimensionality may be a result of the reduction of the number of hydroxyl groups available for hydrogen bonding per C_6 fragment, from three in TMP to two in Di-TMP. The intermolecular hydrogen bonds (1.87(2) and 1.93(2) Å) are within the normal range [22]. As shown in Fig. 2, these hydrogen bonds assemble a two-dimensional infinite network perpendicular to the crystallographic [1,0,−1] axis. The four (2H)C–OH bonds [1.426(2)–1.435(2) Å] are in the same range as those in the TMP structure (1.429(1)–1.433(1) Å) [22].

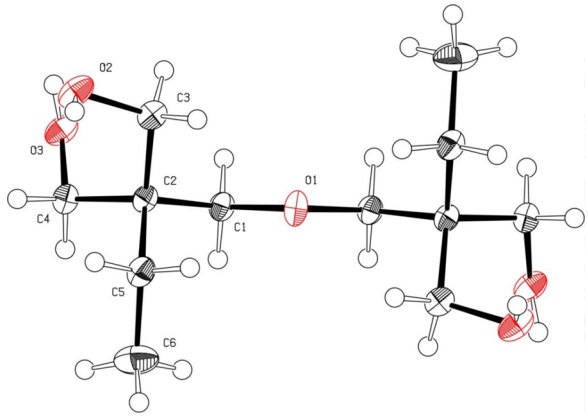


Fig. 1. ORTEP [19] plot of the molecular structure of compound **1** in the solid state, showing 50 % probability displacement ellipsoids and the atom numbering adopted.

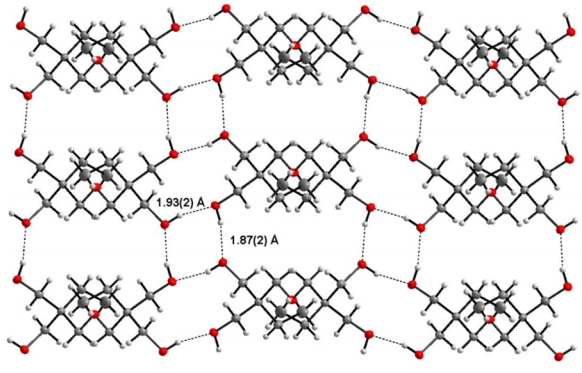


Fig. 2. DIAMOND [23] plot of the packing of **1** in the crystal structure, as viewed perpendicular to the [1,0,−1] axis. Dashed lines indicate the C–H···O interactions.

Experimental Section

Compound **1** was prepared with small adjustments to the procedure reported by Ninomiya *et al.* [18]. In a three-neck double-walled 2 L round bottom flask with an external cooler a suspension of 342 g of 2,2-bis(hydroxymethyl)-1-butanol ("trimethylolpropane", TMP) in 100 g wa-

ter and 63 g of 50 % NaOH solution was added. *Via* two dropping funnels the aqueous formalin solution (37 wt.-%; 195 g) and *n*-butanal (54 g) were added simultaneously to the TMP solution over 2 min. Using the external cooler, we attempted to maintain a reaction temperature of approximately 65 °C, using an external bath temperature of 35 °C (this Aldol-Cannizzaro reaction is particularly exothermic, and high temperatures are useful for the formation of Di-TMP under the current conditions). The reaction was stirred for 3 h and the formalin-water solution was neutralized with formic acid to a pH value of ~ 5. The aqueous solution was extracted three times with 150 mL ethyl acetate. The organic extracts were combined, and the ethyl acetate was slowly removed *via* a rotary evaporator at 80 °C/200 mbar to obtain a yellow oil, which solidifies at r. t. over several days. This oil was distilled *via* a column at high temperature and low pressure. The head fraction was found to be mainly TMP, while the brownish residue in the distillation sump was mainly Di-TMP and some cyclic derivatives of TMP and Di-TMP [24]. The purification and separation of Di-TMP from this residue was accomplished analogously to the procedure by Zey [14], where 150 mL of ethyl acetate was added to the hot residue, and the mixture cooled to 0 °C. After 5 – 6 h a colorless precipitate formed, which was filtered off, washed once more with 20 mL of cold ethyl acetate, and dried under vacuum to obtain 41 g of Di-TMP (**1**) in 9.9 % yield (purity by GC = 98.4 wt.-%). Suitable single crystals for X-ray diffraction studies were grown from a r. t.-saturated methylisobutyl ketone solution by slow evaporation of the solvents and slow cooling to 15 °C. M. p. 109 – 110 °C. B. p. > 300 °C/1013 mbar; 239 °C/4 mbar; 225 °C/3 mbar; 220 °C/2 mbar; 206 °C/1.4 mbar; 160 °C/0.6 mbar; 140 °C/0.3 mbar. – ^{1}H NMR (500.14 MHz, [D$_6$]DMSO): δ = 4.18 (t, ^3J = 5.4 Hz, 4 H, OH), 3.26 (d, ^3J = 5.4 Hz, 8 H, CH_2OH), 3.14 (s, 4 H, CH_2O), 1.23 (q, ^3J = 7.6 Hz, 4 H, CH$_2$), 0.78 (t, ^3J = 7.6 Hz, 6 H, CH$_3$) ppm. – ^{13}C{1H} NMR (125.76 MHz, [D$_6$]DMSO): δ = 71.8 (*C*H$_2$O), 62.0 (*C*H$_2$OH), 43.4 (*C*$_q$), 22.1 (*C*H$_2$CH$_3$), 7.6 (*C*H$_3$) [25] ppm. – Hydroxyl number [26]: 881 – 893 mg KOH g^{-1}. – Acid number [27]: < 0.04 mg KOH g^{-1}. – Gardner Color [28]: 1. – HRMS ((+)-ESI); MeCN/CHCl$_3$ (1 : 1)): *m/z* = 251.18588, 252.18939 (calcd. 251.18585, 252.18920 for C$_{12}$H$_{27}$O$_5$, [M+H]$^+$); *m/z* = 273.16711 (calcd. 273.16779 for C$_{12}$H$_{26}$NaO$_5$, [M+Na]$^+$). – TLC (EtOAc); R_f = 0.17.

*Single-crystal X-ray structure determination of compound **1***

Crystal data and details of the structure determination are presented in Table 3. Suitable single crystals for the X-ray diffraction study were grown from methylisobutyl ketone.

The crystal was fixed on the top of a glass fiber with perfluorinated ether and transferred into a Lindemann capillary, fixed and sealed. Preliminary examination and data collection were carried out on an area detecting system (APEX II, κ-CCD) [29] at the window of a rotating anode (Bruker AXS, FR591) and graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 8342 reflections. Ten data sets were measured in rotation scan modus with $\Delta\varphi/\Delta\Omega$ = 1.0°. The raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects [30]. The structure was solved by a combination of Direct Methods and difference Fourier syntheses [31]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were found in the final difference Fourier maps and allowed to refine freely with isotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(f_o^2 - F_c^2)^2$ with the SHELXL-97 [32] weighting scheme and stopped at a shift over error ratio of < 0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography* [33].

Table 3. Summary of the crystallographic data of compound **1**.

Chemical formula	$C_{12}H_{26}O_5$
Molecular weight	250.33
Crystal color / shape	colorless / plate
Crystal size, mm^3	$0.05 \times 0.25 \times 0.76$
Crystal system	monoclinic
Space group	$C2/c$ (no. 15)
a, Å	20.1202(13)
b, Å	5.8169(4)
c, Å	13.0323(8)
β, deg	114.296(3)
V, Å^3	1390.17(16)
Z	4
$\rho_{calcd.}$, g cm^{-3}	1.20
μ, mm^{-1}	0.1
Wavelength; λ, Å	MoK_α; 0.71073
T, K	123
Θ range, deg	2.22 – 25.56
Reflections integrated	12801
Independent reflections (all data) / R_{int}	1288 / 0.054
Observed reflections [$I \geq 2\sigma(I)$]	1173
Parameters refined	130
$R1$ (observed / all data)[a]	0.0369/0.0403
$wR2$ (observed / all data)[b]	0.0943/0.0965
GOF[c]	1.063
Largest diff. peak / hole, e Å^{-3}	0.29 / −0.17

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

CCDC 846738 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.

Acknowledgement

This work was supported by the DFG for an Eigene Stelle for R. D. D.. E. H. thanks the Lehrstuhl für Anorganische Chemie of the Technische Universität München for X-ray facility support.

[1] N. E. Schnur, E. R. Zehler, WO 93/25628, **1993**.
[2] a) S. P. Gajanan, S. Sivaram, US 2006/251688, **2006**; b) A. P. Verrall, S. G. Friedrich, US 2006/165625, **2006**.
[3] S. P. Gajanan, S. Sivaram, A. Absar, US 2007/53950, **2007**.
[4] T. H. Lee, KR 2011060651, **2011**.
[5] A. Ukai, O. Yamada, JP 51138705 and JP 51118843, **1976**; JP 52048613, **1977**.
[6] A. Ukai, JP 52131513, **1977**.
[7] R. L. Kronenthal, US 2005/65214, **2005**.
[8] I. Rollat-Corvol, H. Samain, US 2005/2887, **2005**.
[9] M. S. Garrison, M. Armstrong, US 2005142079, **2005**.
[10] First examples in the literature: a) M. P. Vysotskii, S. Z. Kaplan, M. M. Ketslakh, E. K. Remiz, D. M. Rudkovskii, M. V. Petrova, G. P. Prokopenko, F. A. Eppel, *Karbonilirovanie Nenasyshchennykh Uglevodorodov* **1968**, 274 – 290; b) V. W. Gash, *J. Org. Chem.* **1972**, *37*, 2197 – 2201.
[11] T. Ninomiya, T. Watanabe, T. Ikebe, EP 1013631, **2000**.
[12] T. Ninomiya, T. Watanabe, A. Iwamoto, S. Miyashita, M. Watanabe, EP 1178030, **2002**.
[13] T. Watanabe, EP 2204356, **2010**; WO 2009/057466, **2009**.
[14] E. G. Zey, DE 2212793, **1972**.
[15] K. S. Herz, DE 2358297, **1974**.
[16] Y. Wada, K. Isihara, DE 2058518, **1971**.
[17] C.-A. Sjögreen, G. Axelsson, WO 92/05134, **1992**.
[18] T. Ninomiya, T. Watanabe, T. Ikebe, A. Iwamoto, DE 69700932, **2000**; EP 799815, **1999**.
[19] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands) **2010**. See also: A. L. Spek, *J. Appl. Crystallogr.* **2009**, *D65*, 148 – 155.
[20] D. S. S. Gowda, N. Federlein, R. Rudman, *J. Chem. Phys.* **1982**, *77*, 4659 – 4665.
[21] D. Chandra, H. Mandalia, W.-M. Chien, D. W. Lindle, R. Rudman, *Z. Phys. Chem.* **2002**, *216*, 1389 – 1400.
[22] a) C. M. Zakaria, J. N. Low, C. Glidewell, *Acta Crystallogr.* **2001**, *E57*, o1081 – o1083; b) D. S. S. Gowda, N. Federlein, R. Rudman, *J. Chem. Phys.* **1982**, *77*, 4659 – 4665; c) D. Chandra, H. Mandalia, W.-M. Chien, D. W. Lindle, R. Rudman, *Z. Phys. Chem.* **2002**, *216*, 1389 – 1400.
[23] K. Brandenburg, DIAMOND (version 3.2c), Crystal and Molecular Structure Visualization, Crystal Impact – K. Brandenburg & H. Putz GbR, Bonn (Germany) **2009**. See also: http://www.crystalimpact.com/diamond/.
[24] Y. Wada, K. Isihara, DE 2058519, **1971**.
[25] First NMR studies were reported in: M. P. Vysotskii, B. I. Ionin, S. Z. Kaplan, M. M. Ketslakh, D. M. Rudkovskii, F. A. Eppel in *Gidroformilirovanie* (Eds.: N. S. Imyanitov), Khimiya, Leningrad **1972**, pp. 178 - -181.
[26] Measured according to the DIN 53240 norm.
[27] Measured according to the DIN EN ISO 2114; ASTM D 1613 norm.
[28] Measured according to the ASTM D1544 norm.
[29] APEX 2 suite of programs (version 2008.4), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2008**.
[30] SAINT (version 7.56a), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2008**; G. M. Sheldrick, SADABS (version 2008/1), Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **2002** and Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2008**.
[31] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, SIR97; see: *J. Appl. Crystallogr.* **1999**, *32*, 115 – 119.
[32] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.
[33] A. J. C. Wilson (Ed.), *International Tables for Crystallography*, Vol. C, Kluwer Academic Publishers, Dordrecht, **1992**, pp. 193 – 199, 219 – 222, 500 – 502.

Druck: AZ Druck und Datentechnik GmbH, Kempten