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Influence of Molecular Structure on Liquid Crystalline Properties and Phase Transitions in These Structures, Part I

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Abstract—Three homologous series of Schiff's base compounds have been prepared to investigate the relationship between chemical constitution and mesomorphism, by condensing *p*-n-alkoxybenzaldehydes with *p*-n-propoxy-, *p*-n-butoxy- and *p*-n-amyloxyanilines respectively and the various transition temperatures are recorded. These series exhibit the general mesomorphic properties as found in other analogous series. It is found that the lower homologues are either non-mesomorphic or nematic while middle members are smectic and nematic both and the higher homologues are purely smectic. In many homologues polymesomorphism in smectic phase is observed.

A number of homologous series[1–7] of organic compounds having a variety of molecular structures have been prepared to investigate the relationship between chemical constitution and mesomorphism. It has been observed that, when the alkyl chains are short, the systems are either non-mesomorphic or nematic; as the chain length increases, smectic properties begin to appear and as the smectic phase increases, the nematic phase decreases with each successive chain increment, till in the higher homologues like hexadecyl and octadecyl ethers only smectic phases are found; of course, it is not possible to postulate very accurately the stage at which smectic properties would first appear in a particular series.

In the present study, the following three series have been prepared and their various transition temperatures are summarized in Tables 1, 2 and 3 respectively.

I *p*-n-Alkoxybenzylidene-*p*-n-propoxyanilines
II *p*-n-Alkoxybenzylidene-*p*-n-butoxyanilines
III *p*-n-Alkoxybenzylidene-*p*-n-amyloxyanilines

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TABLE 1 Series I: *p*-n-Alkoxybenzylidene-*p*-n-propoxyanilines

	Temperature of transition to			
Alkyl group	Smectic$_2$	Smectic$_1$	Nematic	Isotropic
1. Methyl	—	—	(102.0)[a]	119.5
2. Ethyl	—	—	(125.0)	127.5
3. Propyl	—	—	(104.0)[a]	134.5
4. Butyl	—	—	(115.0)[b]	121.0
5. Amyl	—	—	104.5	105.5
6. Hexyl	—	—	98.0	110.0
7. Heptyl	—	—	102.0	107.0
8. Octyl	—	—	100.5	108.0
9. Nonyl	—	(96.5)	105.0	107.0
10. Decyl	(88.5)	(100.0)	103.5	106.7
11. Dodecyl	(91.0)	(103.0)	(104.7)	106.0
12. Hexadecyl	—	(101.5)	—	104.5
13. Octadecyl	—	(100.0)[a]	—	108.5

[a] Values obtained by extrapolating the curve.

[b] Values in the bracket indicate monotropy.

TABLE 2 Series II: *p*-n-Alkoxybenzylidene-*p*-n-butoxyanilines

	Temperature of transition to			
Alkyl group	Smectic$_2$	Smectic$_1$	Nematic	Isotropic
1. Methyl	—	—	(108.5)	115.0
2. Ethyl	—	—	111.0	131.5
3. Propyl	—	—	(114.5)	120.0
4. Butyl	—	—	(122.0)	125.0
5. Amyl	—	—	(115.0)	116.5
6. Hexyl	—	—	102.5	118.5
7. Heptyl	—	—	100.5	115.5
8. Octyl	—	(98.5)	105.0	115.0
9. Nonyl	—	102.0	104.5	113.5
10. Decyl	(92.5)	104.0	108.5	113.0
11. Dodecyl	(95.0)	101.0	111.0	111.5
12. Hexadecyl	—	101.5	—	107.0
13. Octadecyl	—	(104.5)	—	107.5

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TABLE 3 Series III: *p*-n-Alkoxybenzylidene-*p*-n-amyloxyanilines

	Temperature of transition to				
Alkyl group	Smectic$_3$	Smectic$_2$	Smectic$_1$	Nematic	Isotropic
1. Methyl	—	—	—	(101.0)[a]	108.0
2. Ethyl	—	—	—	96.0	121.0
3. Propyl	—	—	—	(105.5)[b]	107.5
4. Butyl	—	—	—	(114.0)	115.5
5. Amyl	—	—	—	(108.5)[a]	114.5
6. Hexyl	—	—	—	104.0	113.0
7. Heptyl	—	—	94.0	98.5	110.0
8. Octyl	(84.0)	91.0	100.5	102.0	111.2
9. Nonyl	(88.5)	—	95.5	104.5	109.7
10. Decyl	(91.0)	94.5	105.5	107.0	109.5
11. Dodecyl	(93.0)	98.0	105.0	—	108.0
12. Hexadecyl	—	(94.5)	98.5	—	105.0
13. Octadecyl	—	—	(103.5)	—	106.0

[a] Values obtained by extrapolating the curve.

[b] Values in the bracket indicate monotropy.

When these values for various transitions are plotted against the number of carbon atoms in the alkoxy chain, the curves represented in Figs. 1, 2 and 3 are obtained for the respective series.

Observation and Discussion

In these three series, all the mesomorphic-isotropic transitions relating to even number of C-atoms in the alkoxy chain lie on one falling curve while similar transitions relating to odd number of C-atoms in the alkoxy chain lie on a curve which rises from C_1-ether to C_7-ether and then falls or shows a falling tendency from C_7-ether to C_9-ether. However, the curve representing these transitions for even number of C-atoms in the chain lies above the one for the same transitions for odd number of C-atoms in the chain. All smectic-nematic transition points, irrespective of odd or even number of C-atoms in the chain, lie on one smooth rising curve which merges with the falling nematic-isotropic curve for the even members. Smectic$_1$-smectic$_2$ transition points also lie on one curve.

Methyl, propyl and octadecyl ethers in the first series are not mesomorphic but the isotropic-nematic transition values can be obtained by extrapolating the respective curves in a legitimate

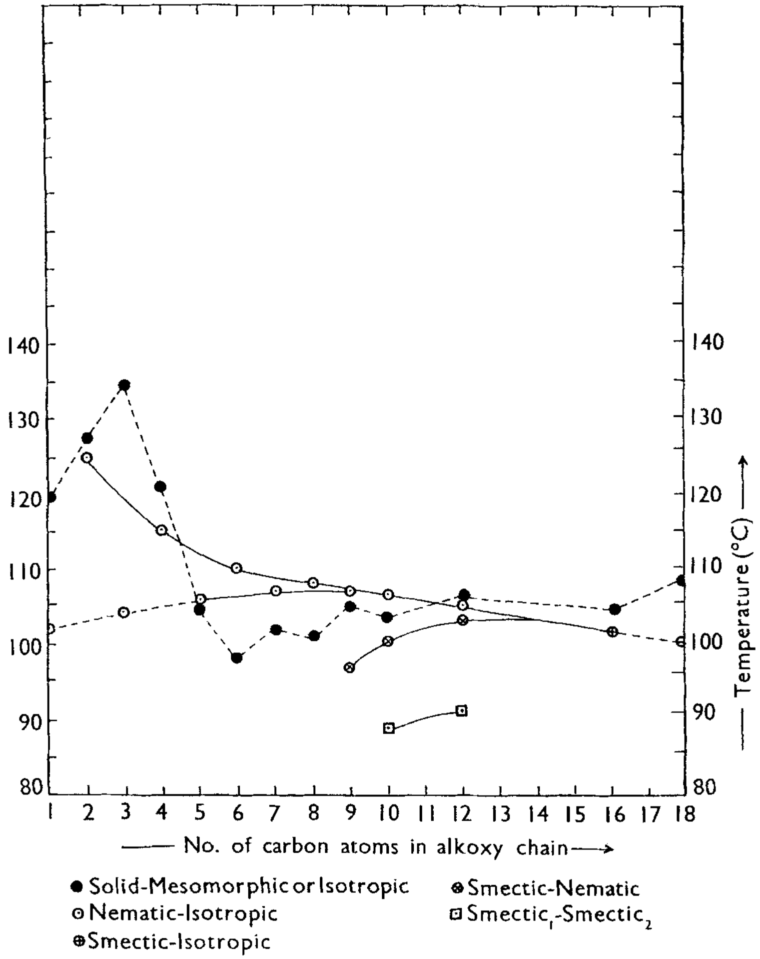

Fig. 1

fashion. When the isotropic liquid of methyl, propyl and octadecyl ether is cooled, crystallization takes place at 108°, 129° and 103.5° C respectively, before giving any mesophase. Weygand and Gabler[1] have reported that *p*-n-propoxybenzylidene-*p*-n-propoxyaniline

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melts at 133° C and they have given the calculated value of 107° for isotropic-nematic change. We, however, find that this compound melts at 134.5° C and the value 107° C is 3° higher than the value obtained by us by extrapolation of the curve for odd members of this series. In this series, smectic phase is found throughout in the undercooled region and has failed to become enantiotropic.

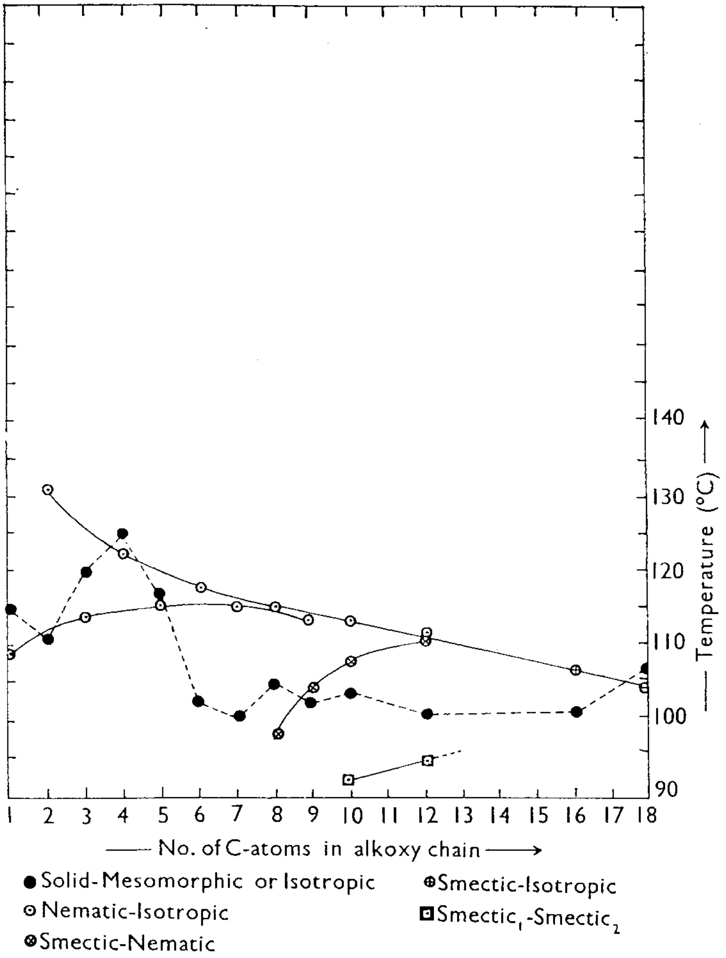

Fig. 2

All the members of the p-n-alkoxybenzylidene-p-n-butoxyaniline series are crystalline liquids—methyl, propyl, butyl, amyl and

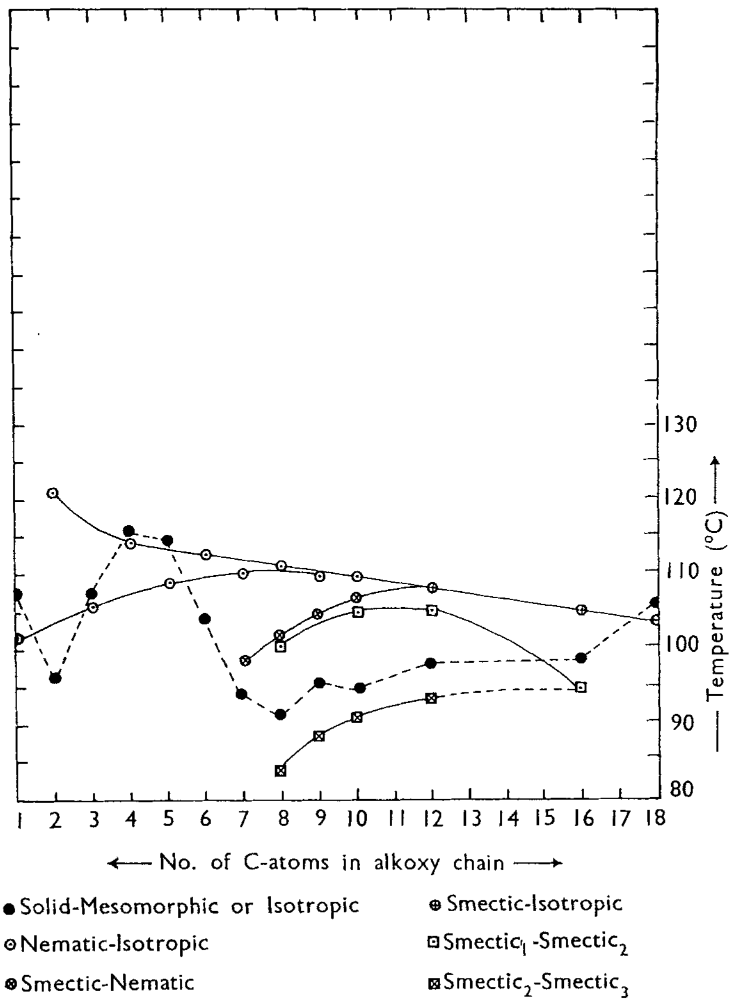

FIG. 3

octadecyl derivatives being purely monotropic. Hexadecyl ether is purely enantiotropic smectic and octadecyl ether is purely monotropic smectic. The smectic property starts from octyl ether

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unlike nonyl ether of series I. The transition temperatures of *p*-n-butoxybenzylidene-*p*-n-butoxyaniline agree with the values given by Weygand and Gabler.[1]

In the series *p*-n-alkoxybenzylidene-*p*-n-amyloxyanilines, methyl and amyl ethers are non-mesomorphic but when the curve passing through nematic-isotropic transitions for the members having odd number of C-atoms in the chain, is drawn and extrapolated towards short carbon chain ethers, it gives 101° C for isotropic-nematic change of methyl ether and 108.5° C for the similar transition of amyl ether. When the isotropic liquid of methyl and amyl ether is cooled, crystallization takes place at about 102.5° C and 110.0° C respectively before giving isotropic-nematic transition. Weygand and Gabler[1] however, give transition temperatures for *p*-n-amyloxybenzylidene-*p*-n-amyloxy-aniline as (103.0°)–113.0° C.

Weygand and Gabler[1] have studied mesomorphism of *p*-n-alkoxybenzylidene-*p*-phenetidine compounds. The series studied here are the higher homologues of this series and naturally similar properties should be expected. In all these series, lower homologues are non-mesomorphic or nematic (either monotropic or enantiotropic) while middle members are both smectic and nematic and the higher homologues like hexadecyl and octadecyl ethers are purely smectic (either enantiotropic or monotropic). It is rather difficult to postulate where the smectic properties should originate in the series, however, in the three series studied here, some regularity regarding the appearance of the smectic phase is observed. In the propyl-ether series, smectic phase first appears at C_9-ether while in butyl- and amyl-ether series, the smectic properties begin at C_8- and C_7-ethers respectively. On this basis, one may expect that in the ethyl-ether series, smectic phase should appear at C_{10}-ether, but as a matter of fact, in ethyl-ether series[1] smectic phase appears at C_9-ether.

As the chain length is increasing, the terminal cohesive forces which account for nematic-isotropic change decrease, as a result of which the nematic-isotropic curve obtained for even-members in these series is a falling one. Similar curve should also be obtained

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for odd-members but in practice, a rising curve is obtained which shows a falling tendency from C_7-ether to C_9-ether. This may probably be due to relative differences between the terminal and lateral cohesions. As the chain length increases, lateral cohesion increases and it may support the terminal forces; this to a certain degree, helps in explaining the rise in the curve which afterwards shows the tendency of becoming a normal falling curve. Still, it is a matter of curiosity as the odd members behave in one way and the even members in the other way. Probably this difference may be due to differences in packing and cohesion between the terminal methyl groups of alkyl chains containing odd and even number of carbon atoms. Here, in these anils two alkoxy groups of different lengths are present, one on each end, and the study of the mode of their end to end arrangement in the crystal lattice may probably help in explaining this type of behaviour. In the middle members (e.g. nonyl to dodecyl ethers in series I, octyl to dodecyl ethers in series II and heptyl to decyl ethers in series III) as the strength of the terminal intermolecular cohesions decreases, the net polarizability of the molecule increases by increasing chain-length and so lateral intermolecular attractions which account for smectic-nematic transition also increase resulting into increasing smectic-nematic transition temperatures up to a stage, where no nematic phase is formed (e.g. hexadecyl ether of series I and II and dodecyl ether of series III). Later, naturally the higher homologues should be purely smectic as the terminal intermolecular attractions become insufficient to maintain parallel molecular orientation necessary for nematic transformation. Of course, after the stage at which smectic-nematic transition disappears, the smectic-isotropic transition must be guided by the weaker terminal attraction, because in practice, it is found that the smectic-nematic transition curve merges with the falling nematic-isotropic curve for even number of carbon atoms in the chain of a homologous series. If the melting points show a rising tendency, the system may become monotropic as found in dodecyl and hexadecyl ethers of series I and in octadecyl ethers of series II and III, or may become non-mesomorphic as in octadecyl ether of series I. Quite analogous

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phenomenon is shown by *p*-n-alkoxybenzylidene-*p*-phenetidine compounds.[1]

One more striking behaviour of these series is the polymesomorphism of smectic phases in at least some higher homologues. In the case of series I and II only decyl and dodecyl ethers exhibit smectic$_1$-smectic$_2$ transitions and so, it is very difficult to understand the nature of the curve passing through these points, but in series III, five members, e.g. octyl, nonyl, decyl, dodecyl and hexadecyl ethers show smectic$_1$-smectic$_2$ and smectic$_2$-smectic$_3$ transitions and hence it has become possible to understand the nature of this curve. Smectic$_1$-smectic$_2$ transition curve rises from octyl to decyl ether and then falls through dodecyl ether to hexadecyl ether while smectic$_2$-smectic$_3$ transition points constitute a rising curve. This behaviour suggests that polymesomorphic transitions among smectic mesophases take place at some definite temperature with certain regularity as the homologous series is ascended.

Comparison of the average nematic thermal stability for butyl to nonyl ethers of the series *p*-n-alkoxybenzylidene-*p*-n-alkoxyanilines, give the following order:

Series	OC_2H_5[1]	>	$-OC_4H_9$ (II)	>	$-OC_5H_{11}$ (III)	>	$-OC_3H_7$ (I)
Average temps. for nematic-isotropic transition (C_4–C_9)	120.5		116.6		111.1		108.7

This order emphasizes the falling nature of the curve passing through nematic-isotropic transition temperatures for the members having even number of carbon atoms in the chain and rising nature of the curve for the similar transitions for the members possessing odd number of carbon atoms in the chain. From this limited data, one cannot postulate that $-OC_9H_{19}$ series would possess higher nematic thermal stability than $-OC_7H_{15}$ series as it is observed in all the series that the nematic-isotropic curve for odd number of carbon atoms in the chain shows a falling tendency from C_7-ether to C_9-ether.

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The order obtained for the smectic thermal stability of the three series examined here is as follows:

Series	$-OC_3H_7$(I) <	$-OC_5H_{11}$(III) <	$-OC_4H_9$(II)
Average temps. for smectic-nematic or smectic-isotropic transition (C_9–C_{12})	101.6	106.6	108.0

Here again series II shows highest smectic thermal stability like nematic thermal stability among the three series in question. This data also suggests that smectic-nematic curve should rise in the initial state and then fall.

Experimental

Determination of Transition Temperatures

Preliminary measurements were made by the optical method of Dave and Dewar.[8] The precise measurements were however made by the polarizing microscope. To prepare the slide, the specimen was melted on a glass slide and a cover-slip was pressed down on the liquid to get a possible thin section of the material. The slide was inserted in the slide slot of the hot-stage fitted Leitz Ortholux polarizing microscope. In this electrically heated block, the sample could be observed continuously under carefully controlled temperatures. The temperature in the neighbourhood of each change was raised at the rate of 1°/2 min and the temperatures for various transitions were recorded by the standard thermometers. The transitions were also checked by lowering the temperature slowly and observing the phase changes.

p-n-Alkoxybenzaldehydes were prepared by the method of G. W. Gray.[3] *p*-n-Alkoxyanilines were prepared by the method of Weygand and Gabler[1] and Gutekunst and Gray.[9]

Schiff's bases: The Schiff's base compounds were prepared by refluxing equimolecular quantities of the corresponding aromatic aldehyde and aniline in alcohol for about 10 to 15 min and recrystallizing the product, several times from ethyl alcohol into fine crystals which give sharp melting point. The analytical data are given in Tables 4 to 6.

TABLE 4 *p*-n-Alkoxybenzylidene-*p*-n-propoxyanilines

Alkyl group	Found % N	Molecular formula	Required % N
1. Methyl	5.349	$C_{17}H_{19}O_2N$	5.204
2. Ethyl	4.966	$C_{18}H_{21}O_2N$	4.947
3. Propyl	4.953	$C_{19}H_{23}O_2N$	4.713
4. Butyl	4.686	$C_{20}H_{25}O_2N$	4.501
5. Amyl	4.366	$C_{21}H_{27}O_2N$	4.307
6. Hexyl	4.277	$C_{22}H_{29}O_2N$	4.129
7. Heptyl	4.086	$C_{23}H_{31}O_2N$	3.966
8. Octyl	3.915	$C_{24}H_{33}O_2N$	3.814
9. Nonyl	3.655	$C_{25}H_{35}O_2N$	3.674
10. Decyl	3.664	$C_{26}H_{37}O_2N$	3.544
11. Dodecyl	3.321	$C_{28}H_{41}O_2N$	3.301
12. Hexadecyl	2.843	$C_{32}H_{49}O_2N$	2.923
13. Octadecyl	2.671	$C_{34}H_{53}O_2N$	2.761

TABLE 5 *p*-n-Alkoxybenzylidene-*p*-n-butoxyanilines

Alkyl group	Found % N	Molecular formula	Required % N
1. Methyl	4.945	$C_{18}H_{21}O_2N$	4.947
2. Ethyl	4.506	$C_{19}H_{23}O_2N$	4.713
3. Propyl	4.418	$C_{20}H_{25}O_2N$	4.501
4. Butyl	4.065	$C_{21}H_{27}O_2N$	4.307
5. Amyl	3.930	$C_{22}H_{29}O_2N$	4.129
6. Hexyl	3.759	$C_{23}H_{31}O_2N$	3.966
7. Heptyl	3.574	$C_{24}H_{33}O_2N$	3.814
8. Octyl	3.516	$C_{25}H_{35}O_2N$	3.674
9. Nonyl	3.376	$C_{26}H_{37}O_2N$	3.544
10. Decyl	3.415	$C_{27}H_{39}O_2N$	3.423
11. Dodecyl	3.267	$C_{29}H_{43}O_2N$	3.204
12. Hexadecyl	2.647	$C_{33}H_{51}O_2N$	2.840
13. Octadecyl	2.654	$C_{35}H_{55}O_2N$	2.688

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TABLE 6 *p*-n-Alkoxybenzylidene-*p*-n-amyloxyanilines

Alkyl group	Found % N	Molecular formula	Required % N
1. Methyl	4.974	$C_{19}H_{23}O_2N$	4.713
2. Ethyl	4.333	$C_{20}H_{25}O_2N$	4.501
3. Propyl	4.262	$C_{21}H_{27}O_2N$	4.307
4. Butyl	3.973	$C_{22}H_{29}O_2N$	4.129
5. Amyl	3.883	$C_{23}H_{31}O_2N$	3.966
6. Hexyl	3.634	$C_{24}H_{33}O_2N$	3.814
7. Heptyl	3.793	$C_{25}H_{35}O_2N$	3.674
8. Octyl	3.358	$C_{26}H_{37}O_2N$	3.544
9. Nonyl	3.234	$C_{27}H_{39}O_2N$	3.423
10. Decyl	3.601	$C_{28}H_{41}O_2N$	3.301
11. Dodecyl	3.277	$C_{30}H_{45}O_2N$	3.104
12. Hexadecyl	2.653	$C_{34}H_{53}O_2N$	2.761
13. Octadecyl	2.487	$C_{36}H_{57}O_2N$	2.617

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