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Synthesis and crystal structure of 2-methoxy-4,6-*bis*(4-nitrophenoxy)-1,3,5-triazine

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ABSTRACT

The novel compound, 2-methoxy-4,6-*bis*(4-nitrophenoxy)-1,3,5-triazine has been synthesized starting from 2,4,6-trichloro-1,3,5-triazine and characterized by ^{1}H NMR, ^{13}C NMR, IR, mass spectroscopy and elemental analysis. The single crystal of the title compound was obtained and subjected to X-ray diffraction analysis. The single crystal data illustrates that it belongs to the monoclinic system, space group C2/c with a = 13.818(3) Å, b = 7.8964(16) Å, c = 30.718(6) Å, β = 96.52(3) °, V = 3330.0(12) Å^3, Z = 8, D_c = 1.537 g/cm^3, $C_{16}H_{11}N_5O_7$, Mr = 385.30, μ ($MoK\alpha$) = 0.124 mm^{-1}, F(000) = 1584, the final R = 0.0489 and wR = 0.1821 for 2491 observed reflections with I>2σ(I).

1. Introduction

Bismaleimides (BMI), as one of the most important types of thermosetting polymers, have received much attention in many industrial fields because of their excellent thermal stability, nonvolatility, and low cost [1-4]. They are widely used in multilayer-printed boards for large-scale computers, as encapsulation resins and passivation layers for integrated circuit (IC) dies, as advanced carbon fiber composites for aircraft [2-4]. However, directly using of the neat BMI resins is limited due to their inherent brittleness. To improve the toughness of the resins, a number of methods have been tried [5-12]. Among those, introducing branched chains and triazine rings into BMI can effectively improve the toughness of the resins [11,12]. The branched chains are "tough" [13] and the triazine rings are "heat resistant" [14,15]. Therefore, the co-reaction between BMI and the modifiers, containing the branched chains and the triazine rings, might give good toughness and thermal stability to the cured resins [11,12].

Our interests are firstly attracted by the triazine fragment, we want to design some other novel BMI resins, containing both the branched chains and the triazine rings, may have better properties than the traditional BMI's. In order to obtain the new BMI, 1,1'-(((6-methoxy-1,3,5-triazine-2,4-diyl) *bis*(oxy))*bis*(4,1-phenylene))*bis*(pyrrolidine-2,5-dione) (**5**), we firstly studied the title compound 2-methoxy-4,6-*bis*(4-nitrophenoxy)-1,3,5-triazine (**3**) (Scheme 1 and 2). Therefore, the novel precursor **3** has also been synthesized, and we also grew and got the corresponding single crystal.

2. Experimental

2.1. Reagents and instruments

All the chemicals were reagent grade and used without further purification. Melting point was determined on a XRC-I-type micro-melting point detector without correction. Mass spectrum and elemental analysis were recorded on Q-TOF-Premimer spectrometer and Euro EA 3000 spectrometer, respectively. IR spectra in KBr pellet was recorded on a NEXUS 670 FT-IR spectrometer in the range 4000-400 cm^{-1}. ^{1}H and ^{13}C NMR were measured on a Bruker Avance α-400 MHz NMR spectrometer (TMS internal standardization, $CDCl_3$ solvent).

2.2. X-ray analysis and refinement

Single crystal data was collected on a Bruker SMART-1000 CCD diffractometer using Mo$K\alpha$ radiation. The crystal structure was solved by direct methods using SHELXS97 [16] and difference Fourier synthesis using SHELXL97 [16]. Full-matrix least-squares refinement based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares techniques, and the hydrogen atoms were determined by theoretical hydrogenation. All calculations were carried out with the SHELXTL-97 program package [16]. Further details concerning data collection and refinement are given in Table 1.

2.3. Synthesis

2.3.1. Synthesis of compound 3

The synthetic route of the compound **3** was shown in Scheme 1. Sodium bicarbonate (25.2 g, 0.30 mol) was slowly added to a solution of methanol (120 mL), water (18 mL) and 2,4,6-trichloro-1,3,5-triazine (27.68 g, 0.15 mol) at 0-5 °C. The mixture was warmed to room temperature and stirred for 30 min.

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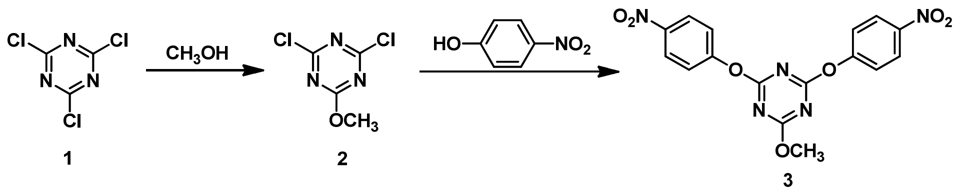
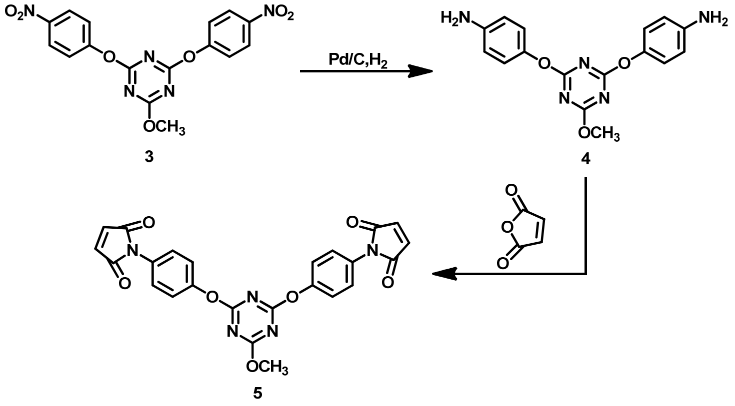


Scheme 1



Scheme 2

Then the reaction mixture was drowned into ice water, filtered off and dried in a desiccator over calcium chloride. The crude product 2-methoxy-4,6-dichloro-1,3,5-trizain (**2**) (16.88 g) was obtained without further purified in a yield of 62.5%.

To a solution of 4-nitrophenol (11.13 g, 0.08 mol), potassium carbonate (22.08 g, 0.16 mol) and acetone (130 mL) was slowly added compound **2** (7.2 g, 0.04 mol). The reaction mixture was refluxed for 1 h. After filtration, the filtrate was poured into water and washed to neutralize. The pure compound **3** (11.51 g) was obtained by recrystallized from acetone in a yield of 91.6%. M.p.: 194-197 °C. Anal. calcd. for $C_{16}H_{11}N_5O_7$: C, 49.88; H, 2.88; N, 18.18. Found: C, 49.83; H, 2.78; N, 18.22 %. IR (KBr, cm^{-1}): 1548, 1390 (C-N), 1513 (NO_2). ^{1}H NMR ($CDCl_3$, 400 MHz, δ, ppm): 8.31 (d, *J* = 8.8 Hz, 4H, Ar-*H*), 7.38 (d, *J* = 8.8 Hz, 4H, Ar-*H*), 4.99 (s, 3H, C*H*$_3$-O-N). ^{13}C NMR ($CDCl_3$, 100 MHz, δ, ppm): 174.06 (1C, *C*-O-CH$_3$), 172.83 (2C, Ar-O-*C*-N), 155.92 (2C, O-*C*-CH), 145.72 (2C, NO$_2$-*C*), 125.47 (4C, NO$_2$-C-*C*H), 122.51 (4C, O-C-*C*H), 56.14 (1C, O-*C*H$_3$). MS (*m/z*): 386.20 [M+1]$^+$.

2.3.2. Synthesis of compound 5

The synthetic route of the compound **5** was shown in Scheme 2. 10% Pd/C (0.06 g) was added to a solution of compound **3** (6.00 g, 15.57 mmol) in DMF (50 mL). The system was stirred at 50 °C under 5 MPa H_2. Upon completion, the mixture was filtered, and the filtrate was concentrated under reduced pressure to remove DMF. Then the concentrate was poured into water. The crude product 4,4'-((6-methoxy-1,3,5-triazine-2,4-diyl)*bis*(oxy))dianiline (**4**) was precipitated and used without further purified in the next step.

To the solution of maleic anhydride (0.60 g, 6 mmol) in 20 mL toluene, a solution of compound **4** (1.00 g, 3 mmol) in 3 mL DMF was added gradually at room temperature. After the mixture was stirred for 1h, *p*-toluenesulfonic acid (0.15 g) was added to the reaction mixture and refluxed to sluice out water for 6 h. Then, the reaction mixture was cooled to room temperature and poured to water. The organic layer was washed with water to pH = 7, dried with anhydrous $MgSO_4$ and concentrated in vacuum. The pure compound **5** (0.81 g) was obtained by recrystallized from THF. Yield: 66.9%. M.p.: 135-139 °C. Anal. calcd. for $C_{24}H_{15}N_5O_7$: C, 59.38; H, 3.11; N, 14.43. Found: C, 59.41; H, 2.98; N, 14.50 %. IR (KBr, cm^{-1}): 1716 (C=O), 1576, 1366 (C-N), 691 (C=C). ^{1}H NMR (400 MHz, DMSO-*d*$_6$, δ, ppm): 3.90 (s, 3H, O-C*H*$_3$), 7.20 (s, 4H, CO-C*H*, hydrogen of maleimide group), 7.38 (d, *J* = 5.2 Hz, 8H, Ar-*H*). ^{13}C NMR (100 MHz, DMSO-*d*$_6$, δ, ppm): 174.04 (1C, *C*H$_3$-O), 173.30 (2C, Ar-O-*C*-N), 170.31 (4C, *C*O-N), 150.87 (2C, O-*C*-CH), 135.18 (4C, CO-*C*H), 129.65 (2C, N-*C*-CH), 128.40 (4C, N-C-*C*H), 122.55 (4C, O-C-*C*H), 56.04 (1C, O-*C*H$_3$). MS (*m/z*): 486.17 [M+1]$^+$.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routs of compound **3** and **5** have been shown in Scheme 1 and Scheme 2, respectively. Compound **3** was synthesized by etherification starting from 2,4,6-trichloro-1,3,5-triazine. Compound **5** was prepared by reduction of compound **3** at 50 °C with Pd/C as the catalyst and then amidation with maleic anhydride through azeotropic dehydration catalyzed by *p*-toluenesulfonic acid in toluene.

Compound **3** and **5** were characterized by IR, ^{1}H NMR, ^{13}C NMR, mass spectroscopy and element analysis. In the IR spectra, the various bands have been assigned to the bending modes of vibration of different groups present in the corresponding compounds for compound **3** and compound **5.** In the IR spectra of compound **3**, the ν(-NO$_2$) vibrations occur as very strong absorptions at 1513 cm^{-1}. The strong sharp absorption of carbonyl group in compound **5** is at 1716 cm^{-1}. And the middle absorption of compound **5** at 690 cm^{-1} is due to the ν(C=C) of maleimide group. ^{1}H NMR spectra of compound **3** and compound **5** are in accord with their corresponding compound.

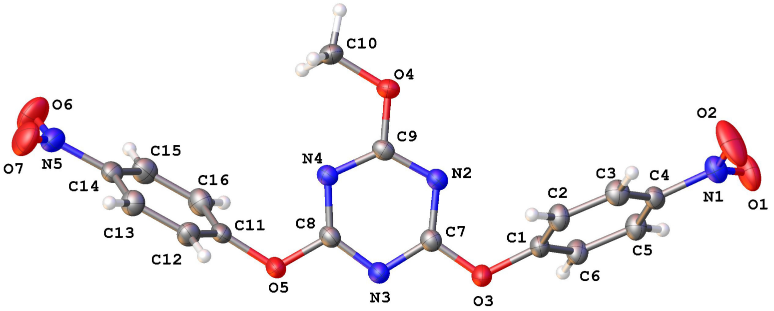


Figure 1. Structure of the compound **3**.

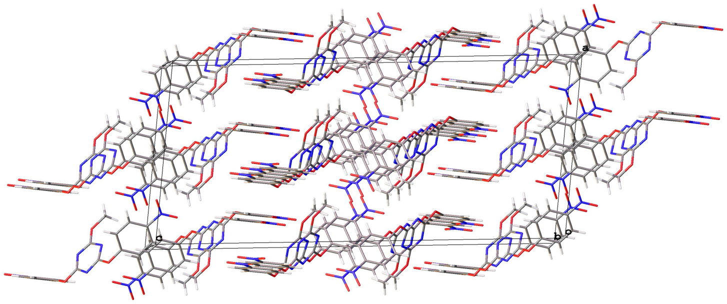


Figure 2. Packing diagram of the compound **3**.

In the ^{1}H NMR spectrum of compound **3**, the proton shifts of the four hydrogen atoms close to the nitro group are δ 7.40 ppm. In compound **5**, the four proton shifts of maleimide group show one singlet at δ 7.20 ppm.

The properties of the new BMI compound **5**, using title compound **3** as precursor, is still studied. The further research of this BMI will be reported shortly.

3.2. Structure description of the title compound

The molecular structure and the packing diagram of the title compound are shown in Figure 1 and Figure 2, respectively. Table 1 gives the crystal data and structure refinement. Selected bond lengths and bond angles are listed in Table 2. What makes interesting is that the crystal structure of the title compound looks like an airplane. The central triazine ring is just like the airframe, while the methoxy group is as the tail and the two phenyl rings are as the wings.

Data in Table 2 show that the bond lengths and angles for the triazine moiety of the title compound are in good agreement with those observed in other triazine derivatives [17,18]. The bond lengths of N2-C7, N2-C9, N3-C8, N3-C7, N4-C8 and N4-C9 are 1.323(2), 1.331(2), 1.319(2), 1.330(3), 1.329(2) and 1.330(2) Å, respectively, indicating that the N-C bonds show partial double bond character in this fragment.

The dihedral angle of the triazine ring and the phenyl ring C1-C6 is -66.3(7)°, while the dihedral angle of the triazine ring and the other phenyl ring C11-C16 is 74.0(7)°. The two phenyl rings lean to two different directions to the central triazine ring. At the end of each wing, the nitro groups are almost coplanar with the corresponding phenyl rings. The nitro plane (N1-O2-O1) forms the dihedral angle of 2.1(6)° with the adjacent phenyl ring, at the other side, the dihedral angle between the other nitro plane (N5-O7-O6) and the corresponding adjacent phenyl ring is 3.5(3)°. The torsion angles of C1-O3-C7-N2 and C11-O5-C8-N4 are 2.7(3) and 0.9(3)^o, respectively. The tail, methoxy group atoms C10-O4, forms a torsion angle -1.5(3)^o with the atoms C9-C4.

From the crystal packing diagrams, in Figure 2, the molecule crystals are composed of dispersive molecules hold together for the most part by Van de Waals forces. These non-covalent interactions, in the title compound, mainly come from the dipole-dipole interaction of NO_2-NO_2 and the dipole-induced dipole interaction of NO_2-phenyl. Additionally, the supramolecular assembly is further stabilized by π-π stacking interaction force between the two phenyl rings C11-C16 of the adjacent molecules with the centroid- centroid distance of 3.079 Å.

Table 1. Crystal data and structure refinement for the title compound.

Empirical formula	$C_{16}H_{11}N_5O_7$
Formula weight	385.30
Temperature	113.15 K
Wavelength	0.710747 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 13.818(3) Å
	b = 7.8964(16) Å
	c = 30.718(6) Å
	β = 96.52(3)°
Volume	3330.0 (12) Å^3
Z	8
Calculated density	1.537 g/cm^3
Absorption coefficient	0.124 mm^{-1}
F(000)	1584
Crystal size	0.24×0.22×0.20 mm
Theta range for data collection	2.67 to 25.01°
Limiting indices	$-16 \leq h \leq -16$
	$-9 \leq k \leq 9$
	$-36 \leq l \leq 36$
Reflections collected	2491
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2917/6/255
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1=0.0489 , wR2 = 0.1650
R indices (all data)	R1= 0.0608 , wR2 = 0.1821
Structure determination	Direct methods (SHELXL-97, SHELXS-97)
CCDC No	831716

Table 2. Selected geometric parameters (Å, º) for the title compound.

Bond lengths			
N2-C7	1.323(2)	N3-C7	1.330(3)
N2-C9	1.331(2)	N4-C9	1.330(2)
N3-C8	1.319(2)	N5-C14	1.468(3)
Bond angles			
C7-O3-C1	118.53(14)	N2-C7-O3	118.95(17)
C9-O4-C10	116.84(15)	N3-C7-O3	113.52(16)
C8-O5-C11	118.04(14)	N3-C8-O5	113.81(16)
O1-N1-O2	123.06(18)	N4-C8-O5	117.61(16)
O6-N5-O7	123.6(2)	O4-C9-N4	118.75(17)
O6-N5-C14	117.81(19)	C13-C14-N5	118.05(19)
C2-C1-O3	120.20(17)	C5-C4-N1	118.81(17)
Torsion angles			
C7-O3-C1-C2	68.6(2)	C9-N4-C8-O5	-176.28(16)
C2-C3-C4-N1	177.52(18)	C10-O4-C9-N4	-1.5(3)
O1-N1-C4-C5	-0.8(3)	C8-N4-C9-O4	177.90(16)
N1-C4-C5-C6	-177.89(18)	C8-O5-C11-C12	-105.6(2)
C1-O3-C7-N2	-2.7(3)	O7-N5-C14-C15	-176.51(19)
C9-N2-C7-O3	-178.10(16)	N5-C14-C15-C16	-178.95(18)
C1-O3-C7-N3	-178.02(16)	C11-O5-C8-N4	0.9(3)
C7-N3-C8-O5	178.52(16)		

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Supplementary material

CCDC 831716 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge at http://www.ccdccam.ac.uk/const/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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