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# Estimation of Nematic-Isotropic Points of Nematic Liquid Crystals

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# Estimation of Nematic-Isotropic Points of Nematic Liquid Crystals[1]

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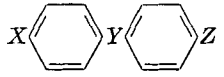
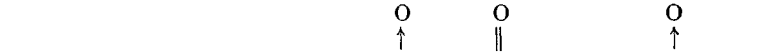
**Abstract**—A survey has been made of reported nematic-isotropic points of nematic liquid crystals having the following structure:



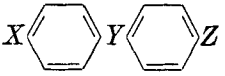
where $X$ and $Z$ are: R—, RO—, $RCO_2$—, $ROCO_2$—, RCO—, ROCO—; R is $n$-alkyl varying from $C_1$ to $C_6$; and $Y$ is:



The variation of the nematic-isotropic points with structure is sufficiently regular to permit the generation of sets of parameters for $X$, $Y$ and $Z$ that can be used to make reasonable predictions of the nematic-isotropic points for all combinations of $X$, $Y$ and $Z$.

## 1. Introduction

The discovery that thin films of certain nematic liquid crystals scatter light under the influence of an electrical field[2] has stimulated considerable interest in these compounds because of their potential value in display technology. The classes of nematic compounds which are currently favored are $p,p'$-disubstituted diphenyl compounds (I) where $Y$ is usually



(I)

azomethine, azoxy or ester linkage.

In addition to other device-related properties, the mesomorphic temperature range is an important parameter and considerable effort is being employed to expand this temperature range to cover anticipated operating requirements. Since the crystal-nematic transition (CN) for nearly all known nematic compounds is above room temperature, lowering of this transition temperature is generally achieved by means of binary or tenary eutectic mixtures of nematic compounds. The nematic-isotropic (NI) liquid transition of nematic mixtures is approximately a linear function of composition.

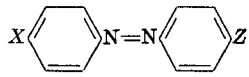
In order to minimize our synthesis requirements we examined reported transition temperatures in a search for structural correlations. We found no useful method for predicting melting points. A literature survey of nematic transition points was more encouraging. Plots of the nematic-isotropic point as a function of substituent chain length give parallel curves for certain analogous nematic compounds. Weygand and Gabler[3] reported this behavior for homologous series of 4,4′-dialkoxyazoxybenzenes, azobenzenes and benzylideneanilines. Similar results were reported for substituted nitrones and anils.[4] These observations suggested the possibility of generating sets of parameters of $X$, $Y$ and $Z$ that could be used for estimating nematic-isotropic points. The incremental effect of certain substituents on the thermal stability of dianils has previously been noted.[5]

We have restricted $X$ and $Z$ to alkyl, alkoxy, acyloxy, alkylcarbonato, cyano and acyl functionalities of no greater than six carbon atoms in the terminus. The central linkage, $Y$, was confined to azo, azoxy, azomethine, nitrone and ester linkages. A total of 137 compounds were used to assign a numerical value to each substituent such that the sum of appropriate substituent values for each compound equaled or approximated the nematic-isotropic point temperature.

## 2. Procedure

Due to the symmetry of the azo linkage, those nematic compounds containing this linkage were used as a point of departure for the determination of parameters for all the $X$, $Y$ and $Z$'s. The azo linkage was arbitrarily assigned a value of zero. From the

TABLE 1 Derivation of Substituent Parameters Based on Nematic-Isotropic Points of Azo Compounds



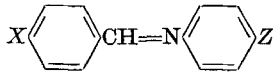
| Ref | X | Z | CN | CI | NI | NI–55 | NI–75 | NI÷2 |
|---|---|---|---|---|---|---|---|---|
| *a* | $CH_3O$ | $CH_3$ | | 110 | 38 | –17 | | |
| *a* | $CH_3O$ | $C_2H_5$ | | 80 | 28 | –27 | | |
| *a* | $CH_3O$ | $C_3H_7$ | 59 | | 69 | 14 | | |
| *b* | $CH_3O$ | $C_4H_9$ | 32 | | 48 | –7 | | |
| *a* | $CH_3O$ | $C_5H_{11}$ | 38 | | 66 | 11 | | |
| *a* | $CH_3O$ | $C_6H_{13}$ | 39 | | 53 | –2 | | |
| *c* | $CH_3O$ | $OC_2H_5$ | | 134 | 131 | 76 | | |
| *c* | $CH_3O$ | $OC_3H_7$ | | 113 | 110 | 55 | | |
| *c* | $CH_3O$ | $OCOCH_3$ | 119 | | 122 | 67 | | |
| *c* | $CH_3O$ | $OCOC_2H_5$ | 91 | | 117 | 62 | | |
| *c* | $CH_3O$ | $OCOC_3H_7$ | 75 | | 117 | 62 | | |
| *c* | $CH_3O$ | $OCOC_4H_9$ | 80 | | 102 | 57 | | |
| *c* | $CH_3O$ | $OCOC_5H_{11}$ | 66 | | 106 | 51 | | |
| *c* | $CH_3O$ | $OCOC_6H_{13}$ | 71 | | 98 | 43 | | |
| *c* | $CH_3O$ | $OCOC_6H_5$ | 162 | | 184 | 129 | | |
| *c* | $CH_3O$ | $OCO_2C_2H_5$ | 90 | | 114 | 59 | | |
| *a* | $CH_3O$ | $OCO_2C_6H_{13}$ | 69 | | 84 | 29 | | |
| *c* | $CH_3O$ | $CO_2C_6H_5$ | 149 | | 177 | 122 | | |
| *a* | $C_2H_5O$ | $C_3H_7$ | 88 | | 100 | | 25 | |
| *b* | $C_2H_5O$ | $C_4H_9$ | 48 | | 81 | | 6 | |
| *c* | $C_2H_5O$ | $OC_3H_7$ | | 144 | 140 | | 65 | |
| *c* | $C_2H_5O$ | $OCOCH_3$ | 120 | | 136 | | 61 | |
| *c* | $C_2H_5O$ | $OCOC_2H_5$ | 103 | | 141 | | 66 | |
| *c* | $C_2H_5O$ | $OCOC_3H_7$ | 90 | | 141 | | 66 | |
| *c* | $C_2H_5O$ | $OCOC_4H_9$ | 79 | | 125 | | 50 | |
| *c* | $C_2H_5O$ | $OCOC_5H_{11}$ | 70 | | 126 | | 51 | |
| *c* | $C_2H_5O$ | $OCOC_6H_{13}$ | 68 | | 118 | | 43 | |
| *a* | $C_2H_5O$ | $OCO_2CH_3$ | 103 | | 145 | | 70 | |
| *c* | $C_2H_5O$ | $OCO_2C_2H_5$ | 96 | | 140 | | 65 | |
| *c* | $C_2H_5O$ | $COCH_3$ | 127 | | 129 | | 54 | |
| *c* | $C_2H_5O$ | $OC_2H_5$ | | 162 | 155 | | | 78 |
| *c* | $C_3H_7O$ | $OC_3H_7$ | | 146 | 112 | | | 56 |
| *c* | $C_4H_9O$ | $OC_4H_9$ | | 135 | 124 | | | 62 |
| *c* | $C_5H_{11}O$ | $OC_5H_{11}$ | | 113 | 108 | | | 54 |
| *c* | $C_6H_{13}O$ | $OC_6H_{13}$ | 102 | | 114 | | | 57 |
| *a* | $C_3H_7$ | $C_3H_7$ | | 82 | 32 | | | 16 |
| *c* | $C_6H_5$ | $C_6H_5$ | | 256 | 255 | | | 128 |
| *a* | $C_2H_5CO_2$ | $OCOC_2H_5$ | | 174 | 140 | | | 70 |
| *c* | $C_6H_5CO_2$ | $OCOC_6H_5$ | 216 | | 268 | | | 134 |
| *a* | $CH_3OCO_2$ | $OCO_2CH_3$ | | 166 | 144 | | | 72 |
| *c* | $C_2H_5OCO_2$ | $OCO_2C_2H_5$ | 98 | | 123 | | | 62 |
| *c* | $C_6H_5OCO$ | $CO_2C_6H_5$ | 219 | | 263 | | | 132 |

*a*. Unpublished results.

*b*. Kelker, H., Scheurle, B., Hatz, R and Bartsch, W., *Angew. Chem. Int. Edn.* 9, 962 (1970).

*c*. Kast, W. in "Landolt-Bornstein," 6th Ed., Vol II, Part 2a, Springer Verlag, Berlin 1960, pp. 266–335.

TABLE 2 Derivation of Substituent Parameters Based on Nematic-Isotropic Points of Benzylideneaniline Compounds




| Ref | X | Z | CN | CI | NI | NI − 55 + 9 |
|---|---|---|---|---|---|---|
| *a* | $CH_3O$ | $C_3H_7$ | 42 | | 57 | 11 |
| *a* | $CH_3O$ | $C_4H_9$ | 20 | | 47 | 1 |
| *a* | $CH_3O$ | $C_5H_{11}$ | 38 | | 58 | 12 |
| *b* | $CH_3O$ | $C_6H_{13}$ | 35 | | 54 | 8 |
| *c* | $CH_3O$ | $C_6H_5$ | 162 | | 177 | 131 |
| *c* | $CH_3O$ | CN | 103 | | 114 | 68 |
| *c* | $CH_3O$ | $OCH_3$ | 146 | 146 | 99 | 53 |
| *c* | $CH_3O$ | $OC_2H_5$ | 128 | 128 | 122 | 76 |
| *d* | $CH_3O$ | $OCOCH_3$ | 83 | | 110 | 66 |
| *d* | $CH_3O$ | $OCOC_2H_5$ | 70 | | 109 | 63 |
| *d* | $CH_3O$ | $OCOC_3H_7$ | 53 | | 112 | 66 |
| *d* | $CH_3O$ | $OCOC_4H_9$ | 55 | | 100 | 54 |
| *d* | $CH_3O$ | $OCOC_5H_{11}$ | 82 | | 100 | 54 |
| *d* | $CH_3O$ | $OCOC_6H_{13}$ | 64 | | 96 | 50 |
| *c* | $CH_3O$ | $OCOC_6H_5$ | 119 | | 178 | 132 |
| *e* | $CH_3O$ | $OCO_2CH_3$ | 85 | | 109 | 63 |
| *e* | $CH_3O$ | $OCO_2C_2H_5$ | 81 | | 104 | 58 |
| *e* | $CH_3O$ | $OCO_2C_3H_7$ | 78 | | 87 | 41 |
| *e* | $CH_3O$ | $OCO_2C_4H_9$ | 66 | | 84 | 38 |
| *e* | $CH_3O$ | $OCO_2C_5H_{11}$ | 45 | | 82 | 36 |
| *e* | $CH_3O$ | $OCO_2C_6H_{13}$ | 66 | | 79 | 33 |
| *b* | $CH_3O$ | $COC_2H_5$ | 115 | | 132 | 86 |
| *b* | $CH_3O$ | $COC_3H_7$ | | 101 | 96 | 50 |
| *b* | $CH_3O$ | $COC_4H_9$ | 87 | | 105 | 59 |
| *a* | $C_3H_7$ | $OCH_3$ | | 59 | 58 | 12 |
| *a* | $C_4H_9$ | $OCH_3$ | 46 | | 49 | 3 |
| *a* | $C_5H_{11}$ | $OCH_3$ | 48 | | 64 | 18 |
| *c* | $C_6H_5$ | $OCH_3$ | | 186 | 176 | 130 |
| *c* | CN | $OCH_3$ | 115 | | 125 | 79 |
| *c* | $C_2H_5O$ | $OCH_3$ | | 123 | 121 | 75 |
| *f* | $C_4H_9O$ | $OCH_3$ | | 111 | 106 | 60 |
| *c* | $CH_3CO_2$ | $OCH_3$ | 112 | | 123 | 77 |
| *g* | $C_2H_5CO_2$ | $OCH_3$ | 86 | | 118 | 72 |
| *c* | $C_6H_5CO_2$ | $OCH_3$ | 119 | | 176 | 130 |

| Ref | $X$ | $Z$ | CN | CI | NI | NI − 55 + 9 |
|---|---|---|---|---|---|---|
| *h* | $C_2H_5O$ | $C_4H_9$ | 36 | | 79 | 13 |
| *c* | $C_2H_5O$ | $C_6H_5$ | 146 | | 192 | 126 |
| *c* | $C_2H_5O$ | CN | 105 | | 124 | 58 |
| *c* | $C_2H_5O$ | $OCH_3$ | | 123 | 121 | 55 |
| *c* | $C_2H_5O$ | $OC_2H_5$ | | 148 | 143 | 77 |
| *d* | $C_2H_5O$ | $OCOCH_3$ | 110 | | 132 | 66 |
| *i* | $C_2H_5O$ | $OCOC_2H_5$ | 111 | | 134 | 68 |
| *j* | $C_2H_5O$ | $OCOC_3H_7$ | 99 | | 137 | 71 |
| *j* | $C_2H_5O$ | $OCOC_5H_{11}$ | 79 | | 110 | 44 |
| *c* | $C_2H_5O$ | $OCOC_6H_5$ | 144 | | 188 | 122 |
| *e* | $C_2H_5O$ | $OCO_2CH_3$ | 86 | | 133 | 67 |
| *e* | $C_2H_5O$ | $OCO_2C_2H_5$ | 94 | | 129 | 63 |
| *e* | $C_2H_5O$ | $OCO_2C_3H_7$ | 86 | | 116 | 50 |
| *e* | $C_2H_5O$ | $OCO_2C_4H_9$ | 82 | | 112 | 46 |
| *e* | $C_2H_5O$ | $OCO_2C_5H_{11}$ | 75 | | 105 | 39 |
| *e* | $C_2H_5O$ | $OCO_2C_6H_{13}$ | 71 | | 103 | 37 |
| *f* | $C_2H_5O$ | $COCH_3$ | | 119 | 115 | 49 |
| *c* | $C_6H_5$ | $OC_2H_5$ | 164 | | 191 | 125 |
| *c* | CN | $OC_2H_5$ | 115 | | 132 | 66 |
| *c* | $CH_3O$ | $OC_2H_5$ | | 128 | 122 | 56 |
| *c* | $C_3H_7O$ | $OC_2H_5$ | | 125 | 124 | 58 |
| *c* | $C_4H_9O$ | $OC_2H_5$ | 106 | | 130 | 64 |
| *c* | $C_5H_{11}O$ | $OC_2H_5$ | 102 | | 119 | 53 |
| *c* | $C_6H_{13}O$ | $OC_2H_5$ | 98 | | 122 | 56 |
| *c* | $C_6H_5CO_2$ | $OC_2H_5$ | 143 | | 187 | 121 |

*a*. Rosenberg, H. and Champa, R. A., *Mol. Cryst. and Liq. Cryst.* **11**, 191 (1970).

*b*. Unpublished results.

*c*. Kast, W. in "Landolt-Bornstein," 6th Ed., Vol. II, Part 2a, Springer Verlag, Berlin 1960, pp. 266–335.

*d*. Castellano, J. A. *et. al.*, private communication.

*e*. Castellano, J. A., Oh, C. S. and McCaffry, M. T., private communication.

*f*. Castellano, J. A., Goldmacher, J. R., Barton, L. A. and Kane, J. S., *J. Org. Chem.* **33**, 350 (1968).

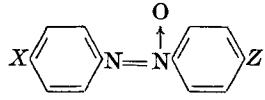
*g*. Goldmacher, J. and Barton, L. A., *J. Org. Chem.* **32**, 476 (1967).

*h*. Fishel, D. L., private communication.

*i*. Steinsträsser, R. and Pohl, L., *Z. Naturforsch.* **26b**, 87 (1971).

*j*. van der Veen, J. and Grobben, A. H., paper presented at III International Liquid Conference, Berlin, Aug. 1970.

TABLE 3 Derivation of Substituent Parameters Based on Nematic-Isotropic Points of Azoxy Compounds




| Ref | X | Z | CN | CI | NI | NI–55 | NI–75 | –21 |
|---|---|---|---|---|---|---|---|---|
| *a* | $CH_3O$ | $CH_3$ | † | | 88 | 33 | | 12 |
| *a* | $CH_3O$ | $C_2H_5$ | † | | 70 | 15 | | –6 |
| *a* | $CH_3O$ | $C_3H_7$ | † | | 94 | 39 | | 18 |
| *b* | $CH_3O$ | $C_4H_9$ | 41 | | 74 | 19 | | –2 |
| *a* | $CH_3O$ | $C_5H_{11}$ | † | | 90 | 35 | | 14 |
| *a* | $CH_3O$ | $C_6H_{13}$ | † | | 78 | 23 | | 2 |
| *c* | $CH_3O$ | $OC_2H_5$ | 96 | | 154 | 99 | | 78 |
| *a* | $CH_3O$ | $OCOC_3H_7$ | † | | 136 | 81 | | 60 |
| *a* | $CH_3O$ | $OCO_2C_5H_{11}$ | † | | 101 | 46 | | 25 |
| *c* | $CH_3O$ | $CO_2CH_3$ | 123 | | 130 | 75 | | 54 |
| *c* | $CH_3O$ | $CO_2C_2H_5$ | 90 | | 92 | 37 | | 16 |
| *c* | $CH_3O$ | $CO_2C_6H_5$ | 123 | | 208 | 153 | | 132 |
| *b* | $C_4H_9$ | $OCH_3$ | 42 | | 77 | 22 | | 1 |
| *c* | $CH_3CO_2$ | $OCH_3$ | 116 | | 132 | 77 | | 56 |
| *c* | $C_6H_5CO_2$ | $OCH_3$ | 148 | | 196 | 141 | | 120 |
| *c* | $C_2H_5O$ | $CO_2CH_3$ | 135 | | 156 | | 81 | 60 |
| *c* | $C_2H_5O$ | $CO_2C_2H_5$ | 102 | | 115 | | 40 | 19 |
| *c* | $C_2H_5O$ | $CO_2C_4H_9$ | 79 | | 88 | | 13 | –8 |
| *c* | $C_2H_5O$ | $CO_2C_6H_5$ | 168 | | 211 | | 136 | 115 |
| *c* | $CH_3OCO$ | $OC_2H_5$ | 111 | | 148 | | 73 | 52 |
| *c* | $C_2H_5OCO$ | $OC_2H_5$ | 76 | | 112 | | 37 | 16 |
| *c* | $C_3H_7CO_2$ | $OC_2H_5$ | 81 | | 151 | | 76 | 55 |
| *c* | $C_6H_5CO_2$ | $OC_2H_5$ | 145 | | 206 | | 131 | 110 |
| *c* | $C_4H_9OCO_2$ | $OC_2H_5$ | 80 | | 128 | | 53 | 32 |
| *c* | $CH_3CO_2$ | $OC_2H_5$ | 95 | | 150 | | 75 | 54 |
| *c* | $C_6H_5OCO$ | $OC_2H_5$ | 146 | | 209 | | 134 | 113 |

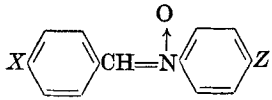
† mixture of isomers

*a*. Unpublished results.

*b*. Berwick, M. A., private communication.

*c*. Kast, W. in "Landolt-Bornstein," 6th Ed., Vol. II, Part 2a, Springer Verlag, Berlin 1960, pp. 266–335.

TABLE 4 Derivation of Substituent Parameters Based on Nematic-Isotropic Points of Nitrones



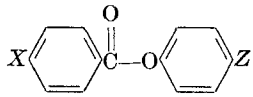

| Ref | X | Z | CN | CI | NI | NI–55 | NI–75 | –8 |
|---|---|---|---|---|---|---|---|---|
| *a* | $CH_3O$ | $C_4H_9$ | | 113 | 53 | –2 | | –10 |
| *b* | $CH_3O$ | $OCH_3$ | | 149 | 120 | 65 | | 57 |
| *b* | $CH_3O$ | $OC_2H_5$ | | 146 | 138 | 83 | 63 | 75 55 |
| *b* | $CH_3O$ | $OC_3H_7$ | | 155 | 109 | 54 | | 46 |
| *b* | $CH_3O$ | $OC_4H_9$ | 123 | | 123 | 68 | | 60 |
| *b* | $CH_3O$ | $OC_5H_{11}$ | 112 | | 120 | 65 | | 57 |
| *b* | $CH_3O$ | $OC_6H_{13}$ | 107 | | 125 | 70 | | 62 |
| *a* | $C_4H_9$ | $OCH_3$ | | 108 | 70 | 15 | | 7 |
| *c* | $CH_3CO_2$ | $OCH_3$ | | 154 | 134 | 79 | | 71 |
| *b* | $C_2H_5O$ | $OCH_3$ | | 129 | 128 | 73 | 53 | 65 45 |
| *b* | $C_2H_5O$ | $OC_2H_5$ | | 178 | 158 | | 83 | 75 |

*a*. Unpublished results.

*b*. Young, W. R., Haller, I. and Aviram, A., *IBMJ. Res.* and *Dev.* **15**, 41 (1971).

*c*. Young, W. R., *Mol. Cryst. and Liq. Cryst.* **10**, 237 (1970).

TABLE 5 Derivation of Substituent Parameters Based on Nematic-Isotropic Points of Ester Compounds

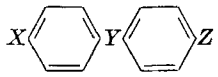



| Ref | X | Z | CN | CI | NI | NI–55 | NI–75 | +35 |
|---|---|---|---|---|---|---|---|---|
| *a* | $CH_3O$ | $OC_2H_5$ | | 96 | 94 | 39 | | 74 |
| *a* | $CH_3O$ | $CO_2C_6H_{13}$ | | 129 | –8 | –63 | | –28 |
| *a* | $CH_3O$ | $CO_2C_6H_5$ | 152 | | 156 | 101 | | 136 |
| *b* | $C_2H_5OCO_2$ | $OCH_3$ | | 110 | 82 | 27 | | 62 |
| *b* | $C_3H_7OCO_2$ | $OCH_3$ | | 78 | 60 | 5 | | 40 |
| *b* | $C_4H_9OCO_2$ | $OCH_3$ | | 70 | 57 | 2 | | 37 |
| *b* | $C_5H_{11}OCO_2$ | $OCH_3$ | | 54 | 53 | –2 | | 33 |
| *b* | $C_6H_{13}OCO_2$ | $OCH_3$ | | 57 | 56 | 1 | | 36 |
| *b* | $CH_3OCO_2$ | $OC_2H_5$ | 86 | | 110 | | 35 | 70 |
| *b* | $C_2H_5OCO_2$ | $OC_2H_5$ | | 104 | 96 | | 21 | 56 |
| *b* | $C_3H_7OCO_2$ | $OC_2H_5$ | | 82 | 79 | | 4 | 39 |
| *b* | $C_4H_7OCO_2$ | $OC_2H_5$ | 49 | | 90 | | 15 | 50 |
| *b* | $C_5H_{11}OCO_2$ | $OC_2H_5$ | 59 | | 74 | | –1 | 34 |
| *b* | $C_6H_{13}OCO_2$ | $OC_2H_5$ | 64 | | 79 | | 4 | 39 |

*a*. Kast, W. in "Landolt-Bornstein," 6th Ed., Vol. II, Part 2a, Springer Verlag, Berlin 1960, pp. 266–335.

*b*. Castellano, J. A., McCaffrey, T. and Goldmacher, J. E., *Mol. Cryst. and Liq. Cryst.* **12**, 345 (1971).

TABLE 6 Substituent Parameters

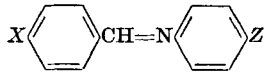



| X,Z | carbon atoms | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |  | CN |
| R | −2 | 5 | 12 | 15 | 14 | 2 | 128 | 68 |
| RO | 55 | 75 | 56 | 61 | 55 | 58 | | |
| RCO | 65 | 67 | 63 | 54 | 50 | 45 | 125 | |
| ROCO | 68 | 61 | 42 | 41 | 43 | 35 | | |
| RC | 52 | 86 | 50 | 59 | † | † | | |
| ROC | 55 | 17 | † | −8 | † | † | 125 | |

† Values not determined

| Y | Parameter |
|---|---|
| N=N | 0 |
| CH=N | −9 |
| N=N→O | 21 |
| CH=N→O | 8 |
| CO | −35 |

TABLE 7 Estimated Nematic-Isotropic Points for *p,p*-Disubstituted Benzylideneanilines




| Ref | *X* | *Z* | CN | CI | NI (exptl) | NI (calcd) | Δ |
|---|---|---|---|---|---|---|---|
| *a* | $CH_3$ | $OCOC_6H_5$ | | 136 | 118 | 114 | −4 |
| *a* | $C_6H_5$ | $CO_2C_2H_5$ | 93 | | 94 | 136 | 42 |
| *b* | $C_3H_7O$ | $C_4H_9$ | 39 | | 56 | 62 | 6 |
| *a* | $C_3H_7O$ | $C_6H_5$ | 154 | | 170 | 175 | 5 |
| *c* | $C_3H_7O$ | $OCOCH_3$ | 94 | | 104 | 112 | 8 |
| *d* | $C_3H_7O$ | $OCOC_2H_5$ | 97 | | 111 | 114 | 3 |
| *d* | $C_3H_7O$ | $OCOC_5H_{11}$ | 85 | | 108 | 97 | −11 |
| *d* | $C_3H_7O$ | $OCOC_6H_{13}$ | 67 | | 116 | 92 | −24 |
| *e* | $C_3H_7O$ | $OCO_2CH_3$ | 98 | | 107 | 115 | 8 |
| *e* | $C_3H_7O$ | $OCO_2C_2H_5$ | 104 | | 106 | 108 | 2 |
| *e* | $C_3H_7O$ | $OCO_2C_3H_7$ | 84 | | 95 | 89 | −6 |
| *e* | $C_3H_7O$ | $OCO_2C_4H_9$ | 69 | | 93 | 88 | −5 |
| *e* | $C_3H_7O$ | $OCO_2C_5H_{11}$ | 58 | | 108 | 90 | −18 |
| *e* | $C_3H_7O$ | $OCO_2C_6H_{13}$ | 53 | | 88 | 82 | −6 |
| *f* | $C_3H_7O$ | $COCH_3$ | 92 | | 102 | 99 | −3 |
| *b* | $C_4H_9O$ | $C_4H_9$ | 36 | | 74 | 67 | −7 |
| *a* | $C_4H_9O$ | $C_6H_5$ | 148 | | 176 | 180 | 4 |
| *a* | $C_4H_9O$ | $OC_4H_9$ | | 125 | 121 | 113 | −8 |
| *g* | $C_4H_9O$ | $OC_6H_{13}$ | 105 | | 119 | 110 | −9 |
| *d* | $C_4H_9O$ | $OCOCH_3$ | 82 | | 113 | 117 | 4 |
| *d* | $C_4H_9O$ | $OCOC_2H_5$ | 85 | | 119 | 119 | 0 |
| *d* | $C_4H_9O$ | $OCOC_3H_7$ | 87 | | 120 | 115 | −5 |
| *d* | $C_4H_9O$ | $OCOC_4H_9$ | 75 | | 112 | 106 | −6 |
| *d* | $C_4H_9O$ | $OCOC_5H_{11}$ | 80 | | 114 | 102 | −12 |
| *d* | $C_4H_9O$ | $OCOC_6H_{13}$ | 71 | | 98 | 97 | −1 |
| *e* | $C_4H_9O$ | $OCO_2CH_3$ | 67 | | 116 | 120 | 4 |
| *e* | $C_4H_9O$ | $OCO_2C_2H_5$ | 90 | | 114 | 113 | −1 |
| *e* | $C_4H_9O$ | $OCO_2C_3H_7$ | 78 | | 106 | 94 | −12 |
| *e* | $C_4H_9O$ | $OCO_2C_4H_9$ | 68 | | 103 | 93 | −10 |
| *e* | $C_4H_9O$ | $OCO_2C_5H_{11}$ | 65 | | 99 | 95 | −4 |
| *e* | $C_4H_9O$ | $OCO_2C_6H_{13}$ | 56 | | 97 | 87 | −10 |
| *h* | $C_4H_9O$ | $COCH_3$ | 85 | | 109 | 104 | −5 |
| *i* | $C_4H_9O$ | $COC_2H_5$ | 86 | | 144 | 138 | −6 |
| *b* | $C_5H_{11}O$ | $C_4H_9$ | 24 | | 68 | 61 | −7 |
| *a* | $C_5H_{11}O$ | $C_6H_5$ | 137 | | 167 | 174 | 7 |
| *a* | $C_5H_{11}O$ | $OC_5H_{11}$ | | 113 | 103 | 101 | −2 |
| *d* | $C_5H_{11}O$ | $OCOCH_3$ | 88 | | 105 | 111 | 6 |
| *d* | $C_5H_{11}O$ | $OCOC_2H_5$ | 82 | | 109 | 113 | 4 |
| *d* | $C_5H_{11}O$ | $OCOC_4H_9$ | 83 | | 105 | 100 | −5 |
| *d* | $C_5H_{11}O$ | $OCOC_5H_{11}$ | 82 | | 111 | 96 | −15 |
| *d* | $C_5H_{11}O$ | $OCOC_6H_{13}$ | 89 | | 104 | 101 | −3 |
| *e* | $C_5H_{11}O$ | $OCO_2CH_3$ | 91 | | 106 | 114 | 8 |
| *e* | $C_5H_{11}O$ | $OCO_2C_2H_5$ | 82 | | 104 | 107 | 3 |
| *e* | $C_5H_{11}O$ | $OCO_2C_3H_7$ | 66 | | 96 | 88 | −8 |

| Ref | $X$ | $Z$ | CN | CI | NI (exptl) | NI (calcd) | Δ |
|---|---|---|---|---|---|---|---|
| *e* | $C_5H_{11}O$ | $OCO_2C_4H_9$ | 71 | | 95 | 87 | −8 |
| *e* | $C_5H_{11}O$ | $OCO_2C_5H_{11}$ | 66 | | 93 | 89 | −4 |
| *e* | $C_5H_{11}O$ | $OCO_2C_6H_{13}$ | 60 | | 91 | 81 | −10 |
| *f* | $C_5H_{11}O$ | $COCH_3$ | 80 | | 106 | 98 | −8 |
| *j* | $C_5H_{11}O$ | $COC_2H_5$ | 83 | | 146 | 132 | −14 |
| *b* | $C_6H_{13}O$ | $C_4H_9$ | 34 | | 78 | 64 | −14 |
| *a* | $C_6H_{13}O$ | $C_6H_5$ | 132 | | 168 | 177 | 9 |
| *e* | $C_6H_{13}O$ | $OCO_2CH_3$ | 62 | | 109 | 117 | 8 |
| *e* | $C_6H_{13}O$ | $OCO_2C_2H_5$ | 64 | | 108 | 110 | 2 |
| *e* | $C_6H_{13}O$ | $OCO_2C_3H_7$ | 64 | | 100 | 91 | −9 |
| *e* | $C_6H_{13}O$ | $OCO_2C_4H_9$ | 69 | | 99 | 90 | −9 |
| *e* | $C_6H_{13}O$ | $OCO_2C_5H_{11}$ | 63 | | 96 | 92 | −4 |
| *e* | $C_6H_{13}O$ | $OCO_2C_6H_{13}$ | 58 | | 96 | 84 | −12 |
| *i* | $C_6H_{13}O$ | $COCH_3$ | 74 | | 111 | 101 | −10 |
| *c* | $C_6H_{13}O$ | $OCOCH_3$ | 88 | | 109 | 114 | 5 |
| *k* | $C_2H_5CO_2$ | $CH_3$ | | 102 | 66 | 56 | −10 |
| *b* | $C_2H_5CO_2$ | $C_2H_5$ | | 80 | 58 | 63 | 5 |
| *b* | $C_3H_7CO_2$ | $C_2H_5$ | | 78 | 64 | 59 | −5 |
| *b* | $C_4H_9CO_2$ | $C_2H_5$ | | 74 | 56 | 50 | −6 |
| *b* | $C_5H_{11}CO_2$ | $C_2H_5$ | | 68 | 66 | 46 | −20 |
| *b* | $C_6H_{13}CO_2$ | $C_2H_5$ | | 76 | 64 | 41 | −25 |
| *b* | $CH_3CO_2$ | $C_4H_9$ | | 60 | 56 | 71 | 15 |
| *b* | $C_2H_5CO_2$ | $C_4H_9$ | 64 | | 70 | 73 | 3 |
| *b* | $C_3H_7CO_2$ | $C_4H_9$ | 68 | | 74 | 69 | −5 |
| *b* | $C_4H_9CO_2$ | $C_4H_9$ | | 86 | 68 | 60 | −8 |
| *b* | $C_5H_{11}CO_2$ | $C_4H_9$ | | 96 | 76 | 56 | −20 |
| *b* | $C_6H_{13}CO_2$ | $C_4H_9$ | | 76 | 74 | 51 | −23 |
| *b* | $CH_3CO_2$ | $COCH_3$ | | 114 | 105 | 108 | 3 |
| *b* | $C_2H_5CO_2$ | $COCH_3$ | 106 | | 113 | 110 | −3 |
| *b* | $C_3H_7CO_2$ | $COCH_3$ | 88 | | 116 | 106 | −10 |
| *b* | $C_4H_9CO_2$ | $COCH_3$ | 101 | | 105 | 97 | −8 |
| *b* | $C_5H_{11}CO_2$ | $COCH_3$ | 92 | | 110 | 93 | −7 |
| *b* | $C_6H_{13}CO_2$ | $COCH_3$ | 100 | | 106 | 88 | −18 |
| *a* | $C_6H_5CO_2$ | $CH_3$ | | 136 | 124 | 114 | −10 |

*a*. Kast, W. in "Landolt-Bornstein," 6th Ed., Vol. II, Part 2a, Springer Verlag, Berlin 1960, pp. 266–335.

*b*. Fishel, D. L., private communication.

*c*. Castellano, J. A. *et. al.*, private communication.

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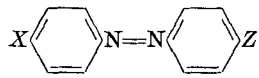
TABLE 8 Estimated Nematic-Isotropic Points for $p,p'$-Disubstituted Azo Benzenes



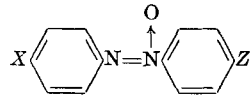
| Ref | $X$ | $Z$ | CN | CI | NI (exptl) | NI (calcd) | $\Delta$ |
|---|---|---|---|---|---|---|---|
| *a* | $C_3H_7$ | $OCO_2CH_3$ | 69 | | 77 | 80 | 3 |
| *a* | $C_3H_7$ | $OCO_2C_2H_5$ | | 82 | 78 | 73 | −5 |
| *b* | $C_4H_9$ | $OC_4H_9$ | 65 | | 75 | 76 | 1 |
| *b* | $C_4H_9$ | $OC_5H_{11}$ | 42 | | 66 | 70 | 4 |
| *a* | $C_6H_{13}$ | $OCO_2C_4H_9$ | 42 | | 52 | 43 | −9 |
| *c* | $CH_3CO_2$ | $OCO_2C_2H_5$ | 119 | | 126 | 126 | 0 |
| *c* | $CH_3CO_2$ | $CO_2C_2H_5$ | 99 | | 102 | 82 | −20 |
| *a* | $C_2H_5CO_2$ | $OCO_2CH_3$ | | 154 | 137 | 135 | −2 |

*a*. Unpublished results.

*b*. Fishel, D. L., private communication.

*c*. Kast, W. in "Landolt-Bornstein," 6th Ed., Vol. II, Part 2a, Springer Verlag, Berlin 1960, pp. 266–335.

TABLE 9 Estimated Nematic-Isotropic Points for *p,p'*-Disubstituted Azoxy Benzenes



| Ref | *X* | *Z* | CN | CI | NI (Exptl) | NI (calcd) | Δ |
|---|---|---|---|---|---|---|---|
| *a* | $C_3H_7$ | $OCO_2C_5H_{11}$ | † | | 79 | 76 | −3 |
| *a* | $C_4H_9$ | $OCO_2C_4H_9$ | † | | 70 | 77 | 7 |
| *a* | $C_4H_9$ | $OCO_2C_5H_{11}$ | † | | 68 | 79 | 11 |
| *a* | $C_5H_{11}$ | $OCO_2CH_3$ | † | | 100 | 103 | 3 |
| *a* | $C_5H_{11}$ | $OCO_2C_2H_5$ | † | | 92 | 96 | 4 |
| *a* | $C_5H_{11}$ | $OCO_2C_3H_7$ | † | | 81 | 77 | −4 |
| *a* | $C_5H_{11}$ | $OCO_2C_4H_9$ | † | | 80 | 76 | −4 |
| *a* | $C_5H_{11}$ | $OCO_2C_5H_{11}$ | † | | 82 | 78 | −4 |
| *a* | $C_5H_{11}$ | $OCO_2C_6H_{13}$ | † | | 81 | 70 | −11 |
| *a* | $C_6H_{13}$ | $OCO_2CH_3$ | † | | 89 | 91 | 2 |
| *a* | $C_6H_{13}$ | $OCO_2C_2H_5$ | † | | 82 | 84 | 2 |
| *a* | $C_6H_{13}$ | $OCO_2C_3H_7$ | † | | 70 | 65 | −5 |
| *a* | $C_6H_{13}$ | $OCO_2C_4H_9$ | † | | 72 | 64 | −8 |
| *a* | $C_6H_{13}$ | $OCO_2C_5H_{11}$ | † | | 72 | 66 | −6 |
| *a* | $C_6H_{13}$ | $OCO_2C_6H_{13}$ | † | | 73 | 58 | −15 |
| *b* | $C_6H_5$ | $C_6H_5$ | 211 | | 206 | 277 | 71 |
| *b* | CN | CN | 215 | | 221 | 157 | −64 |
| *b* | $C_3H_7O$ | $OC_3H_7$ | 116 | | 122 | 133 | 11 |
| *b* | $C_4H_9O$ | $OC_4H_9$ | 107 | | 134 | 143 | 9 |
| *b* | $C_5H_{11}O$ | $OC_5H_{11}$ | 82 | | 119 | 131 | 12 |
| *b* | $C_6H_{13}O$ | $OC_6H_{13}$ | 81 | | 127 | 137 | 10 |
| *b* | $CH_3CO_2$ | $OCOCH_3$ | 163 | | 166 | 151 | −15 |
| *b* | $C_6H_5CO_2$ | $OCOC_6H_5$ | 192 | | >280 | 271 | −9 |
| *b* | $C_2H_5OCO_2$ | $OCO_2C_2H_5$ | 101 | | 138 | 143 | 5 |
| *b* | $C_6H_5OCO$ | $CO_2C_6H_5$ | 202 | | 280 | 271 | −9 |

† mixture of isomers

*a*. Unpublished results.

*b*. Kast, W. in "Landolt-Bornstein," 6th Ed., Vol. II, Part 2a, Springer Verlag, Berlin 1960, pp. 266–335.

TABLE 10 Difference Between Experimental and Estimated Nematic-Isotropic Points

| | ⩽5° | ⩽10° | ⩽15° | >15° | Total |
|---|---|---|---|---|---|
| N=N | 6 (75%) | 7 (87.5%) | 7 (87.5%) | 1 | 8 |
| CH=N | 30 (38%) | 62 (79%) | 70 (90%) | 8 | 78 |
| O ↑ N=N | 10 (40%) | 17 (68%) | 23 (92%) | 2 | 25 |
| Total | 46 (41%) | 86 (77.5%) | 10 (90%) | 11 | 111 |

extrapolated nematic-isotropic point of 110° for 4,4′methoxyazabenzene,[6] the methoxy functionality was assigned a value of 55°. The ethoxy substituent was arbitrarily taken as 75°, a value close to that obtained from the reported nematic-isotropic point of 4,4′-diethoxyazobenzene. By subtracting these values from the reported nematic-isotropic points of unsymmetrically substituted *p,p*-disubstituted azobenzenes containing a methoxy or ethoxy substituent, 30 values were determined for 20 substituents. Additional substituent values were obtained from symmetrically substituted *p,p*-disubstituted azobenzenes. All of these values are shown in Table 1. Crystal-isotropic points (CI) are given for monotropic compounds.

We disregarded the orientation of the central linkage in a series of unsymmetrically substituted *p,p′*disubstituted Schiff's Bases containing methoxy and ethoxy substituents. The values obtained by subtracting 55° or 75° from the nematic-isotropic points of methoxy or ethoxy substituted compounds respectively were, on the average, nine degrees lower than the corresponding values obtained for the azo compounds. A parameter value of $-9°$ was thus assigned to the azomethine linkage (Table 2). In like manner, values of $+21°$, $-8°$ and $-35°$ were assigned to the azoxy, nitrone and ester linkages (Tables 3, 4 and 5).

A total of 137 values were determined for thirty-four substituents. The values were then averaged for each substituent, some substituents having only one value and three substituents as many as eight values. The averaged values are given in Table 6, except that values for three substituents, namely C–2, C–4 alkyl and C–5 carbonate were redetermined to provide better agreement with compounds described under Results.

## 3. Results

The predictive value of the substituent constants (Table 6) was tested for a series of 78 mesomorphic anils, 8 azo compounds and 25 azoxy compounds. These compounds contained neither methoxy nor ethoxy substituents. A comparison of reported and estimated nematic-isotropic points as well as deviations from the reported values are shown in Tables 7, 8 and 9. The average of the absolute deviation values for 111 compounds is 9°. Some statistical data for

these deviations are summarized in Table 10, which shows that 90% of the values were predicted within 15° and 77% within 10° of reported values.

Inspection of compounds whose estimated nematic-isotropic points exhibit deviations of more than 10° from the experimental values reveals that about one-third of these compounds contain an alkyl substituent. Diphenyl and dicyano azoxybenzene show the largest deviations.

## 4. Conclusion

A simple method has been described for estimating the nematic to isotropic transition temperatures for *p,p'*-disubstituted diphenyl compounds containing any combination of 35 substituents and 5 central linkages. With additional experimental data this method can be expanded to cover additional substituents and central linkages.

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