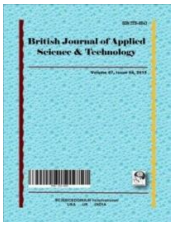

British Journal of Applied Science & Technology
14(1): 1-10, 2016, Article no.BJAST.23494
ISSN: 2231-0843, NLM ID: 101664541

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Synthesis, Characterization and Thermal Properties of New and Known 1,3-Benzo- and Naphtho-Oxazine Monomers Obtained Using a Modified Step-wise Procedure

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Authors' contributions

This work was carried out in collaboration between all authors. Author AUGG designed the study, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Authors MBA, NZ, NAI managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/BJAST/2016/23494
Editor(s):
(1) Jon S. Gold, Department of Chemistry, East Stroudsburg University, East Stroudsburg, PA, USA.
Reviewers:
(1) I. B. Masesane, University of Botswana, Botswana.
(2) Rakesh Choure, Shri Vaishnav Institute of Technology and Science, Indore, India.
Complete Peer review History: http://sciencedomain.org/review-history/12850

Original Research Article

Received 2nd December 2015
Accepted 22nd December 2015
Published 31st December 2015

ABSTRACT

New and known 1, 3-benzo- and naphtho- oxazine monomers were synthesized using a modified step-wise procedure in which formaldehyde which is a suspected human carcinogen and a confirmed animal carcinogen was replaced with methylene bromide for ring-closure reaction. Salicylaldehyde and 2-hydroxy-1-naphthaldehyde were separately condensed with the primary aromatic amines p-toluidine, p-phenylenediamine and 4-butylaniline to give imine compounds which on reduction with $NaBH_4$ yields 2-hydrobenzylamines / 2-hydroxynaphthylamines depending on the 2-hydroxyaldehyde used. The 2-hydroxybenzylamines / 2-hydroxynaphthylamines subsequently undergo ring-closure reaction with methylene bromide in absolute alcohol to give 1, 3-benzoxazine and naphthoxazine monomers in good yields. The chemical structures of the synthesized compounds were confirmed using FT-IR, ^{1}H and ^{13}C NMR spectral analysis and mass spectrometry (GC-MS). The thermal properties of the synthesized compounds were determined

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using Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). From the result of thermal analysis, it may be concluded that the bifunctional monomers show higher glass transition temperature (T_g) and better thermal stability than the monofunctional monomers.

Keywords: Modified step-wise procedure; 1,3-benzoxazine; 1,3-naphthoxazine; synthesis; thermal properties.

1. INTRODUCTION

Benzoxazines are nitrogen and oxygen containing heterocyclic compounds that are developed as alternatives to traditional phenolic resins for high temperature applications [1,2]. The synthesis of these compounds dates back seventy years ago [3-5] but their potentials was only recognized recently [6]. The early synthetic developments were based on monofunctional benzoxazines which later form the basis for the study of bifunctional benzoxazines which were first synthesized in 1994 by Ning and Ishida [7]. Benzoxazine compounds and their corresponding polymers have over the years received much attention of the research community due to their inherent advantages over the traditional phenolic resins. These advantages include near-zero shrinkage upon curing, high thermal stability, high glass transition temperature, low moisture absorption and high molecular design flexibility [8-10]. Furthermore, compounds containing 3,4-dihydro-1, 3-oxazine ring systems show a wide range of pharmacological and antibacterial activities [11,12]. These heterocyclic compounds are therefore studied extensively for the synthesis of biologically active compounds ranging from herbicides and fungicides to therapeutically usable drugs [13]. Biological activities exhibited by these compounds include antimicrobial, antitumor, anthelminthic, antimycobacterial, antituberculosis and Insect Growth Regulatory (IGR) activity among others [14]. Generally, benzoxazine monomers are synthesized by a Mannich-like condensation of phenol, formaldehyde and an amine. Several methods were proposed and used for the synthesis of these heterocyclic monomers using different solvents [15,16]. Among these methods is the three steps procedure which has recently gained considerable interest [17] starting from hydroxyaldehydes, amines or diamines and formaldehyde. In this procedure, imine formation is accomplished between the aldehyde and amino compound followed by reduction to give aminomethylphenols. Lastly, ring-closure between the aminomethylphenols and formaldehyde takes place leading to the benzoxazine monomers. Moreover, this procedure tolerates the use of different functional groups and is therefore used in the synthesis of different benzoxazine compounds [18,19]. In this paper, the three step procedure was modified by replacing formaldehyde which is a suspected human carcinogen and a confirmed animal carcinogen [20] with methylene bromide for ring-closure reaction in the last synthetic step. Methylene bromide can provide the methylene bridge necessary for the ring-closure reaction leading to the formation of 1,3-benzoxazine and 1,3-naphthoxazine compounds.

2. EXPERIMENTAL

2.1 Materials

Salicylaldehyde (98%), 2-hydroxy-1-naphthaldehyde (97%), *p*-toluidine (98%), 4-nitroaniline (97%), *p*-phenylenediamine (98%), 1,6-hexamethylenediamine (97%) and sodium borohydride (99.5%) [Sigma Aldrich Chemical Company]. Absolute ethanol (99.8%) and methanol (98%) [HmbG Chemicals]. Anhydrous sodium sulphate (99%) and ethyl acetate (98%) [Fischer Chemical Company]. All chemicals were used as received without any further purification.

2.2 Characterization

FT-IR spectra were recorded using Perkin Elmer FTIR model 100 series spectrophotometer (KBr Pellet) in the region 280-4000 cm^{-1}. ^{1}H and ^{13}C NMR spectral analysis was conducted on JEOL 500 MHz NMR spectrometer using acetone-d_6 as the NMR solvent. GC-MS analysis was conducted using Shimadzu model QP 5050A GC-MS analyzer.

Differential Scanning Calorimetry (DSC) was performed using a Mettler Toledo DSC 822^{e} calorimeter. Thermogravimetric analysis (TGA) analysis was conducted using a Mettler Toledo TGA/DSC 1 STAR^{e} System at a heating rate of 10°C / min. in nitrogen. Melting points of the

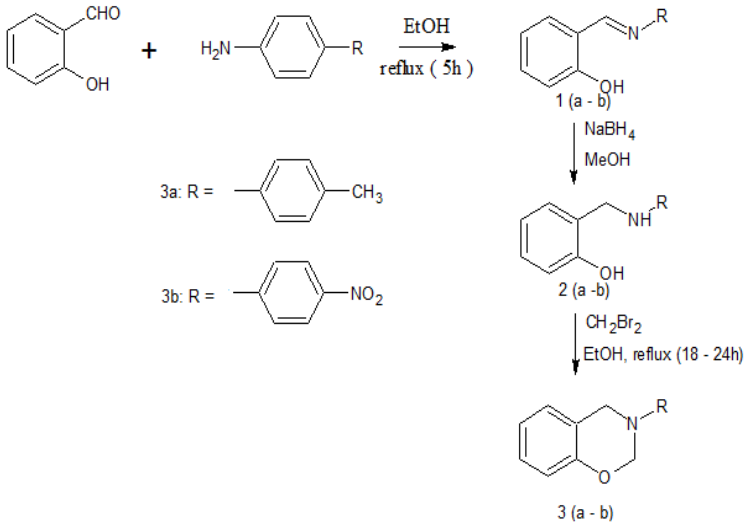
synthesized compounds were determined using a Barnstead electrothermal melting point instrument 9100 Model and are uncorrected.

2.3 Synthesis of Imine compounds 1 (a-e)

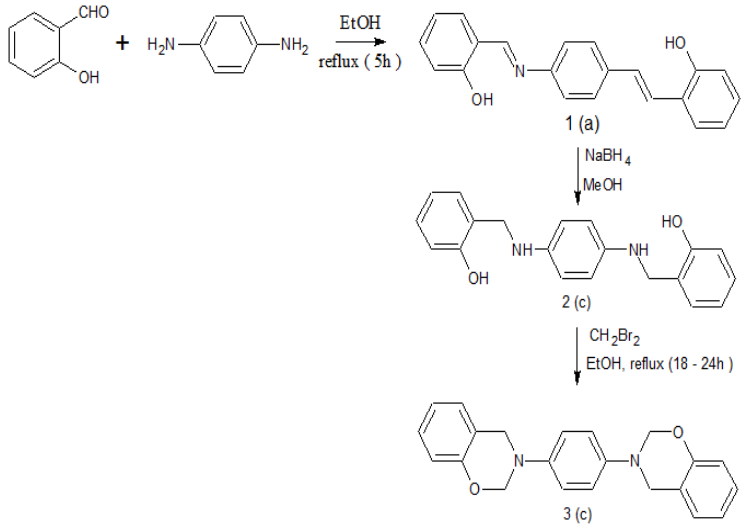
The imine compounds 1 (Scheme 1, 2, 3 and 4) were prepared as reported in literature [17,19] by refluxing 200 mmol of salicylaldehyde / 2-hydroxy-1-naphthaldehyde and individual primary amines in absolute alcohol for 5 h under nitrogen atmosphere.

2.4 Synthesis of 2-hydroxybenzylamines /2-hydroxynaphthylamines 2 (a-e)

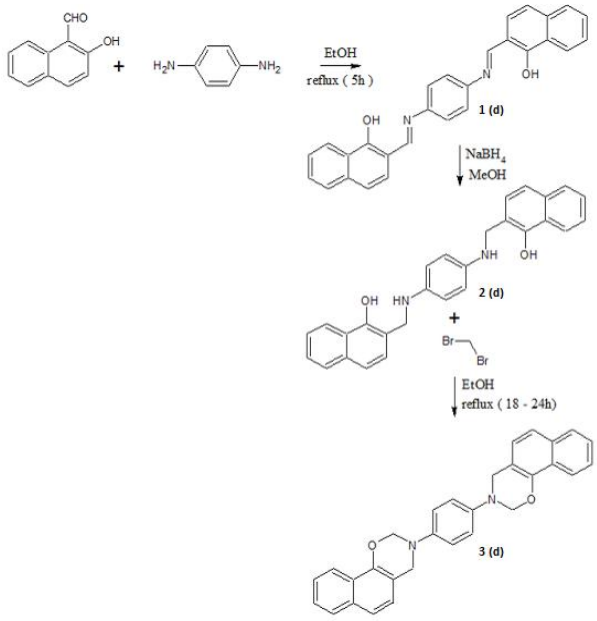
In all cases, 100 mmol of the imine compounds were added into a conical flask containing 150 mL of ethanol. To this solution was added 100 mmol of $NaBH_4$ in small portions at ambient temperature while stirring until the reaction is complete. 150 mL of water was then added and the product was extracted with ethyl acetate, washed with water, dried overnight with anhydrous Na_2SO_4 and concentrated to dryness.



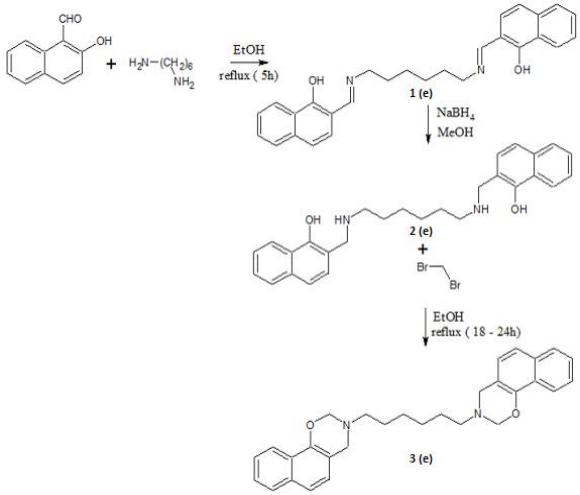
Scheme 1. Synthesis of 1,3-benzo- oxazine monomers (a-b)



Scheme 2. Synthesis of 1,3-benzo- oxazine monomer (c)



Scheme 3. Synthesis of 1,3-naphtho- oxazine monomer (d)



Scheme 4. Synthesis of 1,3-naphtho- oxazine monomer (e)

2.5 Synthesis of 1, 3-benzoxazine and Naphthoxazine Derivatives 3 (a-e)

In all cases, 80 mmol of the 2-hydroxybenzylamines and 150 mmol of methylene bromide were added to 100 mL of absolute ethanol and the mixture refluxed for 18-24 h under nitrogen atmosphere. The mixture was allowed to cool to room temperature and the solvent removed by rotary evaporation. 100 mL of water was then added and the compound extracted with ethyl acetate, washed with water, dried overnight with anhydrous Na_2SO_4 and concentrated to dryness. All the synthesized compounds were purified by recrystallization in 50:50 water: ethanol mixture.

3. RESULTS AND DISCUSSION

3.1 Synthesis of 1,3-benzo- and naphtha-oxazine monomers

All the synthesized compounds showed appropriate characteristic signals necessary to confirm their structures. To illustrate with compound (a), the FT-IR spectrum showed

characteristic absorption bands due to trisubstituted benzene rings at 914 and 1453 cm^{-1} which are characteristic absorptions of benzoxazines and naphthoxazines. In addition, other bands observed are those of asymmetric Ar-H stretching vibration at 3022 cm^{-1}, asymmetric stretching for C-O-C at 1241 cm^{-1} and aliphatic CH_2 stretching bands between 2916 and 2856 cm^{-1}. In the ^1H NMR spectra, the characteristic proton resonance signals of the oxazine ring O-CH_2-N and Ar-CH_2-N were observed at 5.36 and 4.56 ppm. In the ^{13}C NMR spectra, the carbon chemical shifts corresponding to O-CH_2-N and Ar-CH_2-N were observed at 79.6 and 44.8 ppm. Other analytical figures for both the compounds are given as follows.

3-(4-methylphenyl)-3,4-dihydro-2H-1,3-benzoxazine **(a)**: Yield 72%, yellow powder, mp 102-103.2°C. IR (KBr): 3257, 3022, 2916, 2856, 2726, 2576, 1889, 1778, 1592, 1505, 1453, 1399, 1360, 1311, 1241, 1184, 1108, 1047, 971, 914, 814, 748, 712, 610, 543, 516, 479, 459, 396, 361, 334 cm^{-1}; ^1H NMR (500 MHz, Acetone-d_6, ppm): δ_H 8.18-6.68 (4H, Ar-H), 5.46 (O-CH_2-N), 4.60 (Ar-CH_2-N). ^{13}C NMR (500 MHz, Acetone-d_6, ppm): δ_C 154.2-118.4 (Ar-H), 79.6 (O-CH_2-N), 49.9 (Ar-CH_2-N), 19.8 (CH3 aliphatic). MS: m/z 225 (M+).

3-(4-nitrophenyl)-3,4-dihydro-2H-1,3-benzoxazine **(b)**: Yield 74%, bright yellow solid, mp 127-127.8°C. IR (KBr): 3367, 3077, 3174, 3077, 2857, 2433, 1904, 1659, 1589, 1488, 1398, 1322, 1256, 1224, 1197, 1159, 1109, 1014, 952, 856, 825, 753, 689, 629, 577, 535, 493, 441, 336 cm^{-1}; ^1H NMR (500 MHz, Acetone-d_6, ppm): δ_H 8.12-6.81 (4H, Ar-H), 5.58 (O-CH_2-N), 4.79 (Ar-CH_2-N). ^{13}C NMR (500 MHz, Acetone-d_6, ppm): δC 154.8-114.6(Ar-H), 76.6 (O-CH_2-N), 48.6 (Ar-CH_2-N). MS: m/z 256 (M^+).

3-3'-(1,4-phenylene) bis(3,4-dihydro-2H-1,3-benzoxazine) **(c)** Yield 78%, brown powder, mp 178.2-178.8°C. IR (KBr): 2974, 2908, 1584, 1496, 1362, 1205, 932, 826, 748, 635, 541, 437, 308 cm^{-1}; ^1H NMR (500 MHz, Acetone-d_6, ppm): δ_H 7.10-6.82 (Ar-H), 5.36 (O-CH_2-N), 4.58 (Ar-CH_2-N). ^{13}C NMR (500 MHz, Acetone-d_6, ppm): δ_C 127.9-116.2 (Ar-H), 79.9 (O-CH_2-N), 50.0 (Ar-CH_2-N). MS: m/z 344 (M^+).

3, 3'-(1, 4-phenylene) bis (3, 4-dihydro-2H-1, 3-Naphthoxazine) **(d).** Yield 72%, dark red solid, mp = 211-212°C. IR (KBr): 3457, 3012, 2946, 2886, 1601, 1509, 1466, 1377, 1220, 1059, 1000, 938, 809, 745, 680, 629, 556, 489, 422, 367 cm^{-1}; ^1H NMR (500 MHz, Acetone-d_6, ppm): δ_H 8.18-6.46 (Ar-H), 5.82 (2H, O-CH_2-N), 4.90 (2H, Ar-CH_2-N). ^{13}C NMR (500 MHz, Acetone-d_6,ppm):δ_C154.2(C,naphthalene),134.1(C,benzene),132.4(C,naphthalene),25.5(C,naphthalene), 112.7(C,naphthalene), 127.7(CH,naphthalene), 126.9(CH,naphthalene), 125.2(CH,naphthalene), 124.8(CH,naphthalene), 121.4(CH,naphthalene), 119.3(CH,naphthalene), 83.2(2H, O-CH_2-N), 54.2(2H, Ar-CH_2-N). MS: m/z = 444 (M^+).

3, 3'-(1, 6-hexamethylene) bis (3, 4-dihydro-2H-1, 3-Naphthoxazine) **(e).** Yield 68%, beige brown solid, mp = 108.20-119.42. IR (KBr): 3399, 3050, 2925, 2856, 1621, 1513, 1458, 1351, 1260, 1175, 997, 943, 837, 744, 494, 421, 344 cm^{-1}; ^1H NMR (500 MHz, Acetone-d_6, ppm): δ_H 8.32-7.17 (Ar-H), 5.21 (2H, O-CH_2-N), 3.96 (2H, Ar-CH_2-N), 2.42 (CH_2, aliphatic), 1.44 (CH_2, aliphatic), 1.34 (CH_2, aliphatic). ^{13}C NMR (500 MHz, Acetone-d_6, ppm): δ_C 156.2 (C, naphthalene), 134.4 (C,naphthalene), 127.2 (C,naphthalene), 129.6 (CH,naphthalene), 128.2 (CH,naphthalene), 126.2 (CH,naphthalene), 124.6 (CH,naphthalene), 121.6 (CH,naphthalene), 120.4 (CH,naphthalene), 114.1 (CH,naphthalene), 112.8 (C,naphthalene), 78.8 (2H, O-CH_2-N), 52.2 (2H, Ar-CH_2-N), 49.4 (CH_2 aliphatic), 30.6 (CH_2 aliphatic), 28.2 (CH_2 aliphatic). MS: m/z = 452 (M^+).

3.2 Thermal Properties of the Synthesized 1,3-benzo- and Naphtha- oxazine Monomers

Thermal Properties of the synthesized compounds include glass transition temperature (T_g) and thermal stability. DSC was used to determine the glass transition temperature and the transition temperatures of the synthesized monomers. A plot of heat flow versus temperature gives the DSC thermogram from which these three quantities are determined. Figs. 1-5 gives the DSC thermograms of the 1,3-benzoxazine and 1,3-naphthoxazine compounds a-d. The glass transition temperature are 96, 122, 170, 203 and 54°C for compound a, b, c, d and e, respectively. The endothermic peak temperature (melting) [T_m] and the exothermic peak temperature (crystallization) [T_c] are shown in the thermogram of each of the synthesized monomers. The DSC data of all the monomers are summarized in Table 1.

The thermal stability of the synthesized compounds were evaluated using TGA under

nitrogen atmosphere. A plot of weight loss versus temperature gives the TGA thermogram also reffered to as weight loss curves are presnted in Figs. 6-10. From these curves the degradation processes are determined. It can be seen from these thermograms that monomers a, b, c and d exhibits two degradation processes whereas monomer e exhibit three degradation processes. The temperatures corresponding to 5% and 10% weight loss (T_d5 and T_d10) and the char yield (Y_c) are given in Table 1. From the result, it may be concluded that the bifunctional monomers possess better thermal properties than the monofunctional monomers. The TGA data are summarized in Table 2.

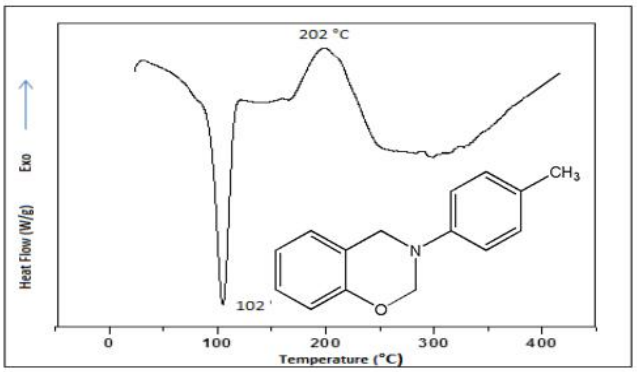


Fig. 1. DSC thermogram of monomer a

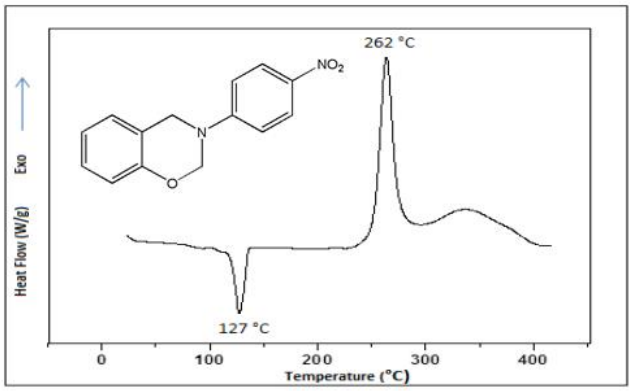


Fig. 2. DSC thermogram of monomer b

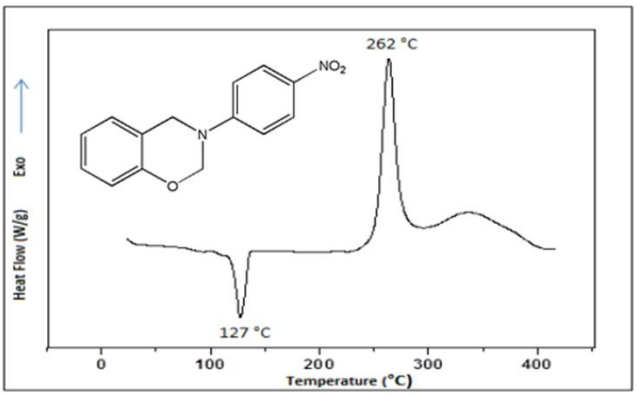


Fig. 3. DSC thermogram of monomer c

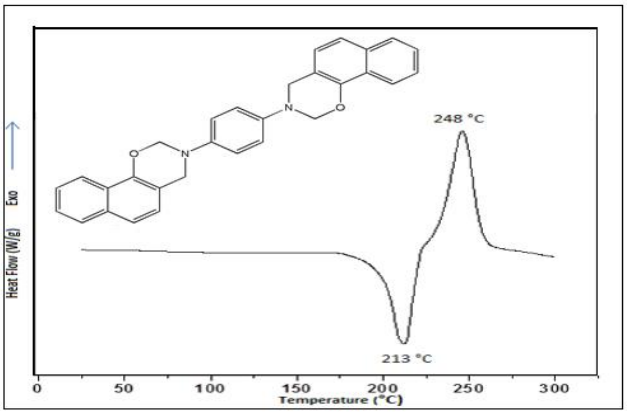


Fig. 4. DSC thermogram of monomer d

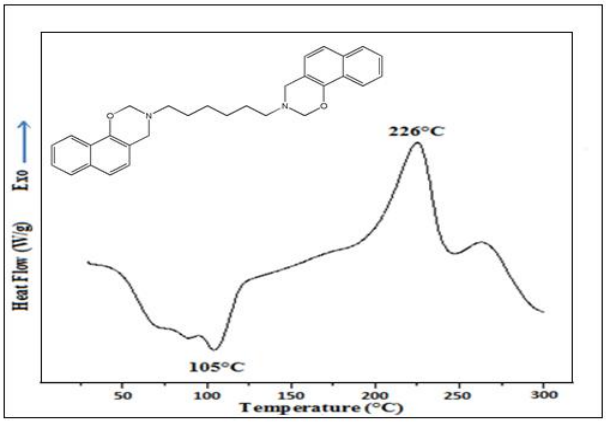


Fig. 5. DSC thermogram of monomer e

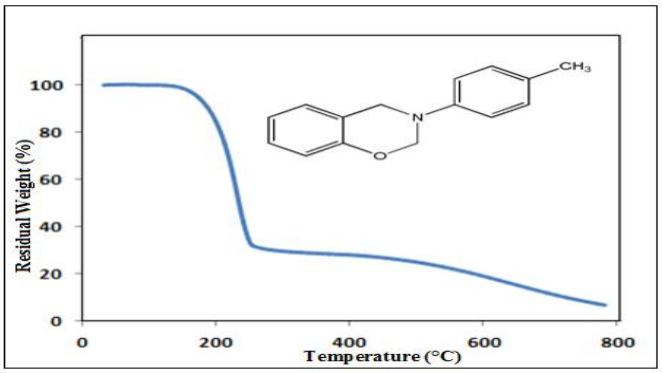


Fig. 6. TGA thermogram of monomer a

Table 1. DSC data of the synthesized monomers (a-e)

Sample (s)	T_g	T_m	T_c
a	98	102	202
b	122	127	262
c	172	178	235
d	202	213	248
e	54	105	226

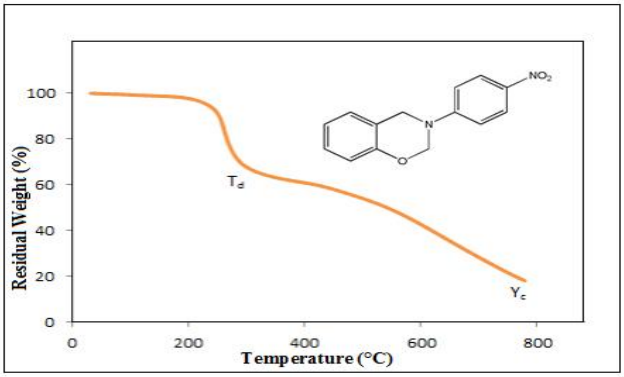


Fig. 7. TGA thermogram of monomer b

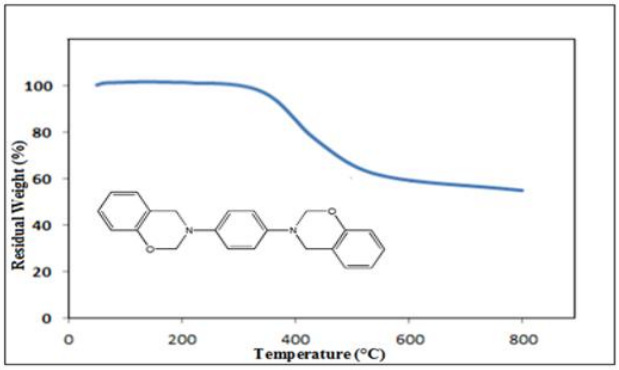


Fig. 8. TGA thermogram of monomer c

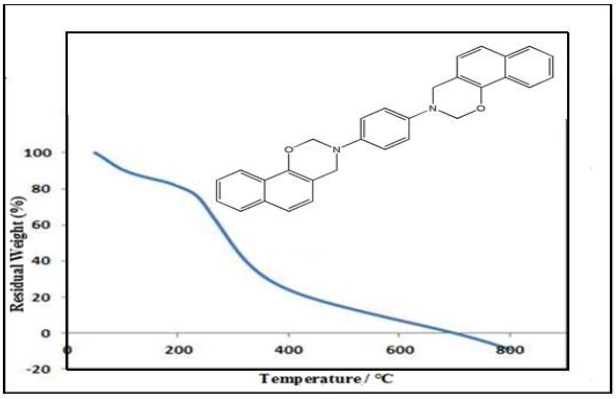


Fig. 9. TGA thermogram of monomer d

Table 2. TGA data of the synthesized monomers (a-e)

Samples (s)	T_d5 (°C)	T_d10 (°C)	T_d (°C)	Y_c (800°c) [%]
a	153	174	262	0
b	232	253	258	18
c	359	383	502	55
d	74	103	394	0
e	100	153	542	0

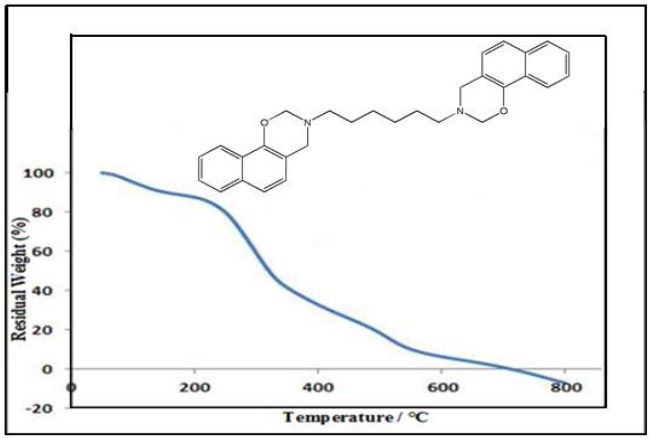


Fig. 10. TGA thermogram of monomer e

4. CONCLUSIONS

New and known 1,3-benzo- and naphtho-oxazine monomers were successfully synthesized using methylene bromide for ring-closure in place of the usual formaldehyde which is a suspected human carcinogen and a confirmed animal carcinogen. Methylene bromide can provide the necessary methylene group between oxygen and nitrogen of the reduced imine compounds leading to ring-closure and elimination of hydrogen bromide. The results obtained are in agreement with what is contained in literature that bifunctional compounds generally show better thermal properties than monofunctional compounds.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the Department of Chemistry, Faculty of Science, Universiti Putra Malaysia for their assistance throughout the work.

DISCLAIMER

This work was presented in the conference “The Fundamental Science Congress 2015” available link is-
“http://math.upm.edu.my/fsc2015/senaraip.php”
date November 12 - 13, Universiti Putra Malaysia.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Nair CPR. Advances in addition-cure phenolic resins. Prog. Polym. Sci. 2004;29: 401-498.
2. Ghosh NN, Kiskan B, Yagci Y. Polybenzoxazines- new high performance thermosetting resins: synthesis and properties. Prog. Polym. Sci. 2007;32: 1344-1391.
3. Holly FW, Cope AC. Condensation products of aldehydes and ketones with *o*-aminobenzyl alcohol and *o*-hydroxybenzylamine. J. Am. Chem. Soc. 1944;66:1875-1879.
4. Burke WJ, Kolbezen MJ, Stephens CW. Condensation of naphthols with formaldehyde and primary amines. J. Org. Chem. 1952;74:3601-3605.
5. Burke WJ, Murdoch KC, Ec G. Condensation of hydroxyaromatic compounds with formaldehyde and primary aromatic amines. J. Am. Chem. Soc. 1954;76:1677-1679.
6. Demir KD, Kiskan B, Aydogan B, Yagci Y. Thermally curable main-chain benzoxazine prepolymers via polycondensation route. React. & Funct. Polym. 2013;73:346-359.
7. Ning X, Ishida H. Phenolic materials via ring-opening polymerization- synthesis and characterization of bisphenol-A-based benzoxazines and their polymers. J. Polym. Sci. Part A: Polym. Chem. 1994; 32:1121-1129.
8. Zhang K, Ishida H. Smart synthesis of high-performance thermosets based on ortho- amide-imide functional

benzoxazines. Frontiers in Materials. 2015;2:1-9.

9. Wang Y, Chang C, Liu Y. Benzoxazine-functionalized multi-walled carbon nanotubes for preparation of electrically-conductive polybenzoxazines. Polymer. 2012;53:106-112.
10. Li S, Zou T, Liu X, Tao M. Synthesis and characterization of benzoxazine monomers from rosin and their thermal polymerization. Designed Monomers and Polymers; 2013.
    DOI: 10.1080/15685551.2013.771317
11. Mathew BP, Kumar A, Sharma S, Shukla PK, Nath M. An eco-friendly synthesis and antimicrobial activities of dihudro-2H-benzo- and naphtha-1,3-oxazine derivatives. European Journal of Medicinal Chemistry. 2010;45:1502-1507.
12. Tang Z, Zhu Z, Xia Z, Liu H, J, Xiao X, Ou X. Synthesis and fungicidal activity of novel 2,3-Disubstituted-1,3-benzoxazines. Molecules. 2012;17:8174-8185.
13. Siddiqui NR, Ali N, Alam MS, Ahsan W. Pharmacological profile of benzoxazine: A short review. J. Chem. Pharm. Res. 2010; 2:309-316.
14. Shakil NA, Pandey A, Singh MK, Kumar J, Awasthi K, Pakaj SK, Srivastavas C, Singh MK, Pandey RP. Synthesis and bioefficacy evaluation of new 3-substituted-3,4-dihydro-1,3-benzoxazines. Journal of Environmental Science and Health Part B. 2010;45:108-115.
15. Li S, Wang L. Curing behavior of 4,4'-diaminodiphenyl methane-based benzoxazine oligomers/bisoxazoline copolymers and the properties of their cured resin. J. Appl. Polym. Sci. 2006;99: 1359-1366.
16. Agag T, Jin L, Ishida H. A new synthetic approach for difficult benzoxazine: Preparation and polymerization of 4,4'-diaminodiphenyl sulfone-based benzoxazine monomer. Polymer. 2009;50: 5940-5944.
17. Lin CH, Chang SL, Hsieh CW, Lee H. Aromatic diamine-based benzoxazines and their high performance thermosets. Polymer. 2008;49:1220-1229.
18. Imran M, Kiskan B, Yagci Y. Concise synthesis and characterization of unsymmetric 1,3- benzoxazines by tandem reactions. Tetrahedron Letters. 2013;54: 4966-4969.
19. Andreu R, Ronda JC. Synthesis of 3,4-Dihydro-2H-1,3-benzoxazines by condensation of 2-Hydroxyaldehydes and primary amines: Application to the synthesis of hydroxy-substituted and deuterium-labeled compounds. Synthetic Communications. 2008;38:2316-2329.
20. Lewis RD Sr. Hazardous chemicals desk reference. John Wiley & Sons, New York; 2008.

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