J Chem Crystallogr (2009) 39:83–86
DOI 10.1007/s10870-008-9471-2

COMMUNICATION

Synthesis and Crystal Structure of 1,3-Bis (*p*-nitrophenoxy)propane

Muhammad Rafique · Sonia Zulfiqar ·
Glenn P. A. Yap · Syed Ismat Shah ·
Muhammad Ilyas Sarwar

Received: 3 March 2008 / Accepted: 12 September 2008 / Published online: 1 October 2008

Abstract The title compound 1,3-bis(*p*-nitrophenoxy)propane was synthesized by nucleophilic substitution of *p*-nitrophenol and 1,3-dibromopropane. Single crystal X-ray diffraction analysis reveals that the molecule in the solid state packs in the monoclinic *P*2/n space group with crystal cell parameters $a = 17.465(5)$ Å, $b = 4.8433(13)$ Å, $c = 17.610(5)$ Å, $\beta = 100.290(6)^\circ$, $V = 1465.6(7)$ Å^3, $D_{calc} = 1.442$ g/cm^{-3}. Two half-molecules are located in the asymmetric unit which are each completed by twofold symmetry making $Z = 4$, $Z' = 1$.

Keywords Nitrophenoxypropane · Crystal structure · Monomer synthon

Introduction

There has been interest in diphenoxypropane and structurally similar compounds as model compounds for oligomer liquid crystals [1]. Several aryl halide, aldehyde, ether, nitrile, and amino derivatives of the parent diphenoxyproprane have also been reported [2–12]. In particular, the reported amino derivative displays a rudimentary dendrimeric form [2]. The nitrile derivative, by coordination to bridging Cu(I) ions, forms a polymer [3]. The phosphine oxide derivative forms a similar polymer via bridging coordination to Cd(II) ions [4]. These suggest that diphenoxypropane derivatives have potential as monomeric synthons for new polymeric materials.

Aryl-nitro compounds are common precursors for amines after reduction [13–17]. Diamino compounds when condensed with diacid chlorides give the corresponding polyamides [18–25]. In order to overcome insolubility of aromatic polyamides in organic solvents, flexible groups can be introduced by incorporating alkyl/ether linkages in the monomer that persist into the final polymer. In addition to enhanced solubility, the incorporation of alkyl/ether linkages generally imparts other desirable physical properties such as improved processability and increased toughness of the polymers without decreasing thermal stability. Soluble polyamides have the added advantage of being more amenable to physical and chemical characterization by common solution-based techniques such as NMR [22, 23, 26–29] and laser light scattering [30–35]. Such soluble polymers can also be utilized for nanocomposite preparation using sol–gel and solution intercalation techniques [24, 25, 36–39].

The title compound, 1,3-bis(*p*-nitrophenoxy)propane, **1**, has the prerequisite alkyl/aryl ether linkages and therefore an attractive synthon, after reduction into the amino derivative, for the preparation of polyamides and polyimides.

M. Rafique · S. Zulfiqar · M. I. Sarwar
Department of Chemistry, Quaid-i-Azam University,
45320 Islamabad, Pakistan

G. P. A. Yap (✉)
Department of Chemistry and Biochemistry,
University of Delaware, Newark, DE 19716, USA
e-mail: gpyap@udel.edu

S. I. Shah
Department of Physics and Astronomy, University of Delaware,
Newark, DE 19716, USA

S. I. Shah · M. I. Sarwar
Department of Materials Science and Engineering,
University of Delaware, Newark, DE 19716, USA

Experimental

Chemicals

p-Nitrophenol (≥99%), anhydrous potassium carbonate (99.99%), *N*,*N*-dimethylformamide (99.8%), toluene (99.8%), 1,3-dibromopropane (99%), methanol (99.8%), and ethanol (99.5%) were procured from Aldrich and used as received.

Synthesis of 1,3-Bis(*p*-nitrophenoxy)propane

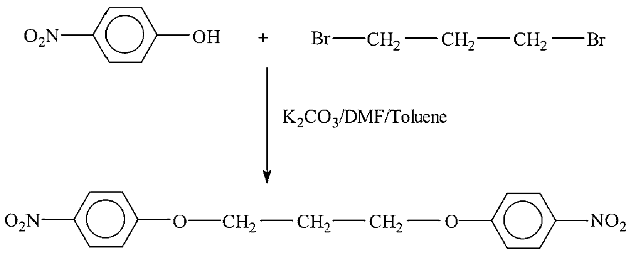
p-Nitrophenol 6.26 g (0.045 mol) and anhydrous potassium carbonate 6.22 g (0.045 mol) were placed in the mixture of *N*,*N*′-dimethylformamide (DMF) 45 mL and toluene 23 mL followed by refluxing at 200 °C using a Dean-Stark trap to remove the water azeotropically. After the removal of toluene, 1,3-dibromopropane 2.3 mL (0.0225 mol) was added to the mixture and then refluxed for 8 h. The resulting solution was allowed to cool to room temperature and was then poured into 200 mL methanol/water (1:1) to give golden yellow precipitate. After being washed thrice with water, the product was collected by filtration and was recrystallized from ethanol, yield 80%; m.p. 122 °C (Scheme 1).

Determination of Crystal Structure

Crystal data and structure refinement details are presented in Table 1. Crystals suitable for X-ray diffraction studies were obtained from a slow evaporation of a saturated solution of the compound in ethanol. A data crystal was selected and mounted on a plastic mesh using Paratone® oil flash-cooled to the data collection temperature. Data were collected on a Brüker-AXS APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were obtained from 60 data frames, 0.3° ω, from three different sections of the Ewald sphere. The systematic absences in the data and the unit cell parameters were consistent with *P*n and *P*2/n. Solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The data-sets were treated with SADABS absorption corrections based on redundant multiscan data [40]. The structures were solved using direct methods and refined with full-matrix, least-square procedures on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Structure factors are contained in the SHELXTL 6.12 program library [40].

Table 1 Crystal data and structure refinement details

CCDC deposit number	678947
Empirical formula	$C_{15}H_{14}N_2O_6$
Formula weight (g/mol)	318.28
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*P*2/n
Unit cell dimensions:	
a (Å)	17.465(5)
b (Å)	4.8433(13)
c (Å)	17.610(5)
β (°)	100.290 (6)
Volume (Å^3)	1465.6(7)
Z, *Z*′	4, 1
Density calculated (g/cm^3)	1.442
Absorption coefficient (mm^{-1})	0.113
F(000)	664
Crystal size (mm)	0.28 × 0.09 × 0.05
θ range for data collection (°)	1.51–28.30
Limiting indices	$-23 \le h \le 22$, $-6 \le k \le 6$, $-23 \le l \le 23$
No. of reflections collected	11,425
No. of unique reflections ($R_{int} = 0.0875$)	3,489
Completeness to $\theta = 25.00°$	99.9%
Absorption correction	Multiscan
Max. and min. transmission	0.9938 and 0.9693
Data/restraints/parameters	3489/0/210
Goodness-of-fit on F^2	1.048
Final *R* indices [$I > 2\sigma(I)$] (*R*1, w*R*2)	0.0787, 0.2416
R indices (all data) (*R*1, w*R*2)	0.0925, 0.2567
Extinction coefficient	0.007(3)
Largest diff. peak and hole (e/Å^3)	0.437 and −0.341



Scheme 1 Reaction for the formation of 1,3-bis(*p*-nitrophenoxy) propane

Results and Discussion

The title compound 3-bis(*p*-nitrophenoxy)propane, **1**, was synthesized in good yield by a facile aromatic nucleophilic substitution reaction of *p*-nitrophenol and 1,3-dibromopropane in the presence of K_2CO_3. Since this compound is a precursor and is easily isolated as crystalline material with a sharp melting point, characterization by single X-ray diffraction was the most straightforward technique to confirm identity (Fig. 1). Compound **1** crystallizes as two symmetry-unique half-molecules in the asymmetric unit with each molecule being completed by twofold symmetry: $-x + 3/2, y, -z + 1/2$ and $-x + 3/2, y, -z + 3/2$. Neither a close inspection of the packing diagram nor the program ADDSYMM [41] suggests any overlooked symmetry.

The molecules may be thought of packing in an interlocked herringbone array. Although it is conceivable that the molecule may adopt a linear conformation or develop bend(s) in the dialkoxy chain at the O atom or the 1 C (or 3 C) atom, consistent with the parent diphenoxypropane solid-state geometry, the molecules bend at the middle 2 C atom. Consequently, a molecular twofold symmetry arises from this bend and the relatively coplanar aryl group with ether O and the 1 and 2 C atoms. The C–C–C angle at the bend are 111.6(3)°, 115.1(3)° which is larger than ideal tetrahedral geometry of an sp^3 hybridized C most likely because of steric bulk of the aryloxy groups. The angles between the phenyl planes are 91.6(2)° and 93.5(2)°. Slight differences between the symmetry-unique molecules can be mostly accounted by rotation around C–C single bonds or steric relief deformations perhaps in order to promote better packing.

The structures of the even C chain analogs 1,3-bis(*p*-nitrophenoxy)ethane, **2**, and 1,3-bis(*p*-nitrophenoxy) butane, **3**, have been previously reported. In sharp contrast with the bent **1**, both **2** and **3** are relatively flat and linear. The angles between the mean planes described by the aryl rings are nil in **2** and **3**. In **3** there is some buckling observed at the butyl chain such that the two aryl rings are located in different but parallel planes. While the molecules exhibit twofold rotation in **1**, the molecules in **2** and **3** are located at inversion centers. The relatively flat **2** and **3** molecules exhibit intermolecular π–π aromatic interactions that are absent in bent **1** [42, 43].

It is well known that aromatic polymers that contain aryl ether or aryl sulfone linkages generally have lower glass transition temperatures, greater chain flexibility and tractability than their corresponding polymers without these groups in the chain. Such polymers are amorphous exhibiting excellent mechanical properties. The lower glass transition temperatures and the improved solubility are attributed to the flexible linkages that provide a polymer chain with a lower energy of internal rotation. The synthesized monomer precursor has alkyl ether linkage that is expected to lower the glass transition temperature with increased flexibility and solubility for ease in further mechanical processing of the resulting polymer.

Conclusion

The synthesis of title compound in good yield allows access to a synthon with the requisite alkyl/aryl linkages in the eventual preparation of soluble polyamides with projected desirable physical properties. The X-ray crystal structure confirms the structural similarity with the parent, unmodified diphenoxypropane but with nitro groups accessible for further chemical modification.

Supplementary Material

CCDC 678947 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting:

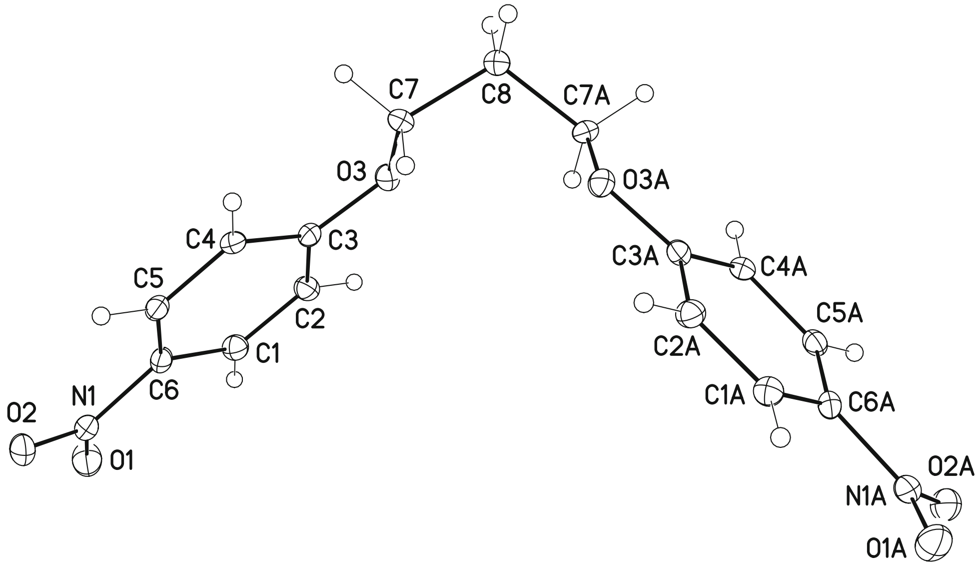


Fig. 1 Molecular diagram of 1.3-bis(*p*-nitroxy)propane with labeling scheme. Atoms are depicted with 30% probability ellipsoids. A second symmetry-unique but chemically equivalent molecule is omitted for clarity. Atoms labeled with A are generated by symmetry operation $(-x + 3/2, y, -z + 1/2)$

The Cambridge Crystalloraphic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336033.

Acknowledgement The authors wish to thank the Higher Education Commission of Pakistan (HEC) for financial support.

References

1. Sasanuma Y, Ono T, Miyazaki E, Hikino K, Arou J, Nakata K et al (2004) J Phys Chem B 108:13163. doi:10.1021/jp040135h
2. Sakellariou EG, Collin J-P, Dietrich-Bucheker CO, Sauvage J-P (2004) Eur J Inorg Chem 575. doi:10.1002/ejic.200300507
3. Berl V, Schmutz M, Krische MJ, Khoury RJ, Lehn JM (2002) Chem Eur J 8:1227. doi:10.1002/1521-3765(20020301)8:5<1227::AID-CHEM1227>3.0.CO;2-0
4. Minacheva LK, Ivanova IS, Kireeva IK, Sakharova VG, Sergienko VS, Tsivadze AY (2002) Crystallogr Rep 45:52
5. Guardigli C, Liantonio R, Mele ML, Metrangolo P, Resnati G, Pilati T (2003) Supramol Chem 15:177. doi:10.1080/1061027031000078248
6. Tooke DM, Lutz M, Spek AL (2005) Acta Crystallogr Sect E Struct Rep 61:o2152. doi:10.1107/S1600536805018532
7. Zhao Q-H, Jiang Z-H, Liao D-Z, Yan S-P, Fang R-B (2001) J Chin Chem Soc (Taipei) 48:723
8. Hu P-Z, Ma L-F, Wang J-G, Zhao B-T, Wang L-Y (2005) Acta Crystallogr Sect E Struct Rep 61:o2775. doi:10.1107/S1600536805023925
9. Fan Z, Diao C-H, Guo M-J, Yu M, Chen X (2005) Acta Crystallogr Sect E Struct Rep 61:o4004. doi:10.1107/S1600536805034665
10. Han J-R, Zhen X-L (2005) Acta Crystallogr Sect E Struct Rep 61:o4069. doi:10.1107/S1600536805036299
11. Seo J, Jin Y, Lee J-E, Park K-M, Lee BY, Lee SS (2004) Anal Sci X-ray Struct Anal 20:x15. doi:10.2116/analscix.20.x15
12. Hokelek T, Bilge S, Demiriz S, Ozguc B, Zilic Z (2004) Acta Crystallogr C 60:o803. doi:10.1107/S0108270104022565
13. Tafesh M, Weiguny J (1996) Chem Rev 96:2035. doi:10.1021/cr950083f
14. Brady ED, Clark DL, Keogh DW, Scott BL, Watkin JG (2002) J Am Chem Soc 124:7007. doi:10.1021/ja0168918
15. Vass A, Dudas J, Toth J, Varma RS (2001) Tetrahedron Lett 42:5347. doi:10.1016/S0040-4039(01)01002-4
16. Firouzabadi H, Tamami B, Kiasat AR (2000) Synth Commun 30:587. doi:10.1080/00397910008087360
17. Hari A, Miller BL (1999) Tetrahedron Lett 40:245. doi:10.1016/S0040-4039(98)02330-2
18. Feng Q-P, Xie X-M, Liu Y-T, Zhao W, Gao Y-F (2007) J Appl Polym Sci 106:2413. doi:10.1002/app.26772
19. Washio I, Shibasaki Y, Ueda M (2007) Org Lett 9:1363. doi:10.1021/ol0702425
20. Liou G-S, Hsiao S-H (2002) J Polym Sci Part A 41:94. doi:10.1002/pola.10552
21. Pan Y, Ford WT (1999) Polymer (Guildf) 40:135
22. Zulfiqar S, Ahmad Z, Sarwar MI (2007) Colloid Polym Sci 285:1749. doi:10.1007/s00396-007-1768-8
23. Zulfiqar S, Sarwar MI (2008) High Perform Polym doi:10.1177/0954008308089114
24. Sarwar MI, Zulfiqar S, Ahmad Z (2007) Colloid Polym Sci 285:1733. doi:10.1007/s00396-007-1760-3
25. Sarwar MI, Zulfiqar S, Ahmad Z (2008) J Sol-Gel Sci Technol 45:89. doi:10.1007/s10971-007-1640-9
26. Hunter CA, Spitaleri A, Tomas S (2005) Chem Commun (Camb) 29:3691. doi:10.1039/b506093a
27. Zhang Q, Dwyer TJ, Tsui V, Case DA, Cho J, Dervan PB et al (2004) J Am Chem Soc 126:7958. doi:10.1021/ja0373622
28. Davis RD, Jarrett WL, Mathias LJ (2000) Polymer (Guildf) 42:2621. doi:10.1016/S0032-3861(00)00501-2
29. Close LG Jr, Fornes RE, Gilbert RD (1983) J Polym Sci 21:1825
30. Zulfiqar S, Lieberwirth I, Sarwar MI (2008) Chem Phys 344:202. doi:10.1016/j.chemphys.2008.01.002
31. Zulfiqar S, Ishaq M, Ahmad Z, Sarwar MI (2008) Polym Adv Technol 19:1250. doi:10.1002/pat.1120
32. Chen X, Xu J, Guo B-H (2006) J Appl Polym Sci 102:3201. doi:10.1002/app.24551
33. Meyer A, Jones N, Lin Y, Kranbuehl D (2002) Macromolecules 35:2784. doi:10.1021/ma010541o
34. Chu B, Ying Q, Wu C, Ford JR, Dhadwal H, Qian R et al (1984) Polym Commun (Guildf) 25:211
35. Pastuska G, Just U, August H (1982) Angew Makromol Chem 107:173. doi:10.1002/apmc.1982.051070113
36. Zhao C, Zhang P, Lu S, He J, Wang XJ (2007) Mater Sci 42:9083. doi:10.1007/s10853-006-0957-z
37. Sengupta R, Bandyopadhyay A, Sabharwal S, Chaki TK, Bhowmick AK (2005) Polymer (Guildf) 46:3343. doi:10.1016/j.polymer.2005.02.104
38. Park Y, Lee D, Kim S (2004) J Appl Polym Sci 91:1774. doi:10.1002/app.13312
39. Zulfiqar S, Sarwar MI, Lieberwirth I, Ahmad Z (2008) J Mater Res 23:2296. doi:10.1557/jmr.2008.0301
40. Sheldrick GM (2008) Acta Crystallogr A 64:112. doi:10.1107/S0108767307043930
41. Spek AL (2003) J Appl Crystallogr 36:7. doi:10.1107/S0021889802022112
42. Butt MS, Khawar Rauf M, Bolte M, Akhter Z, Zafar-uz-Zaman M (2006) Acta Crystallogr Sect E Struct Rep 62:o3440. doi:10.1107/S1600536806027395 Online
43. Qi-Long Z, You-Cai Z, Yun-Qian Z, Sai-Feng X, Zhu T (2007) Acta Crystallogr Sect E Struct Rep 63:o4885. doi:10.1107/S1600536807060114