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Synthesis and Crystal Structure Analysis of Substituted Diethyl Malonate

Shou-xin Liu · Ya-hui Gao · Jian-rong Han · Juan Feng · Xiao-Li Zhen

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Abstract As intermediates of light stabilizer malonate, diethyl 3,5-di-t-butyl-4-hydroxybenzyl phenyl malonates (F.W. 454.58) was synthesized, characterized by ¹H NMR, element analysis and confirmed by X-ray crystal structure analysis. This compound crystallizes in monoclinic class under the space group P21/c with cell parameters, a = 9.8218(4) Å, b = 13.5571(5) Å, c = 19.7233(8) Å; $\beta = 102.3530(10)^{\circ}$, and Z = 4. The structure exhibits inter-molecular hydrogen bonds of the type O–H–O, leading to the formation of one dimensional chains.

Keywords Diethyl malonate · Light stabilizer · Synthesis · Crystal structure · Hydrogen bond

Introduction

Most polymers must be stabilized against the impact of the environment. Antioxidants and ultraviolet (UV) stabilizers are of vital importance to protect polymeric materials from deterioration [1–4]. A highly effective light stabilizer has synergetic effect if used with antioxidant, can raise heat and oxidization stabilities of polymer materials [5]. Savides et al. reported certain phenolic antioxidants, in combination with ultraviolet absorbers, afforded greater light stability to the polymer than the ultraviolet absorbers alone [6, 7].

S. Liu (⊠) · Y. Gao · J. Feng College of Chemical & Pharmaceutical Engineering, Hebei University of Science & Technology, Shijiazhuang 050018, People's Republic of China e-mail: chlsx@263.net

J. Han · X.-L. Zhen

College of Sciences, Hebei University of Science & Technology, Shijiazhuang 050018, People's Republic of China

Otherwise, synergism occurs when mixtures of antioxidants produce a more pronounced activity than the sum of the activities of the individual antioxidants when used separately. With light stabilize improvements, fourth generation of synergistic UV absorber-Hindered Amine Light Stabilizers (HALS) combinations have been the appearance on the market. The results demonstrate a significant performance advantage for the blend product [8]. Therefore, multi-functional light stabilities of polymer materials have received extensive attention. Antioxidants are generally incorporated in polymers to inhibit or minimize oxidative degradation. The malonates products have antioxidant properties and are capable of stabilizing polymers normally subject to oxidative degradation [9]. 3,5-Di-tbutyl-4-hydroxybenzyl malonates derivatives act very efficiently as oxidation inhibitors. So, diethyl 3,5-di-tbutyl-4-hydroxybenzyl phenyl malonate is a potential highly effective HALS intermediate. However, the compound is expensive due to using N,N-dimethyl 3,5-di-tbutyl-4-hydroxybenzyl amine as alkylation reagent during its preparation procedure. In this paper, new synthetic method and crystal structure of the compound were reported. During it's synthesise procedure, the alkyl reagent was replaced by 3,5-di-t-butyl-4-hydroxybenzyl bromide. Its structure is characterized by ¹H NMR and element analysis, and the ester's crystal structure was determined by X-ray diffraction analyses.

Experimental

General

Melting points was measured with an Xt-4 apparatus, thermometer was uncorrected. ¹H NMR spectra were



Scheme 1 Route of synthesis of III

recorded on a Bruker AVANCE II500 instrument in CDCl₃ solution, using tetramethylsilane as an internal reference. Elemental analyses were performed on a Perkin-Elmer 2400C instrument.

Starting material 3,5-di-*t*-butyl-4-hydroxy toluene I diethyl 2-phenylmalonates was commercially available and used without further purification. All chemicals were reagent grade and were used without further purification, unless noted otherwise (Scheme 1).

The Preparation of Substituted Benzyl Bromide II

To a solution of I 3,5-di-t-butyl-4-hydroxy toluene (17.6 g, 0.08 mol) in 200 mL carbon tetrachloride1 was added recrystallized *N*-bromosuccinimide (NBS, 15.8 g, 0.88 mol) and benzoyl peroxide (0.472 g, 0.002 mol). The mixture was refluxed for 3.0 h at which time additional NBS (1.4 g, 0.008 mol) and AIBN (0.24 g, 0.001 mol) were added and the mixture refluxed for another 3 h. When the reaction finished by TLC monitoring, heating was stopped and the mixture was cooled at 0 °C. The mixture was filtered to remove succinimide and the filtrate was concentrated under vacuum. The residue was redissolved in ethyl acetate and washed with saturated solution of sodium bicarbonate, brine, and then dried over MgSO₄. Evaporation of the solvent in vacuo afforded the crude benzyl bromide compound **II** without purification (87.5%).

Synthesis of Substituent Diethyl Malonate (III)

An anhydrous carbon tetrachloride solution (100 ml) of 3,5-di-t-butyl-4-hydroxy benzyl bromide 20.9 g (0.07 mol) was added to an anhydrous carbon tetrachloride (150 ml) of lithium amide (2.3 g, 0.1 mol) and diethyl phenylmal-onate (16.1 g, 0.07 mol). The mixture was refluxed for 4 h.

The solvents were removed in vacuo. The residue obtained was added to a mixture of water (150 mL) and ethyl acetate (100 mL) with stirring vigorously, and the ethyl acetate layer was separated and dried over MgSO₄. The residue obtained upon evaporation of the ethyl acetate was recrystallized from petroleum ether to give colorless crystals of **III** (85%), The colorless single cryatals of the title compound suitable for X-ray analysis were obtained by slow evaporation of an n-hexane solution. m.p 71–73 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.15 (m, 2H), 7.24 (m, 3H), 6.57(s, 2H), 5.02(s, 1H), 4.22(q, 4H, J = 7.5 Hz), 3.47 (s, 2H), 1.30 (s, 18H), 1.23(t, 3H, J = 7.5 Hz). Anal. Calcd for C₂₈H₂₈O₅: C, 42.81; H, 5.03; Found: C, 42.68; H, 5.15.

X-Ray Crystallography

The data of single cryatals of the title compound **III** were collected on a standard Rigaku Saturn 724 CCD Area Detector System equipped with a normal-focus molybde-num-target X-ray tube ($\lambda = 0.71073$ Å). The structure was

Table 1	Crystal	data	and	structure	refinement	for	Ш
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Crystallographic data and structure refinement for complex 3					
Empirical formula	C ₂₈ H ₃₈ O ₅				
Formula weight	454.58				
Temperature (K)	296(2)				
Wavelength (Å)	0.71073				
Crystal system, space group	Monoclinic, P21/c				
Unit cell dimensions	a = 9.8218(4) Å, b = 13.5571(5) Å,				
	c = 19.7233(8) Å;				
	$\beta = 102.3530(10)^{\circ}$				
Volume (Å ³)	2565.46(18)				
Z, calculated density $(g \text{ cm}^{-3})$	4, 1.177				
Absorption coefficient (mm ⁻¹)	0.079				
F(000)	984				
Crystal size (mm ⁻³)	$0.41\times0.24\times0.03$				
Range for data collection	1.84–31.11°				
Limiting indices	$-13 \le h \le 11, -13 \le k \le 18, -27 \le l \le 24$				
Reflections collected/ unique	17131/7093 [R(int) = 0.0253]				
Completeness to $\Theta = 31.11$	85.8%				
Refinement method	Full-matrix least-squares on F ²				
Goodness-of-fit on F ²	1.006				
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0507, wR2 = 0.1258				
R indices (all data) $R1 = 0.0891$, wR2 = 0.1484					
Extinction coefficient	0.0045(8)				
Largest diff. peak and hole 0.283 and 0.216 e Å ⁻³					

solved using direct methods and refined by full-matrix least-squares techniques. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement. All hydrogen atoms were added at calculated positions and refined using a riding model. The structures were refined on F^2 using SHELXTL-97 [10]. The crystals used for the diffraction study showed no decomposition during data collection. The final R values (on F^2) were 0.0404 of the title compound. The crystal data and some details of the structure determination are summarized in Table 1. The fractional co-ordinates and equivalent isotropic displacement parameters are given in Table 2.

Table 2 Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$) for compound III

	х	У	Z	U(eq)
C(1)	4794(3)	3612(2)	-57(1)	88(1)
C(2)	5073(2)	3257(2)	665(1)	62(1)
C(3)	5340(2)	3930(1)	1793(1)	41(1)
C(4)	5785(2)	4860(1)	2226(1)	35(1)
C(5)	4583(2)	5598(1)	1999(1)	39(1)
C(6)	2180(2)	5869(2)	1976(1)	62(1)
C(7)	2125(2)	6432(2)	2614(1)	73(1)
C(8)	6007(2)	4703(1)	3012(1)	37(1)
C(9)	6352(2)	3804(1)	3337(1)	47(1)
C(10)	6611(2)	3730(2)	4049(1)	58(1)
C(11)	6536(2)	4538(2)	4455(1)	66(1)
C(12)	6203(3)	5431(2)	4142(1)	70(1)
C(13)	5945(2)	5518(2)	3429(1)	54(1)
C(14)	7118(2)	5316(1)	2046(1)	38(1)
C(15)	8348(2)	4627(1)	2115(1)	36(1)
C(16)	8647(2)	4192(1)	1529(1)	40(1)
C(17)	9774(2)	3566(1)	1553(1)	41(1)
C(18)	10622(2)	3380(1)	2209(1)	41(1)
C(19)	10362(2)	3796(1)	2818(1)	38(1)
C(20)	9221(2)	4427(1)	2748(1)	38(1)
C(21)	10067(2)	3101(2)	887(1)	55(1)
C(22)	9941(4)	1980(2)	917(1)	99(1)
C(23)	11502(2)	3405(2)	786(1)	88(1)
C(24)	9021(2)	3447(2)	242(1)	85(1)
C(25)	11250(2)	3541(1)	3540(1)	45(1)
C(26)	11040(2)	2446(2)	3694(1)	67(1)
C(27)	12809(2)	3745(2)	3597(1)	76(1)
C(28)	10794(2)	4132(2)	4110(1)	67(1)
O(1)	5344(1)	4097(1)	1130(1)	51(1)
O(2)	4977(2)	3166(1)	1995(1)	77(1)
O(3)	3389(1)	5215(1)	2092(1)	52(1)
O(4)	4706(1)	6402(1)	1779(1)	60(1)
O(5)	11710(1)	2725(1)	2240(1)	63(1)

 $U(\mbox{eq})$ is defined as one third of the trace of the rthogonalized Uij tensor

Results and Discussion

The crystal structure of III is illustrated in Fig. 1. It is composed of two aromatic ring moiety, and two ester group, and two aromatic rings (C8-C13 and C15-C20) makes dihedral angles of 42.3° in malonate derivatives. The five atoms C6.O3,O4,C4.C5 and C2.O1,O2,C3,C4 in two ester groups display an coplanar with a mean deviation to the least square plane 0.0319 Å and 0.0290 Å respectively, and dihedral angle of two planes is $84.9(2)^{\circ}$. Moreover, the bond lengths involving the central atom C4 range from 1.533(2) to 1.556(2) Å, were slightly longer than the corresponding values of reported any other malonate derivatives (1.512–1.528 Å) [11, 12]. The bond angles are in the range of 105.24(12)-114.26(13). Among them, bond angles of two smaller esters group C5-C4-C3 was 105.24 $^{\circ}$, bond angles of C3–C4–C8 was 114.26 $^{\circ}$. The selected bond lengths and bond angles are given in Table 3.

There is an intramolecular O–H...O hydrogen bond in the molecule, while in the crystal O–H...O intermolecular hydrogen bonds lead to the formation of one dimensional chains. The details of hydrogen bonding are given in



Fig. 1 The molecular structures of III, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level

Table 3 Selected bond lengths	(Å)	and a	ngles ((°)	for	Π	0
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C(3)–C(4)	1.533(2)	C(5)-C(4)-C(3)	105.24(12)
C(4)–C(5)	1.539(2)	C(5)-C(4)-C(8)	108.65(13)
C(4)–C(8)	1.533(2)	C(3)-C(4)-C(8)	114.26(13)
C(4)–C(14)	1.556(2)	C(5)-C(4)-C(14)	107.82(13)
C(18)–O(5)	1.380(2)	C(3)-C(4)-C(14)	110.62(13)
O(5)-H(5)	0.8381	C(8)-C(4)-C(14)	109.95(13)

Table 4 Hydrogen bonded geometry, distances and angles are given in Å and $^\circ$

No.	D-HA	d(D-H)	d(HA)	d(DA)	θ (D–HA)	Symmetry code
1	O5-H5O2	0.84	2.56	3.398(2)	179	1 + x, y, z

Fig. 2 The hydrogen bond system between molecular III, The *dashed lines* represented the intermolecular hydrogen bonds (H-bonds are drawn between donor and acceptor atoms)

Table 4. When viewed along the b-axis, the molecules are interlinked by hydrogen bonds as shown in Fig. 2.

Supplementary Material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-82607. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail:deposit@ccdc.cam. ac.uk).

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