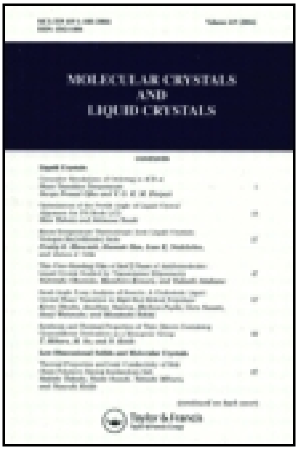


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Dependence Of Nematic-Isotropic Transition Temperatures On The Anisotropy Of Polarizability Of The C-X Bond For Terminal Substituents

Anselm C. Griffin [a]

[a] Department of Chemistry, University of Southern Mississippi, Hattiesburg, Mississippi, 39401

Version of record first published: 28 Mar 2007.

To cite this article: Anselm C. Griffin (1976): The Dependence Of Nematic-Isotropic Transition Temperatures On The Anisotropy Of Polarizability Of The C-X Bond For Terminal Substituents, Molecular Crystals and Liquid Crystals, 34:4, 111-115

To link to this article: http://dx.doi.org/10.1080/15421407608083896

Mol. Cryst. Liq. Cryst., Vol. 34 (Letters), pp. 111-115

Printed in U.S.A.

THE DEPENDENCE OF NEMATIC-ISOTROPIC TRANSITION TEMPERATURES ON THE ANISOTROPY OF POLARIZABILITY OF THE C-X BOND FOR TERMINAL SUBSTITUENTS

ANSELM C. GRIFFIN
Department of Chemistry
University of Southern Mississippi
Hattiesburg, Mississippi 39401

(Submitted for publication September 15, 1976)

Examination of four molecular series of nematogens reveals that Tc is in general related to $\Delta\alpha$ of the C-X bond, but not always directly proportional. Substituents which interact strongly with the remainder of the molecular π-electron system are among notable exceptions

INTRODUCTION

In a recent paper van der Veen[1] used a novel approach to study the relationship between polarizability anisotropy of bonds to small, compact terminal substituents and the nematic-isotropic (N→I) transition temperature of compounds containing these substituents. The basis for the work was the molecular statistical theory of Maier and Saupe[2], in which the following relation obtains at the clearing temperature:

$$Tc = \frac{A}{4.55kV^2} \qquad (1)$$

V is molar volume which is assumed to be constant along a series of molecules differing only in terminal substituents. This assumption obviates the incorporation of excluded volume effects such as those discussed by Kimura[3]. Boltzmann's constant is k and A is the molecular constant, taken as being proportional to the square of Δα, the anisotropy of molecular polarizability, $\alpha_{||} - \alpha_{\perp}$. Van der Veen makes assumptions which lead to the following relation for any series of nematics differing only in terminal substituents:

$$Tc \sim (\Delta\alpha_M)^2 + 2\Delta\alpha_X\Delta\alpha_M + (\Delta\alpha_X)^2 \qquad (2)$$

The term $\Delta\alpha_M$ is the anisotropy of polarizability for all of the molecular structure except the terminal substituent. The polarizability anisotropy of the C_{aryl}-X bond is $\Delta\alpha_X$. If $\Delta\alpha_M$ is much larger than $\Delta\alpha_X$, Tc should show a linear dependence on $\Delta\alpha_X$.

$$Tc \sim 2\Delta\alpha_X \qquad (3)$$

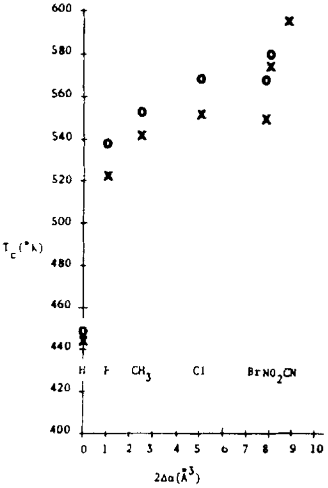
Data[1] were presented for two series of compounds, each differing only in the nature of the terminal substituents. The dependence of Tc on $\Delta\alpha_X$ was reasonably linear for all substituents except bromine.

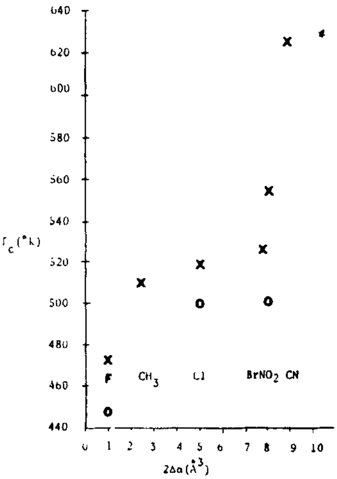
It is the purpose of this work to examine the relation developed by van der Veen more fully by considering additional series and by enlarging the number and type of terminal substituents.

RESULTS

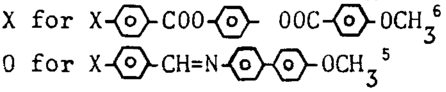
Values of $\Delta\alpha_X$ were taken from Le Fevre[4].

The two series, A and B, presented in GRAPH 1 on the next page were chosen as they each contain a variety of substituents including hydrogen, a substituent not available for examination in the earlier work[1]. Bromine was found[1] to correlate poorly with equation (3). Both series in GRAPH 1 contain bromine as a substituent in order to test for this anomolous behavior.

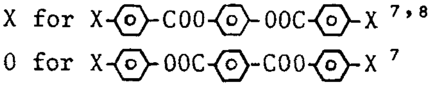




GRAPH 1 Plot showing dependence of Tc on $\Delta\alpha_X$:



GRAPH 2 Plot showing dependence of Tc on $\Delta\alpha_X$:

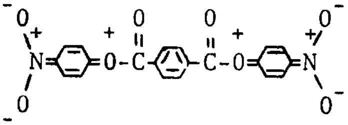


GRAPH 2 presents data for two closely related series of compounds. These series represent extremes in conjugative interaction between a para nitro substituent and other portions of the molecular structure. In series C virtually no mesomeric interaction is possible; in series D, a substantial mesomeric interaction between the sigma-bonded ester oxygen and the terminal nitro substituent is possible.

DISCUSSION

In agreement with van der Veen we find a good correlation with equation (3) for several substituents. There are, however, exceptions. It is apparent from GRAPH 1 that bromine is out of line in both series. The bromo substituent shows the same relative location in both series, suggesting that there is a systematic deviation from linearity for terminally substituted bromo compounds. The Tc of a hydrogen substituted molecule is, in both series, below its anticipated value. As in the case of bromine, both hydrogen substituted compounds have Tc values below the value anticipated by extrapolation of a line established by the linear fit of Tc with $2\Delta\alpha_X$ for the other substituents.

The data in GRAPH 2 are for two series of compounds which differ in location of the ester linkage. Dewar and Griffin[9] demonstrated the influence of location of the carbonyl group of ester linkages on the thermodynamic properties of the N→I transition. Inversion of carbonyl location is also important in the esters considered here. In series C substituents, with the exception of bromine, adhere well to equation (3). Series D, on the other hand, shows a considerable lack of linearity due apparently to the nitro substituent. There is a strong conjugative interaction between the σ-bonded ester oxygens and the nitro groups as shown below.



This interaction negates the validity of the relationship proposed in (3). This non-linearity is not totally unexpected. Le Fevre's[4] data show for *para* nitroanisole that directed polarizability exaltations, due to conjugative interactions along the 1,4-axis in the aromatic ring are quite large. Apparently in such cases the strong conjugative interactions of terminal substituents make invalid the assumption[10] of additivity of polarizability anisotropies. Of the two series of compounds studied by van der Veen[1] and the four presented here, only in our series D are there molecules with strongly electron withdrawing substituents. The relationship between Tc and $\Delta\alpha_X$ as expressed by equation (3) is apparently only applicable in a general sense.

Helpful discussion with Dr. Robert J. Cox is gratefully acknowledged.

REFERENCES

1. J. van der Veen, Journal de Physique, Colloque C1, supplement 3, Volume 36, C1-375 (1975).
2. W. Maier and A. Saupe, Z. Naturforsch., 13a, 564 (1958); 14a, 882 (1959); 15a, 287 (1960).
3. H. Kimura, Phys. Lett., 47A, 173 (1974).
4. M. J. Aroney, R. J. W. Le Fevre, R. K. Pierens, and M. G. N. The, J. Chem. Soc., B, 666 (1969); M. J. Aroney, G. Cleaver, R. K. Pierens, and R. J. W. Le Fevre, J. Chem. Soc. Perkin II, 3 (1974).
5. G. W. Gray, Molecular Structure and the Properties of Liquid Crystals, New York 1962, p. 132.
6. M. J. S. Dewar and A. C. Griffin, J. Chem. Soc. Perkin II, 713 (1976).
7. M. J. S. Dewar and R. S. Goldberg, J. Org. Chem., 35, 2711 (1970).
8. J. P. Schroeder and D. W. Bristol, J. Org. Chem., 38, 3160 (1973).
9. M. J. S. Dewar and A. C. Griffin, J. Chem. Soc. Perkin II, 710 (1976).
10. R. J. W. Le Fevre, Advances in Physical Organic Chemistry, Volume 3, Academic Press, New York, New York, 1965, p. 54.