Synthesis and Spectral Analysis of Some Schiff Bases Containing Long Alkyl Chains

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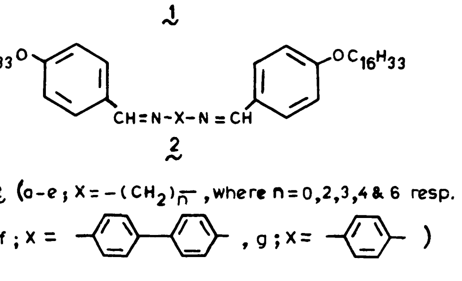
Schiff bases containing hydrophobic alkyl chains have been synthesized and the IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data of some of the compounds have been reported.

In view of the biological importance[1–5] of the Schiff bases, we have reported in this paper the synthesis of Schiff bases (**1** and **2**) from hexadecyloxybenzaldehydes and diamines and have discussed the IR, ^{1}H NMR, ^{13}C NMR, and mass spectra of some of these compounds. Recently Becker et al.[6] have also reported the synthesis of a similar Schiff base derived from 11-*cis*-retinal and have studied their photophysical and photochemical behavior in nonionic micellar solutions.



Experimental

General. Melting points were determined on a sulfuric acid bath and are uncorrected. IR (KBr) spectra were recorded on a Perkin-Elmer 398 spectrophotometer (Table 1). ^{1}H NMR (Table 2) and ^{13}C NMR (Table 3) spectra of the compounds (**1a,b,d** and **2b—e**) were recorded in $CDCl_3$ using TMS as an internal standard. Mass spectra of the compounds (**1a,b** and **2b,d**) were obtained from CDRI Lucknow.

***p*-(Hexadecyloxy)benzaldehyde:** About 0.5 g (0.02 mol) of sodium was dissolved in 50 ml ethanol and to it a solution of *p*-hydroxybenzaldehyde (2.44 g, 0.02 mol) in 20 ml ethanol were added with stirring. To this, hexadecyl bromide (10 ml, 0.02 mol) was added gradually and the total mixture was refluxed at 120 °C for 15 h. A solid separated after cooling the reaction mixture to 0 °C. It was then washed with water, extracted from ether, and crystallized from acetonitrile. Yield 45%; mp 50 °C, IR 2910, 2840 (CH_2), 1690 cm^{-1} (CH=O).

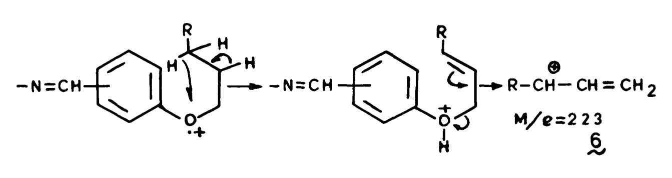
o-(Hexadecyloxy)benzaldehyde was prepared similarly by treating salicylaldehyde with hexadecyl bromide. Yield 45%; mp 46 °C; IR 2910, 2840 (CH_2), 1680 cm^{-1} (CH=O).

***N,N'*-Bis[*p*-(hexadecyloxy)benzylidene]diamines (2b):** A solution of *p*-(hexadecyloxy)benzaldehyde (0.692 g, 0.002 mol) and ethylenediamine (0.06 ml, 0.001 mol) in ethanol (20 ml) was refluxed for 30 min in presence of one to two drops of piperidine. A white compound obtained at room temperature was then crystallized from absolute ethanol. Yield 80%; mp 91 °C.

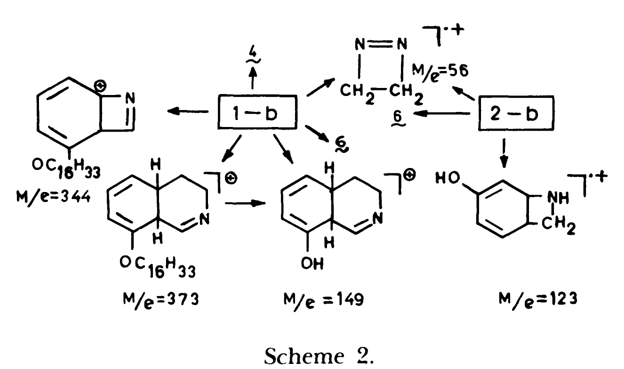
Other Schiff bases (**1** and **2**) were prepared similarly by treating appropriate diamines with *o*- or *p*-(hexadecyloxy)benzaldehyde, respectively, with varying reflux time. Compounds **2a, f, g** were crystallized from benzene and the rest were from ethanol. Compound **1c** was found to be gummy and could not be crystallized. The diamines used for the synthesis of Schiff bases together with mp, analytical, and IR data of the compounds are given in Table 1.

Results and Discussion

IR Spectra: The IR spectra of all the compounds exhibit characteristic absorption in the range of 2920—2840 cm^{-1} for the $-CH_2-$, 1635—1570 cm^{-1} for the -C=N-, 1255—1240 cm^{-1} for the C-O-C, and 770—720 cm^{-1} for the aromatic -C-H. The IR absorption of the C=N group occurs at a lower energy region for compounds **a, f, g**, of both series, which may be due to extended conjugation in the molecule. The absorption due to aromatic C-H groups for Schiff bases **2**

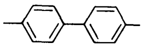
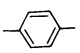
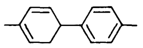
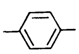


Scheme 1.



Scheme 2.

Table 1. Melting Point, Analytical Data, and IR Spectral Data of the Schiff Bases **1** and **2**

Compound	Schiff base nature of X	Diamines used for condensation	Reflux time h	Mp θ_m/°C
1a	Nil	NH_2NH_2	8	81
1b	$-(CH_2)_2-$	$NH_2(CH_2)_2NH_2$	8	54
1c	$-(CH_2)_3-$	$NH_2(CH_2)_3NH_2$	24	gummy
1d	$-(CH_2)_4-$	$NH_2(CH_2)_4NH_2$	8	66
1e	$-(CH_2)_6-$	$NH_2(CH_2)_6NH_2$	10	44
1f		Benzidine	0.5	75
1g		*p*-Phenylenediamine	0.5	77
2a	Nil	NH_2NH_2	0.5	116
2b	$-(CH_2)_2-$	$NH_2(CH_2)_2NH_2$	0.5	91
2c	$-(CH_2)_3-$	$NH_2(CH_2)_3NH_2$	0.5	75
2d	$-(CH_2)_4-$	$NH_2(CH_2)_4NH_2$	0.5	83
2e	$-(Ch_2)_6-$	$NH_2(CH_2)_6NH_2$	0.5	87
2f		Benzidine	0.5	130(d)
2g		*p*-Phenylenediamine	0.5	127

Compound	Found (Calcd)		IR/cm^{-1}			
	C%	H%	$-CH_2-$	-C=N-	Ar-O-C	Ar-H
1a	80.87	11.12	2920	1625	1255	770
	(80.23)	(11.04)	2850	1605		
1b	80.51	11.20	2910	1630	1245	750
	(80.45)	(11.17)	2840	1595		
1c	—	—	2920	1630	1245	750
			2845	1595		
1d	80.71	11.31	2910	1630	1245	760
	(80.65)	(11.29)	2850	1600		
1e	80.85	11.43	2910	1630	1245	750
	(80.83)	(11.40)	2840	1595		
1f	82.91	10.05	2920	1610	1250	760
	(82.86)	(10.00)	2850	1595		
1g	81.70	10.51	2920	1615	1250	755
	(81.68)	(10.47)	2850	1600		
2a	80.43	11.16	2910	1620	1250	720
	(80.23)	(11.04)	2840	1600		
2b	80.34	11.23	2910	1635	1250	720
	(80.45)	(11.17)	2840	1600		
2c	80.45	11.30	2910	1635	1250	720
	(80.55)	(11.23)	2850	1600		
2d	80.53	11.35	2920	1635	1240	720
	(80.65)	(11.29)	2850	1600		
2e	80.68	11.49	2910	1630	1250	720
	(80.83)	(11.40)	2840	1600		
2f	82.91	10.05	2900	1600	1250	720
	(82.86)	(10.00)	2840	1570		
2g	81.70	10.55	2910	1605	1250	720
	(81.68)	(10.47)	2840	1570		

appears at a lower energy region than that for **1**.

^{1}H NMR Spectra: The ^{1}H NMR spectral data of the compounds are given in Table 2. The chemical shift values indicate that the influence of the 'O' and 'N' atoms is not observed beyond three bonds (i.e. about 4 Å distance). The 'q' and the 'y' protons in the compounds **1d**, **2d**, and **e** appear at the same δ value. Hence, the extent of inductive effect due to the 'O' and 'N' atoms is same at the second carbon (i.e., by a bond distance of about 3 Å). The 'y' protons for the compound **2c**, however, appear at a down field because these protons experience the inductive effect from both the nitrogen atoms to an equal extent whereas in **2d** and **2c** the influence is due to one nitrogen only. The signal due to the methine protons ($-CH_w=N$) is generally shifted downfield for the ortho series

Table 2a. ^{1}H NMR Chemical Shifts (δ) of Schiff Bases **1**

Compound	Nature of X	Positions of proton[a)] o	p	q	r
1a	Nil	0.88, t, 6H, J=6.6	1.25, 52H	1.82, qn, 4H	4.0, t, 4H, J=5.86, 6.6
1b	$-(CH_2)_2-$	0.88, t, 6H, J=5.86, 7.33	1.26, 52H	1.74, qn, 4H	3.92, t, 4H, J=6.6
1d	$-(CH_2)_4-$	0.88, t, 6H, J=6.6	1.26, 52H	1.80, qn, 4H	3.97, t, 4H, J=6.6

Compound	Positions of proton[a)] s	t	u
1a	6.90, d, 2H, J_{st}=8.06	7.36, dt, 2H, J_{st}=8.06, J_{tu}=7.33, J_{tv}=1.47	6.99, t, 2H, J_{tu}=7.33, J_{uv}=8.06
1b	6.83, d, 2H, J_{st}=8.06	7.29, dt, 2H, J_{st}=8.06, J_{tu}=7.33, J_{tv}=1.47	6.91, t, 2H, J_{tu}=7.33, J_{uv}=7.33
1d	6.85, d, 2H, J_{st}=8.06	7.3, dt, 2H, J_{st}=8.06, J_{tu}=7.33, J_{tv}=1.47	6.92, t, 2H, J_{tu}=7.33, J_{uv}=8.06

Compound	Positions of proton[a)] v	w	x	y
1a	8.13, dd, 2H, J_{uv}=8.06, J_{tv}=1.47	9.1, s, 2H	—	—
1b	7.94, dd, 2H, J_{uv}=8.06, J_{tv}=1.47	8.74, s, 2H	3.97, s, 4H	—
1d	7.26, dd, 2H, J_{uv}=7.33, J_{tv}=1.47	8.72, s, 2H	3.67, 2, 4H	1.80, qn, 4H

s=singlet, d=doublet, t=triplet, qn=quintet, dd=doublet of a doublet, dt=doublet of a triplet, J=values in Hz. a) o—r, hexadecyl; s—v, benzene; w, methine; x, y, *N*-methylene.

Table 2b. ^{1}H NMR Chemical Shifts (δ) of Schiff Bases **2**

Compound	Nature of X	Positions of proton[a)] o	p	q
2b	$-(CH_2)_2-$	0.88, t, 6H	1.26, 52H	1.77, qn, 4H
2c	$-(CH_2)_3-$	0.88, t, 6H, J=5.86, 6.6	1.26, 52H	1.78, qn, 4H
2d	$-(CH_2)_4-$	0.88, t, 6H, J=5.86, 7.33	1.26, 52H	1.78, qn, 4H
2e	$-(CH_2)_6-$	0.88, t, 6H, J=5.87, 7.33	1.26, 52H	1.75, qn, 4H

Compound	Positions of proton[a)] r	s+t	u+v
2b	3.94, t, 4H, J=6.6	6.86, d, 4H, J=8.8	7.61, d, 4H, J=8.8
2c	3.96, t, 4H, J=6.6	6.89, d, 4H, J=8.8	7.64, d, 4H, J=8.06
2d	3.97, t, 4H, J=6.6	6.89, d, 4H, J=8.8	7.63, d, 4H, J=8.8
2e	3.96, t, 4H, J=6.6	6.89, d, 4H, J=8.8	7.63, d, 4H, J=8.8

Compound	Positions of proton[a)] w	x	y	z
2b	8.20, s, 2H	3.90, s, 4H	—	—
2c	8.23, s, 2H	3.66, t, 4H	2.08, qn, 4H	—
2d	8.19, s, 2H	3.61, 4H	1.78, qn, 4H	—
2e	8.17, s, 2H	3.56, t, 4H, J=6.6, 7.33	1.75, qn, 4H	1.26, s, 4H

a) o—r, hexadecyl; s—v, benzene; w, methine; x—z, *N*-methylene.

Table 3a. ^{13}C Chemical Shifts (ppm) of Schiff Base **1**

Carbon No.	Chemical shift values		
	1a	**1b**	**1d**
(1) Hexadecyl carbons			
C_1	14.091	14.037	13.983
C_2	22.699	22.615	22.615
C_3	31.950	31.895	31.895
C_4	29.359	29.306	29.306
C_5—C_{11}	29.683	29.629	29.629
C_{12}—C_{14}	26.122	26.068	26.068
C_{15}	29.683	29.629	29.629
C_{16}	68.580	68.420	68.420
(2) *o*-Phenylene carbons			
C_{17}	158.7 (157.7)	158.469	158.199
C_{18}	112.1 (114.3)	111.962	111.962
C_{19}	132.14 (129.0)	131.439	131.331
C_{20}	120.5 (121.0)	120.432	120.540
C_{21}	127.3 (127.5)	127.284	127.284
C_{22}	123.13 (123.60)	125.072	125.126
(3) $-CH=N-(CH_2)_n$ carbons			
C_{23}	157.3	158.307	156.689
C_{24}	—	62.055	61.78
C_{25}	—	—	29.198

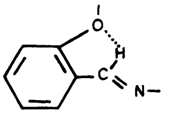
Table 3b. ^{13}C Chemical Shifts (ppm) of Schiff Base 2

Carbon No.	Chemical shift values			
	2b	**2c**	**2d**	**2e**
(1) Hexadecyl carbons				
C_1	14.037	14.091	14.091	14.037
C_2	22.669	22.699	22.723	22.669
C_3	31.895	31.949	31.949	31.895
C_4	29.359	29.350	29.413	29.359
C_5—C_{11}	29.683	29.683	29.683	29.629
C_{12}—C_{14}	26.014	26.014	26.068	26.014
C_{15}	29.683	29.683	29.413	29.359
C_{16}	68.10	68.10	68.30	68.15
(2) *o*-Phenylene carbons				
C_{17}	161.960 (160.4)	161.170	161.170	161.113
C_{18}, C_{19}	114.60 (114.3)	114.60	114.50	114.50
C_{20}—C_{22}	129.30 (127.5)	129.30	129.40	129.40
(3) $-CH=N-(CH_2)_n$ carbons				
C_{23}	161.221	160.40	160.196	159.90
C_{24}	61.80	59.00	61.46	61.515
C_{25}	—	32.216	31.949	30.978
C_{26}	—	—	—	27.149

compared to that for para series because of the possibility of hydrogen bond formation (**3**) in the former. The signal is further shifted downfield in **1a** because its most probable conformation is the H-bonded structure.

^{13}C NMR Spectra: The assignment of the chemical shift values to the carbon atoms has been worked out by applying additive rules proposed by Lindman and Adam.[7] The substituents used are the $-OCH_3$ in place of the $-OC_{16}H_{33}$ and the $-CH=CH_2$ in place of the $-C=N-$ due to unavailability of data and similarity in behavior. The calculated values (given in parentheses) fit well with the observed values within an error of ±0.7 ppm.

Mass Spectra: None of the compounds show a molecular ion peak but the fragmentation pattern conforms to the expected structures of the compounds. The fragmentation pattern due to a straight alkyl chain, peaks at $m/z=43$ due to $C_3H_7^+$, at 105 due to **4** (for ortho series) and **5** (for para series), a prominent peak at 223 (Scheme 1) for all compounds are discernible. The fragmentation pattern of the compounds **1b** and **2b** are given in Scheme 2.



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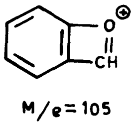

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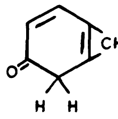

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