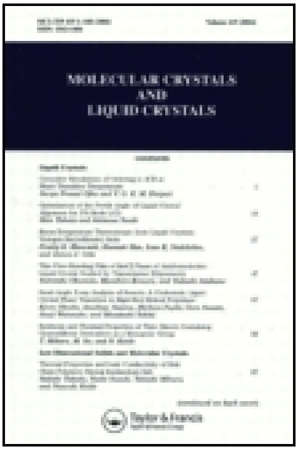


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

A Contribution to the Study of the Nematic—Isotropic Transition. Influence of Polar Terminal Groups

J. Barberá [a] , M. Marcos [a] , M. B. Ros [a] & J. L. Serrano [a]

[a] Quimica Orgánica, Facultad de Ciencias, I.C.M.A. Universidad de Zaragoza-C.S.I.C., 50009-Zaragoza, Spain

Version of record first published: 03 Jan 2007.

To cite this article: J. Barberá , M. Marcos , M. B. Ros & J. L. Serrano (1988): A Contribution to the Study of the Nematic—Isotropic Transition. Influence of Polar Terminal Groups, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 163:1, 139-155

To link to this article: http://dx.doi.org/10.1080/00268948808081994

Mol. Cryst. Liq. Cryst., 1988, Vol. 163, pp. 139–155
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

A Contribution to the Study of the Nematic–Isotropic Transition. Influence of Polar Terminal Groups

J. BARBERÁ, M. MARCOS, M. B. ROS and J. L. SERRANO

Química Orgánica. Facultad de Ciencias. I.C.M.A. Universidad de Zaragoza-C.S.I.C. 50009-Zaragoza. Spain.

(*Received November 11, 1987; in final form January 29, 1988*)

Correlation studies of the T_{N-I} of fifteen 4′-substituted 2-hydroxy-4-*n*-octyloxy-α,α′-dimethylbenzalazines and empirical parameters for the polar end groups [MR (molar refractivity) related to the electronic polarizability and μ (dipole moment)] are presented.

The suitability of the combination of both parameters is checked in order to predict the clearing temperatures in this series.

The validity of these correlations is tested against another series: 4-X-phenyl 4-(*trans*-4-decylcyclohexyl)benzoates (X: —I, —Cl, —Br, —F, —CHO, —$COCH_3$, —NCS, —CN, —NO_2) taken from the literature.

In order to carry out these studies, twelve new 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines with substituents X: —H, —OH, —NH_2, —SH, —$COCH_3$, —$COOCH_3$, —COOH, —$OCOCH_3$, —$OCOC_6H_5$, —NCS, —CF_3, —$NH_3^+Cl^-$ and their analogues: α,α′-dimethyl-2-hydroxy-4-*n*-octyloxy-benzylidene-4′-pyridylmethylenehydrazine and its N-oxide, were synthesized and their mesomorphic properties studied.

The azines with groups X: —NH_2, —SH, —$OCOCH_3$, —$OCOC_6H_5$, —$COCH_3$ and —$COOCH_3$ only show a nematic phase, that with X: —NCS shows nematic and S_A phases, and those with X: —CF_3 and —COOH smectic phases alone.

INTRODUCTION

One of the aims of studies on liquid crystals is to be able to predict the mesomorphic properties of a compound by observing its structure.

Consequently, we can see in the literature a great number of papers about the structure-mesomorphic activity relationship, of which the studies carried out by G. W. Gray[1] and by W. H. De Jeu and J. Van der Veen[2,3] are considered classic.

A quantitative contribution to predictions was made by J. Van der Veen in his paper on the influence of polar terminal substituents on the nematic–isotropic transition temperature.[4]

The starting-point of his work was the molecular statistical theory of Maier and Saupe[5] in which the long-range orientational order of the molecules was attributed to anisotropic dispersion forces alone, inferring that a linear relationship between T_{N-I} and the polarizability anisotropy of the C_{Ar}—X bond must exist.

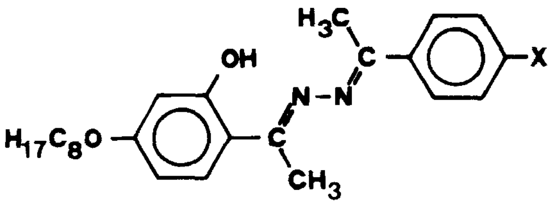
In his paper, Van der Veen demonstrated this linear relationship for two series of nematic compounds with five polar end groups (—CH_3, —F, —Cl, —NO_2, and —CN), and went on to conclude that the anisotropy of the C_{Ar}—X bond for terminal substituents is a valuable instrument for predicting T_c.

However, in similar studies carried out by A. C. Griffin[6] with four new series and a new polar group (—Br), only in two series was this relationship observed and the Br group always had to be omitted.

The fact that the number of terminal substituents used was small and they sometimes showed deviations, leads us to consider these results with reservations.

One of the problems when carrying out this kind of study is that only series with a small number of groups to correlate exist in the literature and consequently we found it was necessary to synthesize a new series of nematic compounds with a higher number of polar terminal substituents.

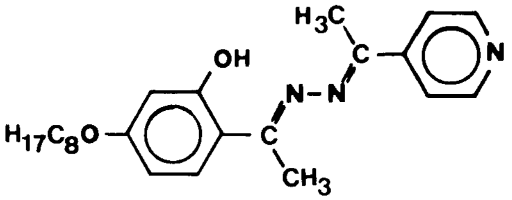
After an initial study of several structures, twenty 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines and the analogous azines with

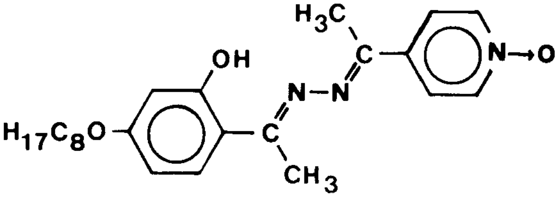


X : H, F, Cl, Br, CN, NO_2, CH_3, OCH_3, $N(CH_3)_2$, CF_3,

NCS, OH, NH_2, SH, $OCOCH_3$, $OCOC_6H_5$, $COOCH_3$,

$COCH_3$, COOH, $NH_3^+Cl^-$.





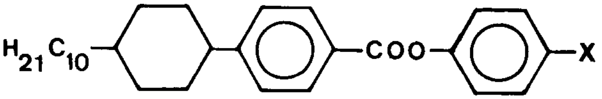
a pyridine ring were selected (the latter azines are represented by Py and Py → O).

Since the mesogenic properties of a compound are a consequence of the balance between the attractive (due to molecular polarizability and polarity) and repulsive forces (essentially governed by steric factors), our aim in this paper is to study the existing correlation between the T_{N-I} of these compounds and empirical parameters of the polar substituents which represent the three factors:

—anisotropy of polarizability
—dipole moment and
—steric effects.

The greater number of factors which influence T_{N-I} taken into account and the number of polar groups used in this work enable us to draw more general conclusions about the influence of the terminal substituents on mesomorphic properties, above all with regard to the clearing temperature.

In order to check the validity of the results obtained, the same studies were carried out on the series of 4-X-phenyl 4-(*trans*-4-decylcyclohexyl)benzoates described by R. Dabrowski *et al.*[7]



X: F, Cl, Br, I, NO_2, CN, NCS, $COCH_3$, CHO.

EXPERIMENTAL

Synthesis

Some of the azines used in the present work have been synthesized and described earlier (X: —OCH_3)[8], (X: —F, —Cl, —Br, —NO_2, —CN and —$N(CH_3)_2$).[9] The rest were prepared as follows:

a) The 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines with groups X: —H and —CF_3, and the α,α′-dimethyl-2-hydroxy-4-*n*-octyloxy-benzylidene-4′-pyridylmethylenehydrazine (Py) were synthesized following the same synthetic scheme used previously.[9]

b) The α,α′-dimethylbenzalazines with groups X: —NH_2, —OH, —SH, —COOH and —$COCH_3$, and the α,α′-dimethyl-2-hydroxy-4-*n*-octyloxybenzylidene-4′-pyridylmethylenehydrazine-N-oxide (Py → O) were synthesized by condensation of the 2-hydroxy-4-*n*-octyloxyacetophenone and the 4-X-acetophenone or 4-acetylpyridine-N-oxide.

c) Synthesis of 2-hydroxy-4′-isothiocyano-4-*n*-octyloxy-α,α′-dimethylbenzalazine (X: —NCS):

This azine was obtained by reaction of 4′-amino-2-hydroxy-4-*n*-octyloxy-α,α′-dimethylbenzalazine with N,N-dimethylthiocarbamoyl chloride in toluene following the method described by Sayigh.[10]

d) Synthesis of 4′-amino-2-hydroxy-4-*n*-octyloxy-α,α′-dimethylbenzalazine hydrochloride (X: —$NH_3^+Cl^-$):

This compound was obtained by passing a stream of HCl through a solution of the 4′-amino-2-hydroxy-4-*n*-octyloxy-α,α′-dimethylbenzalazine in dry ether.

e) Synthesis of 2-hydroxy-4′-methoxycarbonyl-4-*n*-octyloxy-α,α′-dimethylbenzalazine (X: —$COOCH_3$):

This compound was obtained by methylation of the carboxyl group of 4′-carboxy-2-hydroxy-4-*n*-octyloxy-α,α′-dimethylbenzalazine with diazomethane.[11]

f) Synthesis of 4′-acetyloxy and 4′-benzoyloxy-2-hydroxy-4-*n*-octyloxy-α,α′-dimethylbenzalazines (X: —$OCOCH_3$, —$OCOC_6H_5$):

These azines were obtained by esterification of 2,4′-dihydroxy-4-*n*-octyloxy-α,α′-dimethylbenzalazine with the corresponding acid chloride in pyridine.

Techniques

The melting points, transition temperatures, and enthalpies were determined using a Perkin-Elmer DSC-2 Differential Scanning Calorimeter. The heating rate was 10 K/min. and the apparatus was calibrated by measuring the known melting point and heat of fusion of In (429.6 K, 6.8 cal/g).

The optical observations were made using a Meiji polarizing microscope equipped with a Mettler FP82 hot stage and FP80 control processor.

The identification of products was carried out by the usual methods: Perkin-Elmer 240B microanalyzer, U.V. (Perkin-Elmer 200), I.R. (Perkin-Elmer 283), ^{1}H-NMR (Brucker WP-80-CW).

The purity of all compounds was checked by the above-mentioned techniques and by thin-layer chromatography.

Correlation analysis was carried out using a Digital VAX-11780 minicomputer and a subroutine of the SPSS programme[12]: "Multiple regression analysis: Subprogramme regression".

RESULTS

In Table I are gathered the transition temperatures and enthalpies for all the azines described in this paper together with those of the azines described in previous papers[8,9] all of which are used in the following discussion.

The mesomorphic properties of these azines are represented in increasing order of the melting points in Fig. 1.

DISCUSSION

1. Mesomorphic properties of the 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines.

Seventeen of the twenty-two azines studied in this paper show mesomorphic behavior. The azines with end groups X: —H, —OH and —$NH_3^+Cl^-$ (which decomposes) and those derived from pyridine (represented by Py and Py → O) do not form liquid crystals.

The majority of the mesomorphic azines exhibit a nematic phase confirming the "nematic character" of the central core, 2-hydroxy-α,α′-dimethylbenzalazine, which only shows S_A mesophases with long alkyl or alkoxy chains in the 4- and 4′-positions.[8,13] In general, there exists a concordance between the group efficiency order in stabilizing the nematic phase for some of these groups and the order proposed by G. W. Gray.[1]

TABLE I

Transition temperatures and enthalpies for the 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines and some pyridine analogues

X	Transition	Temperature (°C)	Δ*H* (KJ/mol)
F	C—N	97.0	37.87
	N—I	107.2	0.54
Cl	C—N	107.7	37.35
	N—I	135.0	1.13
Br	C—N	109.5	35.16
	N—I	135.0	1.12
NO_2	C—N	97.8	30.65
	N—I	146.3	0.43
CN	C—N	100.6	39.58
	N—I	160.0	1.90
OCH_3	C_1—C_2	97.3	9.05
	C_2—N	101.0	38.06
	N—I	143.8	1.05
CH_3	C—N	88.4	39.49
	N—I	124.1	1.00
$N(CH_3)_2$	C_1—C_2	110.8	1.84
	C_2—N	133.2	27.15
	N—I	144.2	0.88
$OCOCH_3$	C—N	101.9	40.29
	N—I	143.4	1.07
$OCOC_6H_5$	C—N	108.1	45.12
	N—I	193.8	1.35
$COOCH_3$	C—N	126.6	40.13
	N—I	155.3	1.04
$COCH_3$	C_1—C_2	93.3	6.33
	C_3—C_2[a]	103.6	0.69
	C_2—N	112.3	27.59
	N—I	150.3	0.70
SH	C_1—C_2	102.8	9.21
	C_3—C_2[a]	98.6	7.49
	C_2—N	107.2	27.12
	N—I	127.1	0.73
NH_2	C—I	109.4	33.46
	I—N[b]	81.0	
NCS	C—S_A	100.1	35.49
	S_A—N	101.2	0.05
	N—I	167.4	1.14
CF_3	C_1—C_2	74.2	16.80
	C_2—S_A	103.4	19.12
	S_A—I	121.3	4.49

TABLE I (*continued*)

Transition temperatures and enthalpies for the 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines and some pyridine analogues

X	Transition	Temperature (°C)	ΔH (KJ/mol)
COOH	C_1—C_2	110.1	1.79
	C_2—S_C	212.2	25.62
	S_C—S_A	227.3[c]	
	S_A—I	268.4	15.40
H	C—I	83.5	26.11
OH	C_1—C_2	130.2	0.97
	C_2—I	139.0	35.29
Py	C—I	94.3	48.09
Py → O	C_1—C_2	135.2	10.43
	C_2—I	149.7	25.75
$NH_3^+Cl^-$		177.3(Decomp.)	

[a] Data from a second scan
[b] Monotropic transition
[c] Optical microscopic data

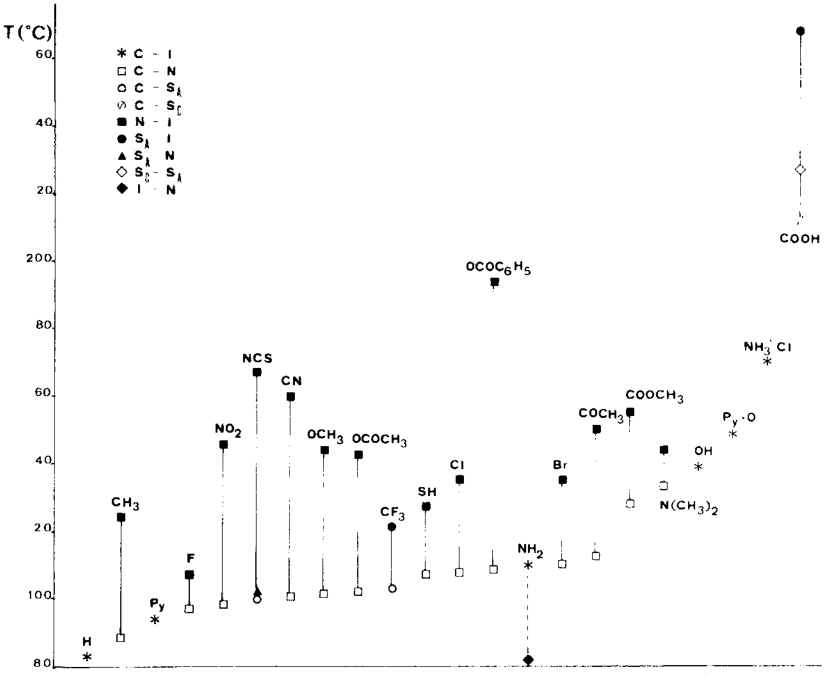


FIGURE 1 Transition temperatures for the 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines and some pyridine analogues.

Only the azines with terminal substituents X: —NCS, —CF_3 (S_A) and —COOH (S_A and S_C) show smectic phases coinciding with the behavior observed by other authors for these groups.[7,14,15]

The different behavior for the azines with end groups X: —OH, —NH_2 and —SH is worth mentioning, as in the case of X: —OH the azine is non-mesomorphic; in the case of X: —NH_2, a monotropic nematic phase and with X: —SH, an enantiotropic nematic are formed.

These groups can form intermolecular hydrogen bonds with very similar structural characteristics. According to G. W. Gray,[16] these bonds may raise the melting points above the mesophase-isotropic liquid transition temperatures and perhaps also favor a non-linear molecular arrangement which is incompatible with mesophase formation.

However, with these azines, the different strengths of these bonds[17]

$$R{-}OH > R{-}NH_2 \gg R{-}SH$$

determine the different mesomorphic behavior of the azines.

In some compounds of this series, crystalline polymorphism before melting (X: —OCH_3, —$N(CH_3)_2$, —CF_3, —COOH, —OH, Py → O) or before and after a first melting (X: —$COCH_3$ and —SH) was observed.

In most cases, the melting points, unlike the clearing points, vary over only a small temperature range (~20°C).

2. Correlation studies between N-I transition temperatures and empirical parameters of the substituents.

2.a. Selection of the parameters. Of the parameters described in the literature,[18] Molar Refractivity (MR) was selected to represent the anisotropy of the polarizability, since this parameter is related to molecular polarizability

$$MR = \frac{4\,\pi\,N\,\alpha}{3}$$

and through this, to the dispersion forces.[18]

Apart from this, MR is an additive-constitutive property of the molecules, enabling us to work with the molar refractivity of polar terminal groups.

Furthermore, as W. J. Dunn[18] in a general discussion of MR has shown, there is a considerable colinearity between MR and Taft's steric parameters E_S^c (n:142. r:0.67), and other studies carried out by us for 14 of the groups studied here (n:14), have shown that a good correlation between MR and some Verloop-Hoogenstraaten's steric parameters (L_1 and B_4)[18] exist (MR-L_1 r:0.90, MR-B_4 r:0.85). In consequence, we used the MR parameter in order to represent both molecular factors: polarizability and steric effects.

In order to represent molecular polarity, the dipole moment of the appropriate monosubstituted benzene measured in benzene solution at 25°C[19] was used.

The MR and μ values for the groups studied and the T_{N-I} for the fifteen α,α′-dimethylbenzalazines which show nematic–isotropic liquid transitions are listed in Table II.

2.b. Correlation between T_{N-I} *and empirical parameters of the substituents.* Since the clearing temperature of a liquid crystal is determined by the polarity, polarizability and steric factors of the molecules, the secondary and tertiary combinations of the MR and μ parameters with T_{N-I} were studied. In a first study, the fifteen α,α′-dimethylbenzalazines with the T_{N-I} values described were used to obtain the results summarized in Table III.

The validity of the results was checked by means of Snedecor's F, defined for a percentage of distribution points, α, of 0.05.[12]

As can be seen, a bad correlation between T_{N-I} and μ was obtained; however, a much better correlation was obtained when MR and

TABLE II

MR, dipole moment and T_{N-I} values used in the correlation studies with the 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines

X	MR	μ(D)	T_{N-I} (K)
F	0.92	1.42	380.4
Cl	6.03	1.56	408.2
Br	8.88	1.56	408.2
CH_3	5.65	0.52	397.3
OCH_3	7.87	1.30	417.0
NO_2	7.36	4.04	419.5
CN	6.33	4.05	433.2
$N(CH_3)_2$	15.55	1.50	417.4
$OCOCH_3$	12.47	1.50	416.6
$OCOC_6H_5$	32.33	1.90	467.0
SH	9.22	1.34	400.3
NCS	17.24	2.85	440.6
$COOCH_3$	12.87	1.90	428.5
$COCH_3$	11.18	2.80	423.5
NH_2	5.42	1.55	354.2

TABLE III

Data from the correlation studies for fifteen 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines

Correlation	r[a]	F[b]	SE[c]	F[d] ν_1/ν_2 (α:0.05)	Groups which deviate
T_{N-I}-MR	0.767	18.50	17.3	F(1/13):4.67	NH_2(−45), CN(30)
T_{N-I}-μ	0.419	2.77	24.5	F(1/13):4.67	$OCOC_6H_5$(55), NH_2(−53), F(−27)
T_{N-I}-MR-μ	0.854	16.20	14.6	F(2/12):3.89	NH_2(−42), OCH_3(16), CN, Cl, CH_3(10)

[a] Correlation coefficient

[b] Snedecor's F

[c] Standard error

[d] Relation of number of independent variables and free degrees: ν_1 number of independent variables; ν_2 free degrees.

TABLE IV

Data from the correlation studies for fourteen 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines

Correlation	r^a	F^b	SE[c]	F^d ν_1/ν_2 (α:0.05)	Groups which deviate
T_{N-I}-MR	0.849	31.0	11.4	$F(1/12)$:4.75	CN(25), F(−14), SH(−13), $N(CH_3)_2$(−12)
T_{N-I}-μ	0.448	3.01	19.3	$F(1/12)$:4.75	$OCOC_6H_5$(49), F(−32), NO_2(−17)
T_{N-I}-MR-μ	0.947	48.20	7.2	$F(2/11)$:3.98	OCH_3(11.9), F(−9.5), CN(8.5), NO_2(−8.5), $N(CH_3)_2$(−7.2)

[a] Correlation coefficient
[b] Snedecor's *F*
[c] Standard error
[d] Relation of number of independent variables and free degrees: ν_1 number of independent variables; ν_2 free degrees.

T_{N-I} were correlated (r: 0.767), and the best correlation coefficient was obtained when both parameters MR and μ were used in the correlation study (r: 0.854).

As can be seen in Table III, the —NH_2 group shows considerable deviations in the three correlations studied, with the predicted clearing temperatures much higher than the real values.

This behavior of the amino-group could be accounted for by the intermolecular hydrogen bonds formed by this group. This bonding gives rise to entities of greater volume and taking into account the Maier and Saupé equation[3]

$$T_{N-I} = \frac{A\,(\alpha_l - \alpha_t)^2\,I}{k\,V^2}$$

a volume increase gives rise to lower transition temperatures.

Due to the anomalous behavior of this group, which the parameters used do not allow for, we studied the same correlations for the fourteen remaining cases, obtaining the results summarized in Table IV.

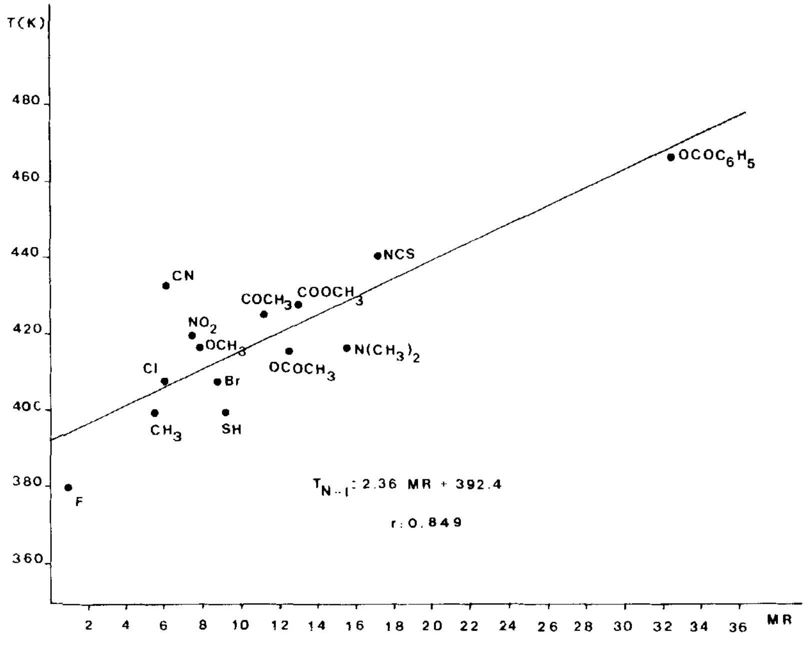


FIGURE 2 Equation and graphic representation of the relation T_{N-I}-MR for fourteen 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines.

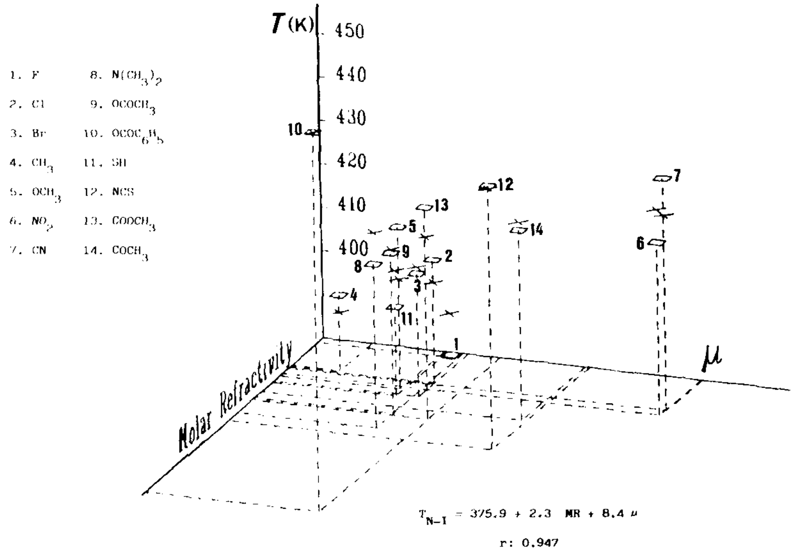


FIGURE 3 Equation and graphic representation of the relation T_{N-I}-MR-μ for fourteen 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines. (☐: experimental values, +: predicted values).

Like the earlier correlations, the best coefficients were obtained when the MR parameter was used.

A good coefficient (*r*: 0.849) was obtained for the correlation between T_{N-I} and MR, with a straight line regression as shown in Figure 2, and an excellent correlation was obtained when both MR and μ parameters were used, with a coefficient *r*: 0.947 and a standard error near to 7°C. The equation and graphic representation are given in Figure 3.

TABLE V

MR, dipole moment and T_{N-I} values used in the correlation studies for the 4-X-phenyl 4-(*trans*-4-decylcyclohexyl)-benzoates

X	MR	μ(D)	T_{N-I} (K)
CN	6.33	4.05	456
NO_2	7.36	4.04	447
CHO	6.88	2.80	435
NCS	17.24	2.85	474
I	13.94	1.29	439
F	0.92	1.42	401
Cl	6.03	1.56	434
Br	8.88	1.56	442
$COCH_3$	11.18	2.80	435

TABLE VI

Data from the correlation studies for the 4-X-phenyl 4-(*trans*-4-decylcyclohexyl)benzoates

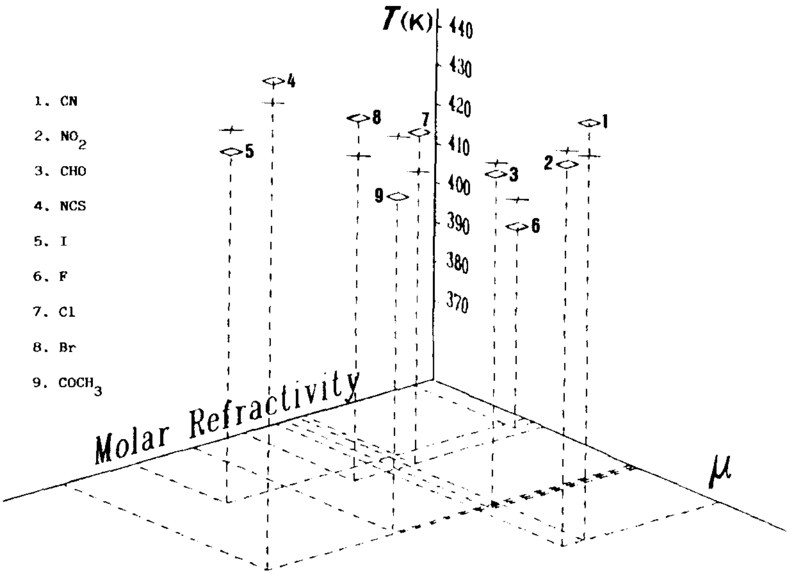
Correlation	r[a]	F[b]	SE[c]	F[d] ν_1/ν_2 (α:0.05)	Groups which deviate
T_{N-I}-MR	0.735	8.25	14.19	F(1/7):5.59	CN(22), I(− 16), F(− 15), $COCH_3$(− 12)
T_{N-I}-μ	0.537	2.84	17.67	F(1/7):5.59	NCS(30), F(− 29)
T_{N-I}-MR-μ	0.890	11.67	10.23	F(2/6):5.14	$COCH_3$(− 15), Cl(9.9), Br(9.7)

[a] Correlation coefficient

[b] Snedecor's F

[c] Standard error

[d] Relation of number of independent variables and free degrees: ν_1 number of independent variables; ν_2 free degrees.



$$T_{N-I} = 392.3 + 2.9\ MR + 9.1\ \mu$$

r: 0.890

FIGURE 4 Equation and graphic representation of the relation T_{N-I}-MR-μ for nine 4-X-phenyl 4-(*trans*-4-decylcyclohexyl)benzoates. (☐: experimental values, +: predicted values).

In order to check the validity of these results, the same correlations were studied for the series 4-X-phenyl 4-(*trans*-4-decylcyclohexyl)-benzoates (X: —F, —Cl, —Br, —I, —CN, —NO_2, —CHO, —NCS, —$COCH_3$) described by R. Dabrowski.[7] The values of MR, μ and T_{N-I} used are listed in Table V and the results from these correlations are summarized in Table VI.

These results are similar to those obtained with the series of azines. A bad correlation between T_{N-I} and μ was obtained; however a good coefficient (*r*: 0.735) for the correlation T_{N-I}-MR and a very good correlation coefficient (*r*: 0.890), much higher than the earlier ones, for T_{N-I}-MR-μ were obtained. The equation and graphic representation of this last correlation are given in Figure 4.

CONCLUSIONS

The central core of the 2-hydroxy-4-*n*-octyloxy-4′-X-α,α′-dimethylbenzalazines studied here fundamentally governs the interactions in the solid phase; consequently the melting points of these compounds are in general similar. The central core is also responsible for the nematic phase shown by most of these compounds.

The polar group, however, plays a more important role in the molecular interactions within the mesophase.

The results obtained from the correlation studies lead to the conclusion that the combination of the empirical parameters—molar refractivity (MR) of the aromatic substituents and the dipole moment (μ) from the monosubstituted benzenes (representative of polarizability-steric factors and polarity respectively)—can be used to predict the clearing temperatures for both of the series.

However, we think that before generalizing these results, the extreme subtlety of the intra- and inter-molecular interactions which govern T_{N-I} should be taken into account, since, in some cases, these interactions are possibly not sufficiently represented by empirical physical aromatic substituent parameters.

Acknowledgments

One of the authors (M. B. Ros) would like to thank the Ministerio de Educación y Ciencia (Spain) for the award of a F. P. I. grant, which made this research possible.

References

1. G. W. Gray, "Advances in Liquid Crystals" Vol. 2, Academic Press, pp. 1–72 (1970).
2. W. H. de Jeu and J. Van der Veen, *Philips Res. Rept.*, **27**, 172 (1972).
3. W. H. de Jeu and J. Van der Veen, *Mol. Cryst. Liq. Cryst.*, **40**, 1 (1977).
4. J. Van der Veen, *J. Phys.* (*Paris*), **36**, C1-375 (1975).
5. W. Maier and A. Saupe, *Z. Naturforsch.*, **14a**, 882 (1959); **15a**, 287 (1960).
6. A. C. Griffin, *Mol. Cryst. Liq. Cryst. Lett.*, **34**, 111 (1976).
7. R. Dabrowski, J. Przedmojski, J. W. Baran and B. Pura, *Cryst. Res. Technol.*, **21**, 567 (1986).
8. J. Barberá, M. Marcos, E. Meléndez and J. L. Serrano, *Mol. Cryst. Liq. Cryst.*, **94**, 367 (1983).
9. M. Marcos, E. Meléndez, B. Ros and J. L. Serrano, *Can. J. Chem.*, **63**, 2922 (1985).
10. A. R. Sayigh, H. Ulrich and J. S. Potts, *J. Org. Chem.*, **30**, 2465 (1965).
11. N. Fisher and G. Opitz, *Synth. Coll. Vol.* **5**, 878 (1973).
12. M. Morrington and C. M. Thompson, *Biometrika*, **33**, 73 (1943).
13. M. Marcos, E. Meléndez and J. L. Serrano, *Mol. Cryst. Liq. Cryst.*, **91**, 152 (1983).
14. P. Le Barny, G. Ravaux, J. C. Dubois and J. P. Parneix, *Mol. Cryst. Liq. Cryst.*, **127**, 413 (1985).
15. D. Demus and H. Zaschke, "Flüssige Kristalle in Tabellen" Vol. II, VEB Deutscher

Verlag für Grundstoffindustrie. Leipzig (1984).
16. G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals," Academic Press, New York, p. 162 (1962).
17. V. P. Pogorelyi, *Russ. Chem. Rev.*, **46**, 316 (1977).
18. C. Hansch and A. Leo, "Substituent Constants for Correlation Analysis in Chemistry and Biology," John Wiley and Sons, New York (1979).
19. A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Company, London (1963).