(10% excess) in dry pyridine and isolated by pouring the solution into ice water.

The fumaric diester (**12a**) was prepared by simultaneous dropwise addition of fumaryl chloride and triethylamine to a solution of *p*-methoxyphenol in dry ether.

The *trans*-β-dihydromuconate diester (**13a**) was prepared by adding the diacid chloride to a solution of *p*-methoxyphenol and pyridine (10% excess of each) in dry ether. This procedure was also used for the furan and thiophene derivatives **16a–19a.**

The thio esters **5b–19b** were prepared in the same way as the corresponding esters, substituting *p*-methoxythiophenol for *p*-methoxyphenol.

Full details of the experimental procedures and references to the literature will be found in a thesis by one of us.[16,17]

References and Notes

[1] This work was supported by the Air Force Office of Scientific Research (Contract No. F44620-71-C-0119) and the Robert A. Welch Foundation (Grant No. F-126).

[2] Robert A. Welch Predoctoral Fellow.

[3] See G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals", Academic Press, New York, N.Y., 1962.

[4] Gray et al. have studied the effects of lateral substituents, and of changes in the terminal groups, on the stability of mesophases: see G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **1**, 333 (1966); **7**, 127 (1969); G. W. Gray and K. J. Harrison, *ibid.*, **13**, 37 (1971); *Symp. Faraday Soc.*, **5**, 54 (1971).

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[7] (a) M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, **30**, 2296 (1965); (b) M. J. S. Dewar and R. S. Goldberg, *ibid.*, **35**, 2711 (1970).

[8] M. J. S. Dewar and A. C. Griffin, *J. Am. Chem. Soc.*, **97**, following paper (1975).

[9] R. B. Bates, R. H. Carninghan, and C. E. Staples, *J. Am. Chem. Soc.*, **85**, 3030 (1963).

[10] For a detailed discussion of the reasons for the low nematic mesophase stability in **14a** see ref 8.

[11] W. Elser, *Mol. Cryst. Liq. Cryst.*, **8**, 219 (1969).

[12] Thus of the 1400 compounds listed by Kast[13] as forming mesophases, less than 1% contain sulfur.

[13] W. Kast in "Landolt-Bornstein", Vol II, Part 2a, 6th ed, Springer-Verlag, Berlin, 1960, p. 266.

[14] A. Bogojawlensky and N. Winogradow, *Z. Phys. Chem.*, **64**, 229 (1908); R. Walter, *Ber. Dtsch. Chem. Ges.*, **58**, 2803 (1925); J. S. Dave and M. J. S. Dewar, *J. Chem. Soc.*, 4305 (1955).

[15] Personal communication, Dr. N. Bodor.

[16] R. M. Riddle, Ph.D. Dissertation, the University of Texas at Austin, Austin, Texas, 1971.

[17] The transition temperatures in the range >250° reported in this dissertation[16] seems to be uniformly too low, in cases where they were determined by the Thomas-Hoover apparatus. The values listed in the tables were determined by Griffin[8] and checked by DTA. The error was probably due to a defective thermometer in the Thomas-Hoover melting point apparatus; we were unable to check this since the thermometer in question had been accidentally destroyed.

A Thermodynamic Study of the Role of the Central Group on the Stability of Nematic Liquid Crystals[1,2]

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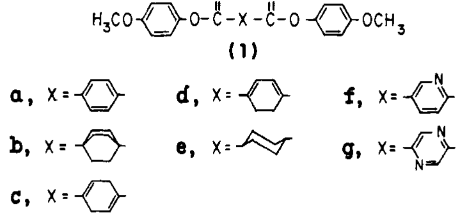
Abstract: Studies of the effect of changes in the central parts of "nematic" molecules indicate that the corresponding changes in nematic → isotropic transition temperatures arise from changes in the entropy of transition, not in the heat of transition as previously supposed. This is true also for the effects of projecting substituents. The results lead to some general conclusions concerning the relationship between structure and mesophase stability.

It has been generally assumed that the stability of nematic liquid crystals depends primarily on the anisotropy of intermolecular forces, the lateral attractions between rod-shaped molecules making them tend to adopt a parallel arrangement. Attempts to correlate structure with mesophase stability have consequently been largely based on considerations of the nature and magnitude of the intermolecular forces favoring such lateral associations. The importance of geometrical factors has of course been recognized but these have been regarded as operating by helping or hindering lateral adhesion of the molecules in question.

Recent work in these laboratories[3] has, however, led to the conclusion that intermolecular forces, due to dipole-dipole attractions, etc., are not the most important factors in determining mesophase stability and that enhanced intermolecular attractions may indeed lead to a decrease in the stability of the nematic phase. The matter is of some practical importance since the strategy followed in searching for new and better liquid crystals must depend on theories concerning the relationship between structure and mesophase stability. The purpose of the work reported here was to study this problem in more detail.

In order to avoid complications from varying end group associations, we decided to study a series of compounds of type **1** where only the central group X is varied. Since our purpose was to determine the relative importance of energetic and other factors in determining mesophase stability, the most promising approach seemed to lie in determining thermodynamic parameters for nematic → liquid phase transitions. We decided to use differential thermal analysis (DTA) since this seems the simplest of the procedures that have been found effective.[4] Few systematic studies had been previously reported on the effect of variations in the central groups of molecules such as **1** on the stability of the corresponding nematic mesophases[3,5-7] and no systematic study of the thermodynamic parameters for their N → I (nematic → isotropic) phase transitions had been reported.



$H_3CO-C_6H_4-O-\overset{O}{\overset{\|}{C}}-X-\overset{O}{\overset{\|}{C}}-O-C_6H_4-OCH_3$

(1)

The first series of compounds studied were those in which X is a 1,4-phenylene group (**1a**) or a group structurally related to this (**1b–g**). The observed melting points, N → I transition temperatures, and thermodynamic parameters

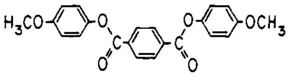
($\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$, $\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$) for the N → I transitions are shown in Table I.

One of these compounds (**1e**) has been studied previously by Andrews and Bacon.[8] It will be seen (Table I) that while their transition temperatures agree with ours, their values for $\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$ and $\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$, determined by adiabatic calorimetry, are much larger. This is because they treated the transition as a specific heat anomaly, integrating the total deviation in ΔH from that calculated on the assumption that the specific heats of both species are constant over a region round the transition. This procedure is incorrect if, as is generally believed, the N → I transition is a first-order phase transition. It is not unusual for specific heats to vary in the neighborhood of a phase transition; Andrews and Bacon included these deviations in their estimate of $\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$, which is consequently much too large. From the internal consistency of results from different runs and from the results of calibration experiments, we are confident that our absolute values for $\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$, are in error by at most 10% and the relative values by at most 2%.

The most striking feature of the results in Table I is the complete lack of any correlation between the N → I transition temperatures ($T_{\mathrm{N}\rightarrow\mathrm{I}}$) and the corresponding heats of transition ($\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$). Since the heats of transition reflect the changes in intermolecular forces on passing from the nematic phase to isotropic liquid, it seems clear that the stability of the nematic phase does not depend primarily on the magnitude of these. Indeed, the compound with the highest $T_{\mathrm{N}\rightarrow\mathrm{I}}$ (**1a**) has the lowest $\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$. Note also that whereas $\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$ is larger for **1f** and **1g** than for **1a**, as would be expected[3] in view of the greater polarity of the central group in the former, their transition temperatures are lower than that for **1a**. The transition temperatures are thus determined mainly by changes in the entropy of transition ($\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$) rather than by changes in $\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$. A plot of $T_{\mathrm{N}\rightarrow\mathrm{I}}$ vs. $\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$ does indeed indicate a definite correlation, though with much scatter; this of course would be expected because of the random variations in $\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$.

Our next problem is to try to relate the changes in $\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$ to changes in molecular structure. Let us first consider the relationship between **1a**, **1f**, and **1g**, all of which are structurally very similar.

The resonance interactions between the aromatic rings and the carboxyl groups will tend to make all three molecules more or less coplanar. Each can then exist in cis and trans forms. In the case of **1a**, these isomers (**2** and **3**, respectively) will have almost identical energies since the ester groups are far apart. Each will also be unchanged by a rotation of any of the 1,4-phenylene groups through 180°. Thus **2** and **3** each have symmetry numbers of eight. An isolated molecule of **1a** in the gas phase can therefore exist in any of 16 energetically equivalent states.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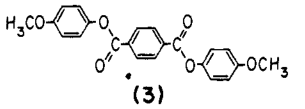

(3)

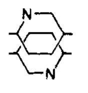
In the isotropic liquid, the energies of **2** and **3** will again be similar. The 16-fold degeneracy will therefore still hold. In the nematic phase, on the other hand, the parallel arrangement of molecules will favor energetically the linear trans form **3**. If this effect were large enough for **1a** to exist exclusively as **3** under these conditions, so that half the 16 possible states were excluded, there would be a decrease in entropy of R ln 2, i.e., 1.38 entropy units, on passing from the isotropic liquid to the nematic phase. Since the observed value of $\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$ is much less than this, the tendency for **3** to be favored in the nematic phase must be quite small, a rather surprising conclusion which contradicts current ideas.[9]

Table I. Thermodynamic Parameters for Di-*p*-anisates

Compd	$T_{\mathrm{C}\rightarrow\mathrm{N}}$[a]	$T_{\mathrm{N}\rightarrow\mathrm{I}}$[b]	$\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$[c]	$\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$[d]
1a	210.6	287.6	0.232	0.414
1b	152.0	268.8	0.288	0.531
1c	205.6	271.8	0.313	0.574
1d	143.7	249.9	0.257	0.491
1e	140.2	243.3	0.292	0.565
	(142.9[e])	(242.8[e])	(0.685[e])	(1.33[e])
1f	173.2	255.3	0.311	0.588
1g	202.6	249.5	0.316	0.605

[a] Melting point (°C). [b] N → I transition temperature (°C). [c] Heat of N → I transition (kcal/mol). [d] Entropy of N → I transition (entropy units). [e] Reference 8.

Next let us consider **1f**. Here again the molecule in isolation can exist in a number of different forms analogous to **2** and **3**. These will, however, fall into two groups of somewhat different energies, depending on whether the carbonyl group in the 2 position of the pyridine ring is cis or trans to nitrogen. There will be a corresponding reduction in the effective symmetry number of the molecule in the isotropic liquid phase, from 16 to 8. There will, however, be a much larger decrease in the nematic phase where the molecules are oriented parallel to one another, for the dipole-dipole interactions between the pyridine rings of adjacent molecules will tend to make them favor orientations such as **4** rather than **5**, **6**, or **7**. There is therefore a larger increase in entropy on passing from the nematic phase to isotropic liquid than in the case of **1a**. Consequently **1f** has a lower N → I transition temperature than **1a**, although $\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$ for **1f** is larger.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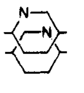
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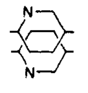
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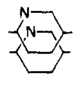

(7)

Similar arguments apply in the case of **1g**. Here two of the pairings analogous to **4**–**7** are favorable and two very unfavorable. In the case of **1f**, three of the pairings are favorable (**4**–**6**) and only one (**7**) is really unfavorable. It is therefore not surprising that $\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$ is greater for **1g** than for **1f** and the nematic → liquid transition temperature correspondingly lower.

Similar arguments can be used in the other cases. Thus $\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$ for **1e** is large because the cyclohexane ring in **1e** is flexible. The parallel arrangement of molecules in the nematic phase limits the ability of the cyclohexane ring to wriggle so there is a corresponding gain in entropy on passing to the isotropic liquid. Likewise the value of $\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$ is larger for **1b** than for **1a** because the ester groups in **1b** are virtually free to rotate about the C-CO bonds whereas those in **1a** are more or less constrained to coplanarity with the central benzene ring. The loss of entropy, due to the tendency for molecules in the nematic phase to adopt linear geometries, is consequently larger for **1b** than for **1c**.

As has been pointed out previously, the double bonds in the central ring of **1c** should be polar, due to resonance interactions with the adjacent carbonyl groups. The situation should therefore be similar to that in **1f**, the resulting dipole-dipole attractions favoring specific pairings of molecules in the nematic phase. As a result, both $\Delta H_{\mathrm{N}\rightarrow\mathrm{I}}$ and $\Delta S_{\mathrm{N}\rightarrow\mathrm{I}}$ are larger for **1c** than for **1a**. The entropy factor again wins out, the transition temperature for **1c** being less than that for **1a**.

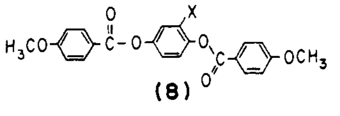
Finally, in the case of **1d**, a new factor appears. As has been pointed out previously,[3] the molecules of **1d** are kinked, due to the nonplanarity of the double bonds in the 1,3-cyclohexadiene ring and the tendency of the adjacent carbonyl groups to lie parallel to them. This lack of linearity will make it harder for the molecules to pack into a nematic structure and will consequently reduce both the difference in energy and the difference in entropy between the nematic and isotropic phases. Here the change in $\Delta H_{N \to I}$ wins, the transition temperature being consequently very low. Loss of rod-shaped structure will probably in general lead to a lowering of the nematic → liquid transition temperature in this way. The same factor may also be responsible for the corresponding lowering in the case of molecules of nonuniform cross-section.[3] Here we are dealing with a factor not present in other molecules of the present series; the transition temperature for **1d** is consequently very much out of line with the rest.

In order to test the correctness of these ideas, we decided to study a series of analogous compounds in which the geometry and polarity of the central ring are disturbed by substituents.

It is well known that introducing lateral substituents into an aromatic ring of a liquid crystalline compound normally lowers the N → I transition temperature. Gray,[9] who pioneered this area, concluded that the monotonic decrease in transition temperature, observed in several such series of compounds as one descends the halogen family, is due to a regular decrease in the intermolecular forces with increasing size of the substituent, leading to a corresponding increase in the mean intermolecular separations. This view has been accepted by most subsequent workers. A recent variant attributes some of the effects of substituents to corresponding changes in polarizability and polarity, due to steric inhibition of conjugation.[10] Here again the effect of substituents in reducing the transition temperature is attributed to a corresponding decrease in the intermolecular forces.

On the other hand Young et al.[11] have found that methyl substituents in the central rings of derivatives of phenyl *p*-benzoyloxybenzoate in some cases raised $\Delta H_{N \to I}$ while lowering the N → I transition temperature. They pointed out that these results were inconsistent with Gray's interpretation of substituent effects and with the interpretation in terms of steric hindrance to conjugation. However, their conclusions in turn have been challenged by a recent study[12] of the thermodynamics of cholesteryl halobenzoates which showed that in this case chlorine substitution in the benzene ring *does* reduce $\Delta H_{N \to I}$.

In order to avoid complications from steric interactions between substituents and the ester groups, we decided to examine a series of analogs (**8**) of **1** in which the carbonyl



a, X = H　**c**, X = Cl　**e**, X = I

b, X = F　**d**, X = Br　**f**, X = CH_3

groups are inverted. Here the substituent will tend to enforce the indicated (**8**) configuration of the adjacent ester group. It was already known[13] that the transition temperature of **8a** is higher than that of **1a**; this difference had been attributed[13] to the greater polarity of the terminal rings in **8a**, due to mutual conjugation between the methoxyl and carbonyl groups. Our results for **8a** and for five derivatives (**8b–f**) are shown in Table II.

It will be seen that both $\Delta H_{N \to I}$ and $\Delta S_{N \to I}$ are much larger for **8a** than for **1a**. The higher transition temperature for the former is due to the fact that the increase in $\Delta H_{N \to I}$ is the greater, implying that greater intermolecular forces are indeed responsible. The arguments given earlier suggest that the large increase in $\Delta S_{N \to I}$ may imply that in the nematic phase the linear trans conformation of **8a** is favored more than is that of **1a** (cf. **3** and **2**), due presumably to the increased intermolecular attractions. If so, esters of type **8a** should provide superior nematic solvents for spectroscopic (e.g., NMR) studies than those of type **1a** because the orientation of solute molecules should be more efficient in the former.

Table II. Effect of Lateral Substituents on the Thermodynamic Parameters for N → I Transitions

Compd	$T_{C \to N}$[a]	$T_{N \to I}$[a]	$\Delta H_{N \to I}$[a]	$\Delta S_{N \to I}$[a]	R,[b] Å
8a	217.0[c]	301.0[d]	0.408	0.711	1.2
8b	173.8	278.5	0.404	0.732	1.35
8c	162.0	252.4	0.463	0.881	1.8
8d	161.4	241.1	0.487	0.947	1.95
8e	173.4	222.9	0.493	0.994	2.15
8f	165.9	252.1	0.529	1.01	2.0

[a] For notation, see Table I. [b] van der Waals radius of ortho substituent (H in case of **1a**). [c] Previously reported values: 213° (ref 5); 222° (ref *e* below). [d] Previously reported values: 297° (ref 5); 300° (ref e). [e] M. J. S. Dewar and J. P. Schroeder, *J. Org. Chem.*, 30, 2296 (1965).

Table III. Relative Enthalpy Changes for the Monotropic Nematic–Smectic Transition of Some Laterally Substituted Diesters

Compd	$T_{N \to S}$	$\Delta H_{N \to S}$
8a	178	5
8b	140	4
8f	123	1

In the case of the halogen derivatives **8b–e** there is, as expected,[9] a steady decrease in the N → I transition temperature with increasing size of the halogen. However, this is due *not* to a decrease in $\Delta H_{N \to I}$ along the series but to a steady increase in $\Delta S_{N \to I}$. Indeed, $\Delta H_{N \to I}$ shows a small but significant and uniform *increase* with increasing size of the substituent. Introduction of a methyl substituent (**8f**) also leads to a large decrease in the N → I transition temperature, again as a result of a large increase in $\Delta S_{N \to I}$. This decrease in the transition temperature is, however, somewhat less than would have been expected in view of the van der Waals radius of methyl (see last column of Table II).

The simplest explanation of these results seems to be that the substituent reduces the entropy of the nematic phase by limiting the mobility of molecules in it. The interlocking of substituents on different molecules should hinder motions parallel to their long axes in the nematic phase. The effect would of course be much less pronounced in the corresponding isotropic liquid where the molecules are randomly oriented. This locking together of molecules in the nematic phase will also tend to reduce the mean intermolecular distance and hence somewhat increase the corresponding intermolecular forces. The result will be a relatively large increase in $\Delta S_{N \to I}$ and a smaller increase in $\Delta H_{N \to I}$, as observed.

While this paper has been concerned with the effects of structure on the nematic → isotropic transition, the conclusions reached should apply with even more force to nematic → smectic (N → S) transition in view of the high degree of orientation of molecules forming a smectic phase. We have recently been able to observe monotropic N → S transitions in some of the molecules studied here and have made some preliminary DTA measurements for them. Since our instrument is not yet calibrated for the cooling mode, only relative values for ΔH are as yet available; these are shown in Table III, together with the observed transition tempera-

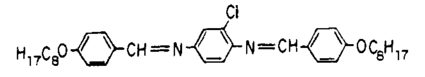
Table IV. Properties of Di-*p*-methoxybenzoates of 2-Substituted Hydroquinones

Compd	Yield, %	Mass spectrum (*m/e*)	Ir spectrum, cm^{-1} (KBr pellet)	NMR spectrum (δ) in TFA
8b	28	396[a], 135[b]	3060[c], 2940[c], 2835[d], 1705[e]	8.17–8.40[f], 7.03–7.34[f], 4.03[g]
8c	36	414[a], 412[a], 135[b]	2945[c], 2845[d], 1720[e]	8.15–8.39[f], 7.00–7.37[f], 4.01[g]
8d	44	456[a], 458[a], 135[b]	2950[c], 2845[d], 1720[e]	8.15–8.42[f], 7.01–7.40[f], 4.02[g]
8e	29	504[a], 135[b]	2940[c], 2840[d], 1722[e]	8.17–8.45[f], 7.01–7.41[f], 4.05[g]
8f	47	392[a], 135[b]	2940[c], 2840[d], 1710[e]	8.30–8.46[f], 6.98–7.26[f], 4.01[g], 2.03[h]

[a] Parent peak. [b] Base peak ($MeOC_6H_4CO^+$). [c] Aromatic CH stretch. [d] Methoxyl CH stretch. [e] Carbonyl stretch. [f] Multiplets; 11 H together (aromatic CH). [g] Singlet, 6 H (methoxyl groups). [h] Singlet, 3 H (methyl group).

tures. Since the latter do not vary greatly, it is evident that there is a huge decrease in the entropy of transition when hydrogen is replaced by methyl but not when it is replaced by the much smaller fluorine substituent. According to our views, the order of the nematic phase in **8** is increased greatly by an increase in the size of X and methyl proved especially effective in this, increasing ΔS for the N → I transition; the same effect should of course *decrease* ΔS for the N → S transition, as we observe.

This suggestion seems to be supported by some recent work by De Vries,[14] who found that the Schiff's base **9**,



(9)

analogous to **8**, formed a nematic phase in which the molecules tended to have a staggered arrangement that might be expected if they were interlocked in the manner we have suggested.

The relatively low efficiency of methyl in relation to its van der Waals radius (Table II) can be explained likewise. Bonds between carbon and halogen are highly polar, in the sense $C^{\delta+}-X^{\delta-}$. The negatively charged halogen atoms in different molecules of **8b–e** will therefore repel each other strongly. The effective radius of halogen, in relation to intermolecular interactions of the type we are considering, will then be considerably greater than its van der Waals radius. In the case of the relatively neutral methyl group no such long range coulomb forces will operate.

These arguments concerning the effects of projecting substituents should apply equally to any other deviation in the shape of the molecule from a cylinder of uniform cross-section. In particular, they should apply to the effects of bends, bulges, and waists. Previous work here[3] has shown that such distortions from cylindricality do indeed lower N → I transition temperatures. We believe that in each such case the decrease will be found to be due to an increase in $\Delta S_{N\rightarrow I}$, accompanied by a smaller increase in $\Delta H_{N\rightarrow I}$.

Our arguments suggest that polarity in the central part of a linear molecule is also likely to reduce the N → I transition temperature through a reduction in the effective symmetry number. Polarity in the terminal groups on the other hand is known[9] to favor nematic stability; our results for **1a** and **8a** suggest that current intuition is correct in attributing this to enhancement of intermolecular forces, i.e., an increase in $\Delta H_{N\rightarrow I}$. The ideal structure for a nematic molecule thus seems to be a linear nonpolar cylinder of uniform cross-section with polar ends. We would for example attribute the superiority of the ester (-COO-) and azoxy (-NO=N-) linking groups over vinylene (-CH=CH-) or azo (-N=N-) to their greater width rather than to their greater polarity. It is interesting in this connection that acetylene appears to be a poor linking group in spite of its linearity and rigidity. It is of course the slenderest of all possible linking groups.

Our conclusions also lead to the prediction that molecules with unfavorable geometries should form mesophases of correspondingly high density and viscosity. This could be checked by measurements of the changes in density and viscosity during the N → I transition.

Experimental Section

Melting points (corrected) were determined either with a Thomas-Hoover melting point apparatus or, in the case of mesomorphic compounds, by DTA. Proton NMR were obtained on a Varian A-60 Spectrometer and infrared spectra were run on a Beckman IR-8 spectrometer. Mass spectra were measured with electrons of 70 eV energy. All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. All the compounds reported here had satisfactory elemental analyses (errors <0.2%). The thermodynamic data were obtained with a Stone differential thermal analyzer, Model 202, SH-11BR2 aluminum sample holder, platinel differential thermocouple, and aluminum disks. The temperature scale of the analyzer was calibrated against known standards and the heats of transition were obtained on the same instrument calibrated against ultrapurity indium and lead reference standards. These materials span the temperature range of the compounds under consideration.

Compounds **1a–f** and **8a** were prepared as previously.[3]

Pyrazine-2,5-dicarbonyl Chloride. Pyrazine-2,5-dicarboxylic acid (we are grateful to S. B. Brown for a supply of this) (1.0 g) was added to thionyl chloride (10 ml) containing one drop of dimethylformamide and the mixture refluxed overnight. Evaporation and crystallisation from hexane gave yellow strands (0.53 g, 43%) of the acid chloride, mp 145° (lit.[15] 143–144°).

Bis(*p*-methoxyphenyl) Pyrazine-2,5-dicarboxylate (1g). A solution of *p*-methoxyphenol (0.248 g, 0.002 mol) in dry pyridine (5 ml) was added dropwise with stirring to pyrazine-2,5-dicarbonyl chloride (0.205 g, 0.001 mol) in dry pyridine (5 ml) at room temperature. Next day the **1g**, isolated with acid, was crystallized from ethanol-chloroform: 0.11 g (29%); mp 202.6°; $T_{N\rightarrow I}$, 249.5°; ir (KBr pellet) 3070 (pyrazine CH), 3005 (ArCH), 2840 (OCH_3CH), 1750 (C=O), 1250 (C-CO) cm^{-1}; NMR (TFA) δ 9.52 (s, 2 H, pyrazine ring), 6.86 (m, 8 H, phenylene), 3.57 (s, 6 H, OCH_3); mass spectrum *m/e* 380 (parent ion), 229 (base peak).

2-Halohydroquinones. 2-Chlorohydroquinone and 2-methylhydroquinone were commercial samples. 2-Bromohydroquinone was prepared by the method of Dakin,[16] mp 113° (lit.[16] 113–115°). 2-Fluoro- and 2-iodohydroquinones were prepared by persulfate oxidation of the 2-halophenols, by the procedure used by Baker and Brown[17] for the preparation of other hydroquinone derivatives. 2-Iodohydroquinone, 8.9% yield after crystallization from chloroform, had mp 114° (lit.[18] 115–116°). 2-Fluorohydroquinone: 14.5% yield after crystallization from chloroform, had mp 126°; ir (KBr pellet) broad bands centered at 3000 and 1260 cm^{-1}; NMR (D_2O) δ 6.37–7.04 (m); mass spectrum *m/e* 128 (parent ion and base peak).

Hydroquinone Di-*p*-methoxybenzoates (8a–f). These were prepared by dropwise addition of a solution of the hydroquinone (0.01 mol) in dry pyridine (20 ml) to one of *p*-anisoyl chloride (0.02 mol) in dry pyridine (20 ml) at room temperature. The esters were isolated by adding water and acid, washed with bicarbonate, and crystallized from chloroform. The properties of **8a** have been reported (but see Table II). Those of **8b–f** are shown in Tables II and IV.

References and Notes

(1) This work was supported by the Air Force Office of Scientific Research (Contract No. F44620-71-C-0119) and the Robert A. Welch Foundation (Grant F-126).

(2) (a) A preliminary account of some of this work was given at the third

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Circularly Polarized Luminescence and Energy Transfer Studies on Carboxylic Acid Complexes of Europium(III) and Terbium(III) in Solution

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Abstract: Circularly polarized luminescence (CPL) and total (unpolarized) luminescence measurements are reported for a number of Eu^{3+} and Tb^{3+} complexes of optically active carboxylic acids in aqueous solution under a variety of physical conditions. Additionally, Tb^{3+} → Eu^{3+} energy transfer is studied as a function of pH for aqueous solutions which are 1:5:1 in Tb^{3+}-carboxylic acid-Eu^{3+}. Efficiency of Tb^{3+} → Eu^{3+} energy transfer is related to the possible formation of dinuclear or polynuclear complex species either through multiple binding sites on a single carboxylic acid ligand or through ligand + OH$^-$ bridging groups between Tb^{3+}-Eu^{3+} pairs. The results of this study demonstrate the sensitivity of Tb^{3+} and Eu^{3+} CPL to the detailed nature of ligand environment. Changes in ligand type and in donor atom availability (through changes in pH conditions) lead to easily discernible alterations in the sign and intensity patterns of the CPL spectra. Additionally, the extensive splitting of the various ^7F_J multiplet levels of Tb^{3+} and Eu^{3+} due to the low-symmetry ligand fields in Tb^{3+} and Eu^{3+}-carboxylic acid complexes is readily apparent in the CPL spectra, whereas these splittings generally are not resolved in the total luminescence spectra.

I. Introduction

Recently, there has developed considerable interest in the use of the spectroscopic and magnetic properties of lanthanide ions as probes of biomolecular structure and function, particularly for those systems which bind calcium. For example, Birnbaum and Darnall[2-5] have suggested that the visible absorption spectra of lanthanide ions provide a sensitive probe of electrostatic binding sites in proteins and enzymes, and Morallee et al.[6] have emphasized the potential of lanthanide cations as nuclear magnetic resonance probes of biological systems. Additionally, Luk[7] has demonstrated the utility of lanthanide ion emission spectra for characterizing the metal binding sites of a protein (transferrin). More recently, the metal binding sites of several protein structures have been studied by the relatively new spectroscopic emission technique, circularly polarized luminescence (CPL). Gafni and Steinberg[8] have reported the CPL spectra of Tb^{3+} bound to transferrin and to conalbumin, and the CPL of Tb^{3+} bound in a Ca^{2+} site of a carp muscle parvalbumin has been examined in our laboratory.[9]

To better characterize the nature of the lanthanide-ligand linkages in biomolecular systems, a number of recent studies have focused on the structural characteristics of complexes formed by hydroxy- and amino-substituted carboxylic acids with lanthanide ions in aqueous solution. Since it is likely that the lanthanide binding sites of most proteins present -OH, -NH$_2$, or -COO$^-$ as ligating groups, it might be expected that carboxylic and amino acid complexes can provide appropriate model systems for studying Ln^{3+}-protein interactions. Katzin and coworkers[10-12] have carried out extensive studies on the circular dichroic properties of Pr^{3+} and Eu^{3+} complexes of α-amino acids and of many hydroxy-substituted carboxylic acids. The circular dichroism (CD) spectra of these systems are highly structured in the region of the metal ion f ↔ f transitions and are comprised of many more components or bands than the corresponding absorption spectra, reflecting the low-symmetry environment of the metal ion in these complexes. Katzin's studies also revealed that the CD spectra are extraordinarily sensitive to pH changes, suggesting that CD provides a sensitive measure of ligand binding modes in cases where the ligands have several potential donor groups with different pK_a's in aqueous solution. More recently, Martin and coworkers[13] have examined the titration and CD behavior of 12 trivalent lanthanide ions and 15 amino acid ligands in aqueous solution. They noted that although the amino acids form only weak complexes with Ln^{3+} ions, the CD signatures associated with f ↔ f transitions are very sensitive to the detailed chemical nature of the ligand environment. Furthermore, they concluded from their titration studies that in basic solution the complexes tend to form polynuclear species making the interpretation of the CD data in terms of specific spectra-structure relationships somewhat difficult. Polynuclear complex formation and the simultaneous occurrence of several complex species are problems commonly encountered in solution studies of Ln^{3+} complexes.

Birnbaum and Darnall[14] used difference absorption spectroscopy to study the interaction of Nd^{3+} with acetate, alanine, histidine, benzoate, and anthranilate ligands in aque-