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Preliminary communication

Development of an incremental system for the prediction of the nematic–isotropic phase transition temperature of liquid crystals with two aromatic rings

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It is possible to express the transition temperature nematic–isotropic (T_{NI}) for nematogens with just two aromatic ring systems as the sum of incremental values of substructural elements, denoted as substituents and bridging moieties. Of the 1426 mesogens that can be constructed by the elements for which the increments have been given, the T_{NI} values of most can be predicted to within 10°C, the only notable exception being the 1,2-diphenylethenes.

In recent times, several approaches have been adopted for the investigation of a quantitative relationship between the structure of a thermotropic liquid crystal material and its transition behaviour. The molecular approach has been tried frequently, relating the temperature of the transition nematic–isotropic (T_{NI}) of a compound to its molecular polarizability ($\Delta\alpha$) [1], its geometrical anisotropy [1], and other electronic and/or stereochemical factors [2]. As more and more liquid crystal materials have been studied over the years (50 000 by 1990), they have become the subject of statistical evaluation. With the compilation of the available data on liquid crystals [3] and the development of data bases (such as LiqCryst) [4] it has become possible to predict transition temperatures of mesogens by cross-comparison with a large number of similar structures. Within this statistical evaluation of physical properties in relation to structures, it is possible to differentiate among three different methods:

(*a*) The direct comparison of similar compounds to seek for a structure–property relationship within a series of molecules [5]. Here, the work on the dependence of T_{NI} on the number of atoms in the terminal groups of liquid crystals must be noted (even–odd effect within a homologous series).

(*b*) A more dynamic approach is the comparison of a compound with a larger set of different molecules, where the dependence of the relationship of similar structures on other physical values, such as on T_{NI} itself, is included [4]. Both methods (a) and (b) are suited to predict transition temperatures of molecules, where there is a linear relationship between molecular structure and transition temperature.

(*c*) Where no linear relationship exists, the use of artificial neural networks may be preferred [6].

Clearly, for the molecular approach towards estimating T_{NI}, a good approximation of the molecular characteristics is needed. These are not always easy to obtain and are also highly dependent on the conformation of the molecules. While the lowest energy conformation can be calculated for one molecule, it can only be *approximated* for that molecule in a mesophase. Methods (b) and (c) involving the statistical approach evidently need powerful computational tools.

If, on the other hand, compounds show an additive structural–property relationship, i.e. if the substructures of a molecule contribute a fixed value to the transition temperature of that molecule as a whole, it should be possible to put in hand a simple incremental system developed from the analysis of as many structural comparisons as obtainable. Indeed, it could be shown that certain classes of thermotropic liquid crystals show such an additive behaviour. In 1972 Knaak *et al.* [7] developed a system of increments for the influence of substituents and bridging moieties on the T_{NI} of liquid crystal materials with two aromatic rings. This incremental system was based on a set of roughly 160 compounds. While the system is easy to use for the

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evaluation of the T_{NI} of substances, it has two main limitations:

(1) The calculated values of T_{NI} do not always correlate well with the experimental values. The two sets of values have an average deviation of about 9°C [2, 7], and compounds with long alkyl (alkoxy) chains as terminal groups cannot be evaluated accurately.

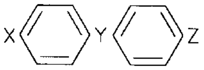
(2) The increments for certain important classes of liquid crystal materials, even within the restriction of compounds with two aromatic rings, have not been listed.

The aim of the present communication is a refinement of the incremental values given by Knaak *et al.*, but the method is now based on comparisons within a set of about 940 known liquid crystalline substances. The requirement that the molecules are aromatic with two aryl rings remains. Secondly, the incremental values for the calculation of T_{NI} for biphenyls, aromatic thioesters and diphenylacetylenes (tolanes) will be given for the first time.

The increments as given by Knaak *et al.* [7], where available, were taken as the starting values for further refinement. Calculated NI temperatures using these increments were compared with listed NI temperatures for compounds tabulated in LiqCryst [4]. Deviations between the two sets of temperatures were minimized by iterative adjustment of the increment for one substructural element. Successive and iterative treatment of all substituents and bridges provided the new values for the increments listed below.

Tables 1 and 2 give the new, refined incremental values based on 1426 known liquid crystalline compounds possessing two aromatic rings. Knaak *et al.* [7] have set the incremental parameter of the azo linkage to zero as a point of reference. The authors have found that the values for the azo compounds of Knaak as evaluated within a larger set of data do not show the best fit. To offer a link of reference to the parameters of Knaak, the increment for imines (as in benzylideneanilines) as a bridging element was maintained at a value of −9·0°C and all other parameters were altered accordingly. New in the list are increments for the nitro-, chloro-, isothiocyanato-, heptyl-, heptoxy-, 2-methylbutoxy- and 2-methylbutoxycarbonyl substituents (table 1) and for

Table 1. Substituent parameters (°C).



(Number of carbon atoms *n* in the terminal group, where *R* is of the general formula C_nH_{2n+1}).

X, Z	1	2	3	4	5	6
R	17·0	5·8	22·1	11·0	25·1	15·9
*R*O	50·8	72·6	54·7	63·1	55·1	61·0
*R*COO	60·3	66·1	64·9	55·9	58·7	53·4
*R*OCOO	69·6	64·1	49·6	48·3	45·3	43·6
*R*CO	59·0	90·9	61·3	71·1	[a]	[a]
*R*OOC	66·5	46·7	19·9[b]	23·8	[a]	[a]

–CN	$-NO_2$	– Cl	– NCS	$-OC_8H_{17}$
72·0	31·6[b]	30·3[b]	54·3[b]	61·1[b]
$-C_7H_{15}$	OC_7H_{15}	$-OC_5H_{11}$[c]	$-COOC_5H_{11}$[c]	
26·6[b]	56·2[b]	13·9[b]	– 0·7[b]	

Table 2. Parameters of bridge elements (°C).

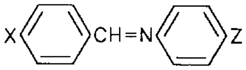
Y					
N=N	CH=N	N=N(O)	CH=N(O)	COO	C=C
–3·5	– 9·0	13·9	8·7	– 30·5	27·6[b]
COS	C≡C				direct link
– 3·2[b]	– 14·4[b]				– 56·6[b]

[a] Values not determined.

[b] Increments not found in [7].

[c] C_5H_{11} = 2-methylbutyl.

Table 3. Calculated nematic—isotropic transition temperatures for *p*,*p*′-disubstituted benzylideneanilines.



X	Z	(°C) $T_{\mathrm{NI\ exp}}$	$T_{\mathrm{NI\ calc}}$[7]	$T_{\mathrm{NI\ calc}}$[8]	Δ[8] (Δ[7])
C_3H_7O	C_4H_9	55·7	62	56·7	1·0 (6)
C_4H_9O	C_4H_9	75·0	67	65·1	−9·9 (−8)
$C_5H_{11}O$	C_4H_9	69·2	61	57·1	−12·1 (−8)
$C_6H_{13}O$	C_4H_9	77·8	64	63·0	−14·8 (−14)
C_4H_9O	OC_4H_9	122·0	113	117·2	−4·8 (−9)
C_4H_9O	OC_6H_{13}	119·0	110	115·1	−3·9 (−9)
C_3H_7O	$OOCCH_3$	108·0	112	106·0	−2·0 (4)
C_3H_7O	$OOCC_2H_5$	113·0	114	111·8	−1·2 (1)
C_3H_7O	$OOCC_5H_{11}$	109·0	97	104·4	−4·6 (−12)
C_3H_7O	$OOCC_6H_{13}$	100·0	92	99·1	−0·9 (−8)
C_4H_9O	$OOCCH_3$	114·2	117	114·4	0·2 (3)
C_4H_9O	$OOCC_2H_5$	120·0	119	120·2	0·2 (−1)
C_4H_9O	$OOCC_3H_7$	119·0	115	119·0	0·0 (−4)
C_4H_9O	$OOCC_4H_9$	113·0	106	110·0	−3·0 (−7)
C_4H_9O	$OOCC_5H_{11}$	115·5	102	112·8	−2·7 (−14)
C_4H_9O	$OOCC_6H_{13}$	110·0	97	107·5	−2·5 (−13)
$C_5H_{11}O$	$OOCCH_3$	105·0	111	106·4	1·4 (6)
$C_5H_{11}O$	$OOCC_2H_5$	109·0	113	112·2	3·2 (4)
$C_5H_{11}O$	$OOCC_4H_9$	110·5	100	102·0	−8·5 (−11)
$C_5H_{11}O$	$OOCC_5H_{11}$	111·0	96	104·8	−6·2 (−15)
$C_5H_{11}O$	$OOCC_6H_{13}$	104·0	91	99·5	−4·5 (−13)
$C_6H_{13}O$	$OOCCH_3$	109·0	114	112·3	3·3 (5)
C_3H_7O	$COCH_3$	101·7	99	104·7	3·0 (−3)
C_4H_9O	$COCH_3$	111·0	104	113·1	2·1 (−7)
C_4H_9O	COC_2H_5	146·0	138	145·0	−1·0 (−8)
$C_5H_{11}O$	$COCH_3$	109·0	98	105·1	−3·9 (−11)
$C_6H_{13}O$	$COCH_3$	114·5	101	111·0	−3·5 (−14)
C_3H_7O	$OCOOCH_3$	108·0	115	115·3	7·3 (7)
C_3H_7O	$OCOOC_2H_5$	106·0	108	109·8	3·8 (2)
C_3H_7O	$OCOOC_3H_7$	95·0	89	95·3	0·3 (−6)
C_3H_7O	$OCOOC_4H_9$	93·0	88	94·0	1·0 (−5)
C_3H_7O	$OCOOC_5H_{11}$	90·0	90	91·0	1·0 (0)
C_3H_7O	$OCOOC_6H_{13}$	88·0	82	89·3	1·3 (−6)
C_4H_9O	$OCOOCH_3$	114·0	120	123·7	9·7 (6)
C_4H_9O	$OCOOC_2H_5$	114·0	113	118·2	4·2 (−1)
C_4H_9O	$OCOOC_3H_7$	106·0	94	103·7	−2·3 (−12)
C_4H_9O	$OCOOC_4H_9$	103·0	93	102·4	−0·6 (−10)
C_4H_9O	$OCOOC_5H_{11}$	100·0	95	99·4	−0·6 (−5)
C_4H_9O	$OCOOC_6H_{13}$	96·0	87	97·7	1·7 (−9)
$C_5H_{11}O$	$OCOOCH_3$	105·0	114	115·7	10·7 (9)
$C_5H_{11}O$	$OCOOC_2H_5$	104·0	107	110·2	6·2 (3)
$C_5H_{11}O$	$OCOOC_3H_7$	96·0	88	95·7	−0·3 (−8)
$C_5H_{11}O$	$OCOOC_4H_9$	95·0	87	94·4	−0·6 (−8)
$C_5H_{11}O$	$OCOOC_5H_{11}$	93·0	89	91·4	−1·6 (−4)
$C_5H_{11}O$	$OCOOC_6H_{13}$	93·0	81	89·7	−3·3 (−12)
$C_6H_{13}O$	$OCOOCH_3$	113·0	117	121·6	8·6 (4)
$C_6H_{13}O$	$OCOOC_2H_5$	108·0	110	116·1	8·1 (2)
$C_6H_{13}O$	$OCOOC_3H_7$	100·0	91	101·6	1·6 (−9)
$C_6H_{13}O$	$OCOOC_4H_9$	99·0	90	100·3	1·3 (−9)
$C_6H_{13}O$	$OCOOC_5H_{11}$	96·0	92	97·3	1·3 (−4)
$C_6H_{13}O$	$OCOOC_6H_{13}$	96·0	84	95·6	0·4 (−12)
C_3H_7COO	C_4H_9	56·5	71	62·3	5·8 (15)
C_2H_5COO	CH_3	66·5	56	74·1	7·6 (−11)
C_2H_5COO	C_2H_5	58·0	63	62·7	4·7 (5)
C_2H_5COO	C_4H_9	71·2	73	68·1	−3·1 (2)
C_3H_7COO	C_2H_5	63·5	59	61·5	−2·0 (−5)

Table 3. (*Continued*)

X	Z	(°C) $T_{\mathrm{NI\ exp}}$	$T_{\mathrm{NI\ calc}}$[7]	$T_{\mathrm{NI\ calc}}$[8]	Δ[8] (Δ[7])
C_3H_7COO	C_4H_9	74·0	69	66·9	−7·1 (−5)
C_4H_9COO	C_2H_5	56·0	50	52·5	−3·5 (−6)
C_4H_9COO	C_4H_9	68·0	60	57·9	−10·1 (−8)
$C_5H_{11}COO$	C_2H_5	66·5	46	55·3	−11·2 (−21)
$C_5H_{11}COO$	C_4H_9	76·0	56	60·7	−15·3 (−20)
$C_6H_{13}COO$	C_2H_5	64·5	41	50·0	−14·5 (−24)
$C_6H_{13}COO$	C_4H_9	74·5	51	55·4	−19·1 (−24)
CH_3COO	$COCH_3$	105·0	108	110·3	5·3 (3)
C_2H_5COO	$COCH_3$	113·0	110	116·1	3·1 (−3)
C_3H_7COO	$COCH_3$	115·5	106	114·9	−0·6 (−10)
C_4H_9COO	$COCH_3$	105·5	97	105·9	0·4 (−9)
$C_5H_{11}COO$	$COCH_3$	110·5	93	108·7	−1·8 (−18)
$C_6H_{13}COO$	$COCH_3$	107·0	88	103·4	−3·6 (−19)

the bridge elements ethene, ethyne, thioester, and the direct link (biaryls).

Table 3 is a representation of an original table by Knaak *et al.* [7] of estimated transition temperatures (T_{NIcalcd}) for *p,p'*-benzylideneanilines to facilitate a direct comparison of the quality of the transition temperatures calculated (see the figure) using the increments of Knaak *et al.* [7] and ours. All compounds carrying a phenyl substituent (*R*=phenyl) have been excluded. The reason for this is that some of these compounds were shown to have a smectic and not a nematic phase. Also those compounds of the original table have been excluded where transition temperatures were reached by interpolation and have not been measured experimentally. Also, it must be noted that certain experimental values of transition temperatures (T_{NIexp}) have been revised since 1972. All transition temperatures tabulated in table 3 are those found in [3, 4]. Of the 69 compounds evaluated, the use of Knaak's parameters led to a better prediction in 17 cases with a mean deviation of 8·3°C overall; the use of the newly refined increments led to a better prediction in 51 cases with a mean deviation of 4·3°C.

Table 4 gives another indication of the quality of T_{NI} prediction using the newly refined increments evaluated over all compounds found in [4], for which Knaak [7] has given increment values. Lastly, table 5 gives an overview of the quality of T_{NI} prediction evaluated over all compounds found in [4] for which we have given increments in this communication.

It is of interest to note that for 1,2-diarylethenes (stilbenes), no increment could be found that generally satisfies prediction of T_{NI} for these compounds. Apart from the comparatively small available data set on which the parameters can be based, the major reason for this is that the values for a homologous series of dialkoxystilbenes on the one hand and those of many of the other tabulated stilbenes on the other hand are divergent. Of course, the stilbenes may constitute one of the systems where a general additivity of substructural increments does not apply. Furthermore, the inclusion of short chains as terminal groups, for example methyl or especially methoxy, is a source of some error in the statistical evaluation of a homologous series.

From table 1 it can be seen that the accepted order [9] of priority for terminal groups is reflected. Thus, the transition temperature decreases in the following relative order:

CN	>	OCH_3	>	NO_2	>	Cl	>	CH_3
72°C		50·8°C		31·6°C		30·3°C		17·0°C

Even–odd effects in the homologous series can be noted. Compounds with an odd number of carbon atoms in their terminal group (C_nH_{2n+1}) give higher transition temperatures than compounds with an even number. For ethers of the general formula $O(C_nH_{2n+1})_2$ the situation is reversed. Branched terminal groups depress the transition temperature as compared with non-branched termini with the same number of carbon atoms, as noted by Vorländer [10] many years ago.

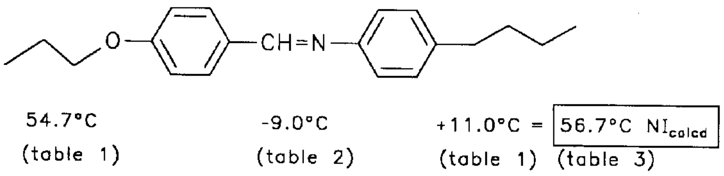


Figure. Example of a calculation of $\mathbf{T}_{\mathrm{NI}}$ using the system of increments from tables 1 and 2.

Table 4. Difference between experimental and estimated nematic–isotropic transition temperatures.

Ref.	≤5°	≤10°	>15°	Total	
[7]	322 (34%)	563 (60%)	726 (77%)	215	941
[8]	502 (53%)	769 (82%)	877 (93%)	64	941

[a] Liquid crystals possessing bridges and substituents, for which incremental parameters have been given both by [7] and by us [8]. This excludes compounds with substituents or bridges marked by [b] in tables 1 and 2. In all, 941 known compounds have been reviewed.

Table 5. Difference between experimental and estimated nematic–isotropic transition temperatures (°C)[a].

Bridge	≤5°	≤10°	≤15°	>15°	Total
N=N	96 (55%)	148 (84%)	165 (94%)	11	176
CH=N	219 (52%)	339 (79%)	394 (92%)	35	429
N=N(O)	94 (43%)	157 (72%)	196 (90%)	22	218
COO	185 (51%)	300 (83%)	338 (90%)	22	360
C=N(O)	5 (42%)	10 (83%)	11 (92%)	1	12
C=C	1 (4%)	3 (12%)	6 (24%)	19	25
C=C	33 (46%)	55 (77%)	62 (87%)	9	71
COS	49 (44%)	87 (78%)	108 (96%)	4	112
direct link	15 (65%)	21 (91%)	22 (96%)	1	23

[a] Liquid crystals possessing bridges and substituents, for which the increments have been provided, have been screened. In all, 1426 known liquid crystalline compounds have been reviewed.

The bridge elements –O–, $-CH_2CH_2-$, $-CH_2O-$, which are known to give low transition temperatures, have not been included in this survey. Nevertheless, for nematic compounds with two aromatic units and the general form given, the priority of the bridging groups in the order of decreasing transition temperature is as follows:

N=N(O); CH=N(O) > N=N; CH=N
13·9°C; 8·7°C −3·5°C; −9·0°C

> COO > direct link;
−30·5°C −56·6°C

COS > COO
−3·2°C −30·5°C

In conclusion, it is possible to express the T_{NI} values for nematogens with two aromatic ring systems as the sum of incremental values of substructural elements, denoted as substituents and bridging moieties. Of the 1426 tabulated liquid crystals that can be constructed by the elements for which the increments have been given,† the T_{NI} of more than 90% can be predicted correctly within a value of 15°C. The T_{NI} of most classes (75% or more) can be predicted to within 10°C, the only notable exception being the 1,2-diphenylethenes.

References

[1] De Jeu, W. H., and Van Der Veen, J., 1977, *Mol. Cryst. liq. Cryst.*, **40,** 1 and references therein.

[2] Liu, C. T., 1981, *Mol. Cryst. liq. Cryst.*, **74,** 25 and references therein.

[3] Vill, V., 1992–1995, *Liquid Crystals*, Vol. IV/7, Landolt-Boernstein, New Series (Berlin: Springer).

[4] Vill, V., 1996, *LiqCryst 2.1—Database of Liquid Crystalline Compounds for Personal Computers*, Fujitsu Kyushu System (FQS) Ltd., Fukuoka, Japan (Hamburg: LCI Publisher).

[5] Blair, T. T., Neubert, M. E., Tsai, M., and Tsai, C.-C., 1991, *J. phys. chem. ref. Data*, **20,** 189.

[6] Schroeder, R., Kränz, H., Vill, V., and Meyer, B., 1996, *J. chem. Soc. Perkin Trans. II*, 1685.

[7] Knaak, L. E., Rosenberg, H. M., and Servé, M. P., 1972, *Mol. Cryst. liq. Cryst.*, **17,** 171.

[8] This communication.

[9] Gray, G. W., Winsor, P. A., 1974, *Liquid Crystals and Plastic Crystals* (New York: John Wiley and Sons); Sage, I., *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. A15, p. 359.

[10] Vorländer, D., 1907, *Ber.*, **40,** 1970.

† The authors believe that it should be possible to calculate incremental values for hetarenes and certain rigid cycloalkanes.