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SHORT COMMUNICATION

Synthesis, spectral and thermal study of (2E,6E)-2,6-bis(4-aminobenzylidene)cyclohexanone

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ABSTRACT

(2E,6E)-2,6-bis(4-aminobenzylidene)cyclohexanone (BABC) was synthesized by two-step reaction of p-nitrobenzaldehyde and cyclohexanone followed by its reduction. The structure of BABC was supported by UV-Vis, FTIR, ¹HNMR and mass spectral data. DSC endothermic transition at 230.6 °C is assigned as melting transition followed by decomposition reaction. BABC is thermally stable up to 240 °C and followed three step degradation kinetics. Various kinetic parameters were determined by Anderson-Freeman method and discussed.

Keywords: Photoactive diamine, thermal stability, kinetic parameters, Anderson-Freeman method, (2E,6E)-2,6-bis(4-aminobenzylidene)cyclohexanone

1. INTRODUCTION

Aromatic diamines are important materials for dyes, agrochemicals, varnishes, antioxidants, coatings, pesticides, fertilizers, etc. industries. They are also useful for manufacturing thermally stable polyimides, poly(ester-imides), Schiff bases, bactericides, antitubercular, antifungal and antibacterial and curing agents for epoxy resins [1-3]. The alkalinity of amines depends on aromatic ring substituents.

Photochemical reactions of photosensitive materials can induce changes in solubility, optical transparency, dielectric constant, and refractive index [4-7]. Chalcone, cinnamate, coumarine, thymine, dibenzal acetone, cinnamylidene, 1,4-phenylenediacrylate, 2-styryl pyridine and their derivatives are photo sensitive materials. Among photosensitive materials chalcone derivatives are highly sensitive to UV radiation in the wavelength range 300-360 nm. They are used for the synthesis of photocrosslinkable and photopolymerization [8]. They are used in different polymer fields especially in photoresist technology. To the best of our knowledge no work has been reported on (2E,6E)-2,6-bis(4-aminobenzylidene)cyclohexanone.

The main objective of the present work was to synthesize photosensitive diamine for curing epoxy resins. We have synthesized (2E,6E)-2,6-bis(4-aminobenzylidene)cyclohexanone (BABC) by two-step reaction of p-nitrobenzaldehyde and cyclohexanone followed by its reduction. BABC is characterized by spectral and thermal techniques.

2. EXPERIMENTAL

2. 1. Materials

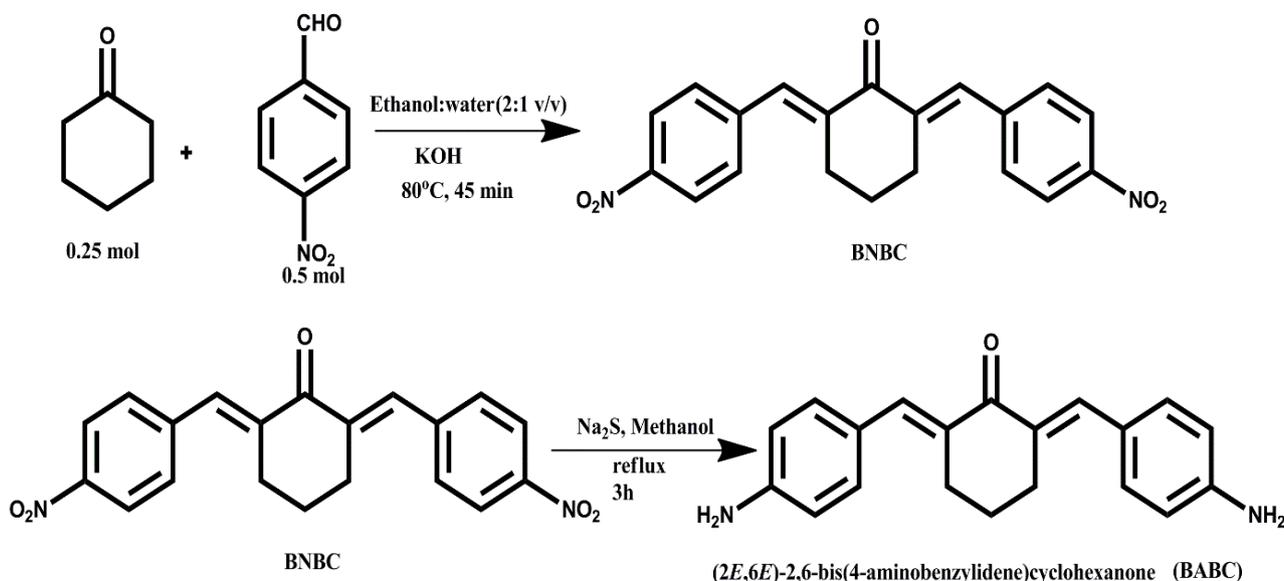
Solvents and chemicals used were of laboratory grade and purified prior to their use [9]. 4-Nitrobenzaldehyde, sodium bicarbonate, potassium hydroxide, and sodium sulfide were supplied by Spectrochem Mumbai, methanol, ethyl acetate, n-hexane, diethyl ether, N,N-dimethylformamide, acetone, chloroform, tetrahydrofuran, 1,4-dioxane, 1,2- dichloroethane and dimethylsulfoxide were supplied by Allied Chemicals Mumbai and used as received.

2. 2. Synthesis of (2E,6E)-2,6-bis(4-nitrobenzylidene)cyclohexanone

A 0.25 mol cyclohexanone, 0.5 mol 4-nitrobenzaldehyde and, 300 ml ethanol-water (2:1V/V) were placed into a three neck flask equipped with a mechanical stirrer and thermometer. The mixture was heated to 80 °C with stirring for 45 min and then 0.1g KOH catalyst was added and refluxed with stirring for 1h. The reaction was monitored by TLC using ethyl acetate-n-hexane (3:2 V/V). The reaction mixture was cooled to room temperature and poured in excess of diethyl ether. Yellow precipitates were filtered, washed well with diethyl ether and dried in an oven at 50 °C. (2E,6E)-2,6-bis(4-nitrobenzylidene)cyclohexanone (BNBC) was crystallized four times from chloroform-n-hexane. The yield and mp were 93% and 182 °C, respectively.

2. 3. Synthesis of (2E,6E)-2,6-bis(4-aminobenzylidene)cyclohexanone

(2E,6E)-2,6-Bis(4-aminobenzylidene)cyclohexanone (BABC) was synthesized by reducing BNBC (Scheme-I). A 51 mmol Na₂S and 20.8 mmol NaHCO₃, 1.5 lit of the mixture of CH₃OH·H₂O (2:1 V/V) were placed into a 2lit three necked flask equipped with a mechanical stirrer and a thermometer. The reaction mixture was stirred at room temperature for 1h. A light blue precipitates formed were filtered and filtrate was transferred into another 2lit three necked flask. To this solution 35.7 mmol of BNBC in 100 ml CH₃OH was added and refluxed with stirring for 3h. The reaction was monitored by TLC using ethyl acetate-n-hexane (3:2V/V). Brown product was filtered, washed well with water and dried in an oven at 50 °C. BABC was crystallized four times from DMF-water. The yield and mp of BABC were 89 % and 220 °C, respectively.



Scheme I. Synthesis of (2E,6E)-2,6-bis(4-aminobenzylidene)cyclohexanone (BABC)

2. 4. Characterization methods

Ultraviolet-Visible (UV-Vis) spectra of BNBC and BABC in THF were scanned on a Shimadzu UV1700 over wavelength range from 250-500 nm. Fourier transform infrared (FTIR) spectra (KBr pellet) of BNBC and BABC were scanned on a Shimadzu FTIR-8400 spectrometer over the frequency range from 4000 to 400 cm⁻¹. ¹HNMR spectra of BNBC (400 MHz) and BABC (500 MHz) in DMSO-d₆ were scanned on a Bruker FTNMR spectrometer by using TMS as an internal standard. Mass spectra of BNBC and BABC were scanned on a Shimadzu GC-MS QP 2010 spectrometer using EI (0.7kV) detector. The ion source temperature was 220 °C and interface temperature was 240 °C. Differential scanning calorimetric (DSC) and thermogravimetric thermograms of BABC were scanned on a Shimadzu DSC60 (Kyoto, Japan) at 10 °C min⁻¹ heating rate under nitrogen atmosphere (100 mlmin⁻¹ flow rate). A known mass of BABC was taken in an aluminum cup covered empty aluminum cup and sealed by a crimper. DSC and TG thermograms were scanned over the temperature range from room temperature to 350 °C and 800 °C, respectively.

3. RESULTS AND DISCUSSION

3. 1. Spectral analysis

BNBC: UV-Vis (THF): 339 nm; IR (KBr): 3232 (=C-H str.), 2922(C-H asym str.), 2843 (C-H sym. str.), 1763 (C=O str.), 1591 (C=C str.), 1510 (N=O str.), 1437 (C-H def.), 1155 (C-H ipd) and 854 (C-H oopd); ¹HNMR (DMSO-d₆, 400 MHz): 1.770-1.741 (t, 2H, CH₂) 2.947-2.921 (t, 4H, CH₂), 7.695 (s, 2H, =C-H), 7.822-7.801(d, 4H, ArH, J = 8.4), and 8.293-8.271 (d, 4H, Ar H, J = 8.8); MS: 365 (M⁺), 364 (M-1), 363 (M-2), 348, 347 (Base peak), 318, 317, 289, 215, 128, 115, 102, 89, 77, 63, 51.

BABC: UV-Vis (THF): 258 and 405 nm; IR (KBr): 3358 (N-H str.), 3101 (=C-H str.), 2928 (C-H asym str.), 2843 (C-H sym. str.), 1712 (C=O str.) 1587 (C=C str.), 1435 (C-H def.), 1157 (C-H ipd) and 837 (C-H oopd); ^1H NMR (DMSO d_6 , 500 MHz): 1.719-1.697 (t, 2H, CH $_2$) 2.835-2.815 (t, 4H, CH $_2$), 5.674 (s, 4H, NH $_2$), 6.623-6.606 (d, 4ArH, J 8.5), 7.281-7.264 (d, 4ArH, J = 8.5) and 7.474 (s, 2H, =CH); **MS**: 306 (M+2) $^+$, 305 (M+1) $^+$, 304 (M $^+$, Base peak), 302 (M-2) $^+$, 288, 276, 247, 182, 144, 130, 117, 106, 93, 77, 65.

Both π - π^* and n - π^* transitions in BNBC and BABC are possible due to presence of double bonds and lone pair of electrons on nitrogen atoms. The combined π - π^* and n - π^* transition of BNBC is shifted from 339 nm to 258 nm in case of BABC. The shifting of combined π - π^* and n - π^* transition of BNBC and appearance of new peak in visible region suggested transformation of nitro groups to amino groups. Disappearance of IR absorption peak of BNBC at 1510 cm^{-1} (N=O str.) and appearance of new absorption peak of BABC at 3358 cm^{-1} (N-H str.) supported complete reduction of BNBC. The appearance of a new peak at 5.674 ppm due to amino groups confirmed complete reduction of BNBC. As compared to BNBC the relevant protons of BABC are appeared in somewhat up field due to electronegativity difference between two compounds. The mass spectra of BNBC and BABC showed expected M+ peak at 365 and 304, respectively. Other expected fragments confirmed the structure of both the compounds. Thus UV-Vis, IR, NMR and MS data confirmed the structure of the synthesized compounds.

3. 2. Thermal analysis

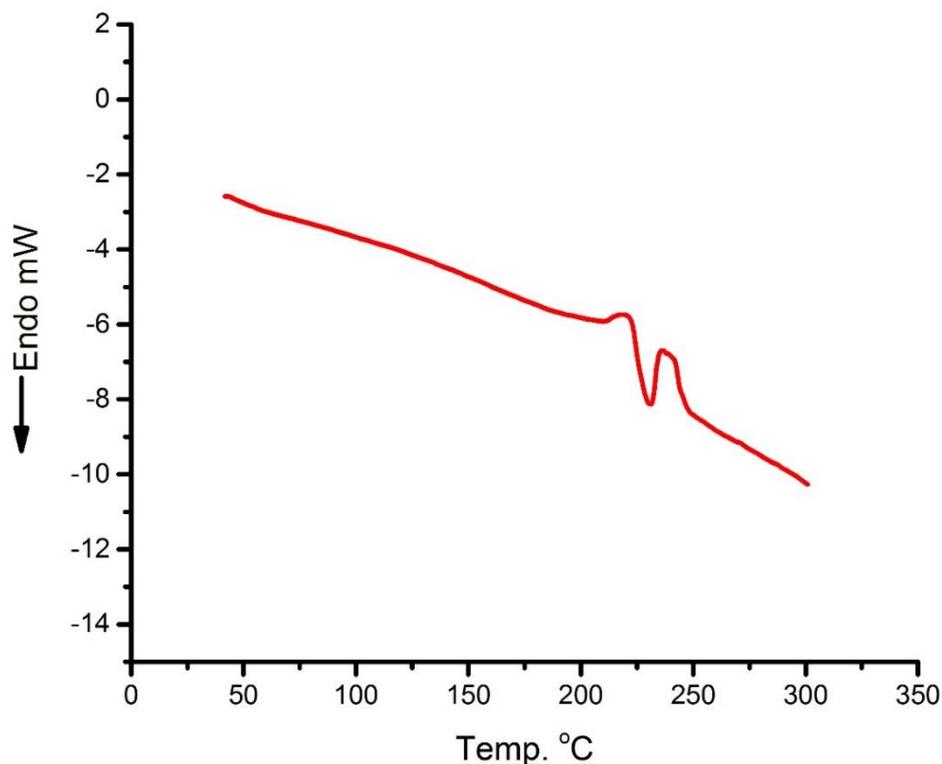


Figure 1. DSC thermogram of BABC at 10 °C /min heating rate in nitrogen atmosphere.

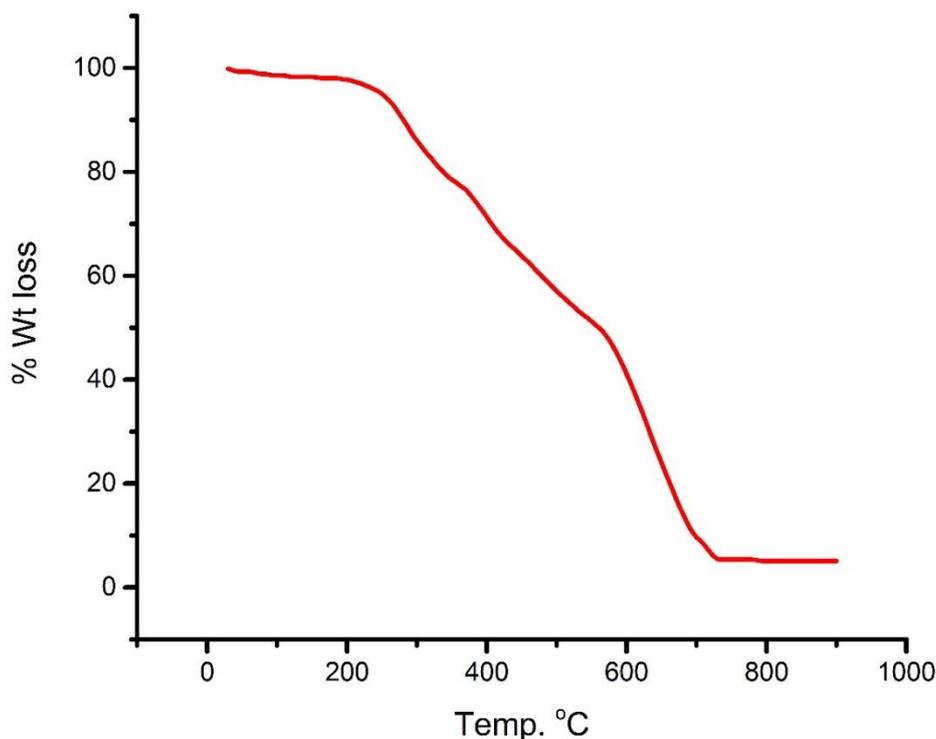


Figure 2. TGA thermogram of BABC at 10 °C/min heating rate in nitrogen atmosphere.

DSC and TG thermograms of BABC at the heating rate of 10 °C min⁻¹ in nitrogen atmosphere are presented in Figures 1 and 2, respectively. DSC endothermic transition at 230.6 °C is assigned as melting transition followed by decomposition reaction. BABC is thermally stable up to 240 °C and followed three step degradation kinetics. Initial decomposition temperature (T_o), decomposition range, temperature of maximum weight loss (T_{max}), and % weight loss are presented in Table 1. The T_{max} values were derived from dW/dt against Temperature plots. BABC showed 5% residue at 800 °C.

Table 1. Thermal and kinetic parameters of BABC.

T_o , °C	Decomp. range, °C	T_{max} , °C	% Wt loss	n	E_a , kJmol ⁻¹	A, s ⁻¹	ΔS^* , JK ⁻¹ mol ⁻¹	R ²
240	240-350	288.7	17.3	0.33	182.08	9.83×10^{14}	36.84	0.993
	360-435	398	11.9	1.22	148.07	2.21×10^9	-72.78	0.980
	550-720	636	44.53	1.18	132.36	1.29×10^5	-156.32	0.963

Associated kinetic parameters such as energy of activation (E_a), frequency factor (A), order of reaction (n) and entropy change (ΔS^*) were determined according to Anderson-Freeman method [10]:

$$\Delta \ln dW/dt = n \Delta \ln W - (E_a/R) \Delta (1/T) \quad (1)$$

$$A = E_a \beta / RT^2 e^{E_a/RT} \quad (2)$$

$$\Delta S^* = R \ln(Ah/kT) \quad (3)$$

where: dW/dt is the weight loss with time, W is the active weight of the substance, β is the heating rate, R ($8.314 \text{ JK}^{-1}\text{mole}^{-1}$) is the gas constant, h ($6.626 \times 10^{-34} \text{ Js}^{-1}$) is the Planck's constant, T is the temperature and k ($1.380 \times 10^{-23} \text{ JK}^{-1}\text{mol}^{-1}$) is the Boltzmann constant. The derived least square values of n , E_a , A and regression coefficients R^2 for all the three steps are reported in Table 1. The values of ΔS^* were determined at corresponding T_{\max} . The first step degradation reaction followed apparently fractional order (0.33) degradation kinetics, while second step (1.22) and third step (1.18) degradation reactions followed apparently first order degradation kinetics. The observed trend of E_a , A and ΔS^* is Step-I > Step-II > Step-III. The degradation reaction of organic compounds is a complex process and involves variety of reactions namely recombination, branching, crosslinking, rearrangement, etc. The degradation starts from weak linkages depending upon bonds strength and form free radicals, which further undergo a variety of reactions to form new compounds, which further degrade at elevated temperatures. A 95 % of BABC was degraded into small hydrocarbon products, water, ammonia, etc. The observed 5% residue at 900 °C confirmed formation of highly thermally stable cross-linked product. Thermal study of BABC indicated its use as a high temperature curing agent for epoxy resins. We have indeed use BABC as a curing agent for multifunctional epoxy resin of bisphenol-C and data will be published in near future.

4. CONCLUSIONS

In the present investigation photosensitive aromatic diamine was synthesized and analyzed by spectral and thermal techniques. BABC is a high melting compound and thermally stable up to 240 °C. It followed three step degradation kinetics. The synthesis of BABC and its use as a curing agent for epoxy resin was our part of research program.

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References

- [1] N. Singh, J. Pandey, A. Yadav, V. Chaturvedi, S. Bhatnagar, A. N. Gaikwad, *Eur. J. Med. Chem.* 44 (2009) 1705
- [2] M. H. Yi, W. Huang, M. Y. Jin, K. Y. Choi, *Macromol.* 30 (1997) 5606
- [3] K. Y. Choi, M. H. Yi, M. Y. Jin, *Polymeric Materials Encyclopedia* Vol 7, CRC Boca Raton, New York, London.1996; p. 5379.

- [4] S.-J. Sun, G. Schwarz, H. R. Kricheldorf, T.-C. Chang, *J. Polym. Sci., Part A, Polym. Chem.* Ed. 37 (1999) 1125
- [5] A. Rehab, Salahuddin, *Polymer* 40 (1999) 2197
- [6] N. Kawatzuki, T. Yamamoto, H. Ono, *Appl. Phys. Lett.* 74 (1999) 935
- [7] Y.K. Gong, F. Nakanishi, K. Abe, *Mol. Cryst. Liq. Cryst.* 327 (1999) 123
- [8] A. Reiser, *Photoreactive Polymers*; Wiley-Interscience: New York, 1998.
- [9] A. I. Vogel, A. R. Tatchell, B. S. Funis, A. J. Hannaford, P.W.G. Smith, Vogel's Textbook of Practical Organic Chemistry, 5th Ed., Addison Wesley Longman Ltd., U. K. (1998), p. 395.
- [10] D. A. Anderson, E. S. Freeman, *J. Polym. Sci.* 54 (1961) 253