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Mesogenic Properties as an Analytical Tool for the Pyrolytic Transformation of Substituted Aryl Aldehyde Semicarbazones to Corresponding Benzalazines

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The evaluation of semicarbazones for the mesogenic properties revealed that it undergoes transformation to azine at elevated temperatures. The transformation products were identified by modern tools. The diazines of 4-*n*-alkoxy benzaldehydes are reported to be mesogenic. It was planned to use mesomorphism as a tool for analysis. We had established that transformation of a semicarbazone of aldehyde gives diazine. With this in view fourteen 4-*n*-alkoxybenzaldehyde semicarbazones were synthesized and heated at 260°C in an oil-bath. The pyrolized products were purified and evaluated for their mesogenic properties. The mesogenic properties of pyrolized products exactly tally with the diazines reported by Shaw and Brown.[1] A few diazines which were not reported are also obtained in present study and are characterized. They also exhibit mesomorphism. The study indicates that if the transformation products can be designed which are conducive to mesomorphism, the mesogenic properties can be the tool to understand it and identify the products. The calorimetric study is carried out and enthalpy values are obtained to understand thermodynamic behavior.

Keywords: benzalazines, mesogenic, compounds, analytical

INTRODUCTION

Recently we have reported the synthesis and mesogenic properties of the semicarbazones and amino oxadiazoles.[2] The evaluation of semicarbazones for the mesogenic properties revealed that it undergoes transformation to azine at elevated temperatures.[3] In the present study we are reporting the synthesis of mesogenic diazines by the new route which can even act as analytical tool for the transformation reaction products in question.

EXPERIMENTAL

Microanalysis of compounds were performed on Coleman instrument. IR spectra were recorded on Shimadzu IR-408. NMR spectra were recorded on Perkin-Elmer R-32. Mass spectra were recorded on Kratos MS Spectrometer. Liquid crystalline properties were investigated on Leitz-Labourlux polarizing microscope provided with heating stage. DSC were investigated on the Perkin Elmer DSC-4.

p-n-alkoxy benzaldehydes[4] and *p-n*-alkoxy benzaldehyde semicarbazones[5] were synthesized by the method described in the literature.

Procedure

Preparation of 4,4′-Di-*n*-alkoxybenzalazines from the *p-n*-alkoxy benzaldehyde semicarbazones:

Respective *p-n*-alkoxy benzaldehyde semicarbazone was heated at 255–260°C in an oil-bath for five minutes. The mass was allowed to cool up to room temperature. The crude product was extracted in chloroform and filtered. Filtrate was absorbed on the silica-gel and subjected to column chromatography to remove by-products, if formed. The mixture of petroleum ether: ethyl acetate (95:5%) was used as an eluent. The products were purified by repeated crystallization till constant transition temperatures were obtained. The yield of purified diazines vary between 65 to 70%.

The synthesized compounds give satisfactory elemental analysis.

Spectral aspects of *p-n*-heptyloxy benzaldehyde semicarbazone.

IR ν 3500, 3150, 2900, 2850, 1675, 1600, 1510, 1480, 1450, 1400, 1365, 1305, 1250, 1180, 1130, 1105, 1040, 1015, 960–950 (doublet), 870, 800, 760 cm^{-1}.
NMR ($CDCl_3$ + DMSO d^6): δ, 7.5 (*s*, 1H, azomethane, H), 7.3 (*d*, J = 8 Hz, 2H, aromatic H), 6.8 (*d*, J = 8 Hz, 2H, aromatic H), 5.85 (brs, 2H, NH_2), 3.95 (*t*, 2H, —O—CH_2—CH_2), 3.2 (*s*, 1H, NH), 1.35 (brs, 10H, CH_2, *s*), 0.9 (br *t*, 3H, CH_3, *s*).

MS: m/z 277 (M^+), 260 ($M^+ - NH_3$), 204 ($M^+ - NH_3 + N_2 + CO$), 136 (base peak), 120, 106, 94, 78, 57.

Spectral aspects of 4-4′-Di-*n*-heptyloxybenzalazine.

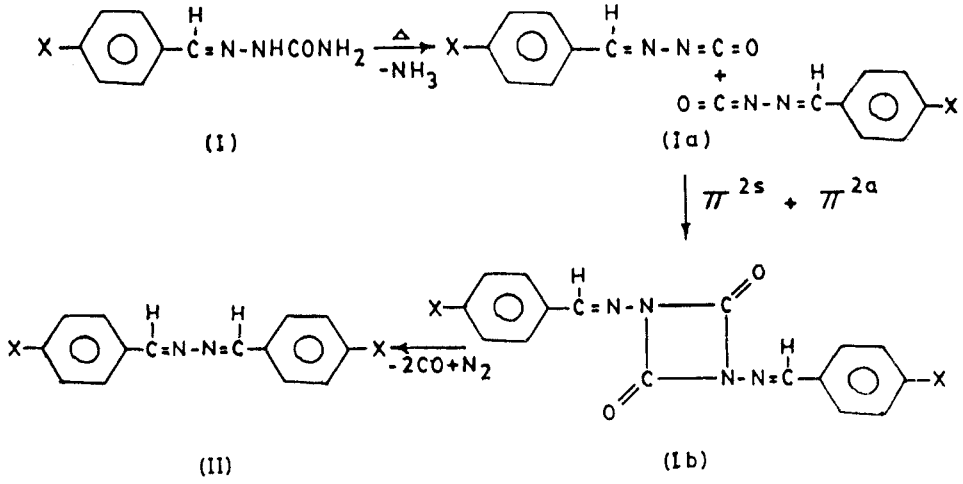
IR ν 2900, 2850, 1620, 1600, 1580, 1510, 1470, 1422, 1400, 1325, 1310, 1295, 1250, 1170, 1075, 1040, 1015, 990, 960, 870, 840, 815 cm^{-1}.

NMR ($CDCl_3$): δ, 8.4, (*s*, 2H, H—C=N), 7.6 (*d*, J = 8 Hz, 4H, aromatic H), 6.85 (*d*, J = 8 Hz, 4H, aromatic H), 4.0 (*t*, 2H, —O—CH_2—CH_2), 1.35 (brs, 10H, CH_2, *s*), 0.4 (brt, 3H, CH_3, *s*).

MS: m/z 436 (M^+), 337 ($M^+ - C_7H_{15}$), 245 ($M^+ - C_7H_{15} + C_6H_4O$) (base peak), 147 ($M^+ - C_7H_{15} + C_6H_4O + C_7H_{15}$), 120 ($M^+ - C_7H_{15} + C_6H_4O + C_7H_{15}$ + HCN), 94, 57.

RESULTS AND DISCUSSION

The formation of diazines during the thermolysis of benzaldehyde semicarbazones might be proceeding by the following mechanism:



Mechanism

The mechanism is proposed based on the characterized gaseous decomposition product by GC and identifying —N=C=O group by spectral method as well as by trapping the group in Situ with reactive agents and characterizing the resultant products formed. However, for the further confirmation of the mechanism suggested above, other experiments have been undertaken and these results will be published soon.

The formation of diazines as final product are confirmed by different techniques. However, it was thought that if terminal substituent-X is selected in such a way that resultant diazines are mesogenic then characterization is automatically achieved as many of the mesogenic diazines are known.

A few representative diazines, obtained in the present study by the new route, were characterized by elemental and spectral analysis. Moreover they were independently synthesized by simple reaction of *p-n*-alkoxybenzaldehydes with hydrazine. The transition temperatures of all the diazines tally (Table I) well with the literature[1] which were obtained by the new route.

Reference to Table I shows that dodecyloxy to octadecyloxy members of the present series are reported for the first time. The nematic phase persists up to the last members of the series. Phase transitions of all the diazines are studied by using DSC method. The transition temperatures obtained by optical method and DSC method tally well. Dodecyloxy to octadecyloxy derivatives exhibit additional solid-solid transition. The enthalpy values of the system exhibits a normal trend similar to other mesogenic series.

The study has provided new route of diazine synthesis and has highlighted the use of mesogenic properties as an analytical tool.

TABLE I

Transition temperatures obtained by optical and DSC methods and enthalpies for 4-4'-Di(*n*)alkoxybenzalazines

Compound No.	Alkyl group	Transition	Transition temperature °C		ΔH kcal/mol
			Optical	DSC	
1	Methyl	C—N	173.0	171.9	4.67
		N—I	186.0	184.2	0.18
2	Ethyl	C—N	175.0	174.3	5.62
		N—I	201.0	200.0	0.36
3	Propyl	C—N	151.5	149.2	3.92
		N—I	156.0	155.6	0.15
4	Butyl	C—N	150.0	147.1	1.28
		N—I	172.0	169.7	0.06
5	Pentyl	C—N	129.0	128.7	7.77
		N—I	153.5	153.4	0.16
6	Hexyl	C—N	128.0	128.0	6.78
		N—I	153.0	152.4	0.22
7	Heptyl	C—S	82.0	80.4	0.66
		S—N	133.0	132.0	4.93
		N—I	145.0	143.6	0.25
8	Octyl	C—S	97.0	95.4	4.19
		S—N	132.5	131.9	4.33
		N—I	145.0	143.6	1.96
9	Nonyl	C—S	81.0	79.0	4.66
		S—N	135.0	133.1	8.24
		N—I	144.0	143.6	1.96
10	Decyl	C—S	84.5	81.1	4.04
		S—N	128.5	124.0	4.32
		N—I	138.0	136.3	0.25
11	Dodecyl	C—S	122.0	121.2	5.84
		S—N	129.0	128.9	1.01
		N—I	134.0	132.0	0.75
12	Tetradecyl	C—S	110.0	106.9	5.67
		S—N	122.0	119.8	8.19
		N—I	132.0	128.0	2.17
13	Hexadecyl	C—S	114.0	110.9	4.11
		S—N	120.5	117.9	3.77
		N—I	126.0	124.6	1.66
14	Octadecyl	C—S	113.0	112.7	5.06
		S—N	118.0	115.2	4.39
		N—I	125.0	122.0	2.89

C = Crystal.
N = Nematic.
S = Smectic.
I = Isotropic liquid.

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References

1. W. G. Shaw and G. H. Brown, *J. Am. Chem. Soc.*, **81**, 2532 (1959).
2. N. K. Chudgar, S. N. Shah and R. A. Vora, *Mol. Cryst. Liq. Cryst.*, **172**, 51 (1989).
3. N. K. Chudgar, S. N. Shah, V. K. Singh and R. A. Vora, (unpublished results).
4. G. W. Gray and B. Jones, *J. Chem. Soc.*, 1467 (1954).
5. Adams Johnson and Wilcox, *Lab. Expt. in Org. Chem.* (The Macmillan Company, Collier Macmillan Limited, London), p. 219 (1969).