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Mesogenic and Non Mesogenic Central Rigid Cores

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Mesogenic and Non Mesogenic Central Rigid Cores

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The mesogenic power of several central rigid cores is measured by means of depolarized Rayleigh scattering. It is shown that there is a close relation between the angular correlation parameter J and the mesogenic power that lead us to define mesogenic and non mesogenic rigid cores. An attempt is made to explain these facts by consideration of certain different structural aspects.

INTRODUCTION

During the last few years, a large number of studies have been centred around the problem of establishing relations between molecular structure and mesomorphic properties.[1–6] It must still be said, at present, that the mesomorphic phenomenon remains mysterious! Especially if we attempt to "explain" this phenomenon whilst being aware that the successful preparation of liquid crystals follows an empirical approach involving some element of chance. For example, it was considered for some time, that it was an absolute necessity that the rigid core should contain at least two or three benzene rings; Jacques *et al.*,[7] however, have recently prepared different mesomorphic cholestanes where no polarisable grouping is evident; at the same time Pohl *et al.*[8] were successful in synthesising mesogenic compounds built from one and two cyclohexane rings!

In our laboratory we have developed a different approach to this problem; it was hoped that certain features of the problem could be predicted, using as a basis some specific physical characteristic of these substances. For example, it is now well known that the angular correlations are drastically higher for a mesogenic substance than for a non-mesogenic one.[9] More precisely, we have asked the question: "is it possible to find, in the central rigid part, some

specific property having the potential induce mesomorphism"?,† and to characterize it by means of the depolarized light scattering technique. This article attempts to provide a more precise answer to this question.

Brief review of the depolarized Rayleigh scattering technique (DRS)

The DRS technique involves the measurement and interpretation of the depolarized scattered intensity i of a liquid. The comparison of the molar intensity ($y = Ki/c$) measured for a given compound at infinite dilution in an inert solvent (Y^{∞}) and also in the pure sample ($Y^{\oplus}$) lead to the angular correlation parameter J. In the microscopic model of Kielich[10]

$$J = \frac{Y^{\oplus} - Y^{\infty}}{Y^{\infty}}$$

where $J = \frac{1}{2}Z\langle 3\cos^2\theta - 1\rangle$, θ is the angle between the symmetric axes of one molecule with its Z neighbours.

Three different situations may arise:

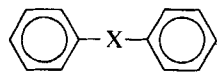
i) $J > 0$; this indicates a tendency of the molecules to organize their axes of higher symmetry parallel to one another, called "paratropic comportment."

ii) $J < 0$; the tendency of the molecules to organize their axes perpendicular to one another, called "diatropic comportment."

iii) $J = 0$; corresponds to isotropic repartition of molecules, called "atropic comportment."‡

EXPERIMENTAL RESULTS

We have measured the J value for several central rigid groups having the general formula,



the results are listed in Table I in order of decreasing J.

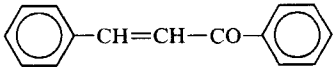
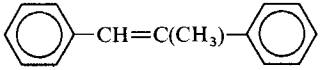
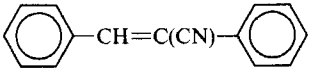
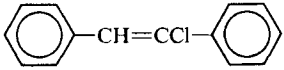
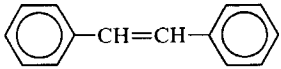
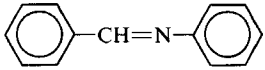
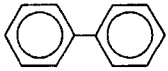
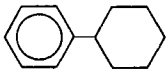
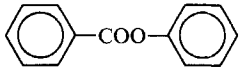
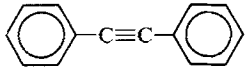
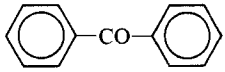
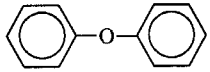
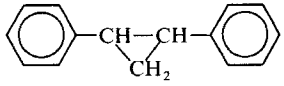
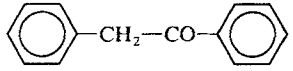
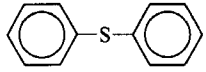
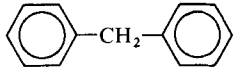
Careful examination of these results show that one can find two distinct groups of rigid cores. Let us first examine those having J values between 0.39 and 0.78. The values show that these cores exhibit fairly strong molecular

† This idea has been suggested to us by Professor J. Billard.

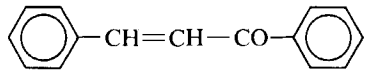
‡ For more technical and theoretical detail see Ref. (10).

TABLE I

Fusion temperature and JA_{22} values for the different rigid cores

Noyau	$t_K \rightarrow I$ °C	JA_{22}
	62	1.08
	81.5	0.78
	86	0.73
	50	0.62
	124	0.58
	52	0.53
	70	0.43
	Liquide	0.43
	69	0.40
	60	0.39
	48	0.30
	28	0.18
	Liquide	0.08
	60	0.03
	Liquide	0
	27	−0.17

correlations in the isotropic phase, or more precisely, a paratropic comportment. This is consistent with the fact that these cores, by suitable disubstitution, generally give mesogenic substances. It should be remarked upon that one of these cores prepared here, i.e.:



has a J value outside of the domain 0.39–0.78. A specific study of the mesogenic power of this core will be presented. We should also point out that the phenylcyclohexane is exactly in the range of the "good rigid core" domain; indeed, at the time of this measurement, the "good rigid core" argument was an accepted criterion for attempts to build new mesomorphic compounds. Pohl *et al.*[8] have recently proved the correctness of our argument. This confirms that for any substance, the measured value of the J parameter can be used to predict the mesogenic properties.

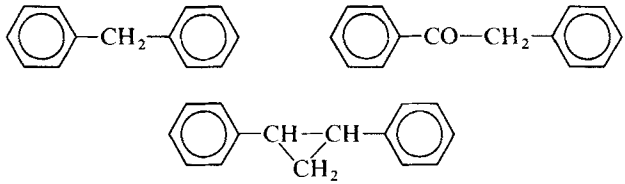
Thus in the first instance we have presented a description of what we term "mesogenic central rigid cores" (cores able to give mesogenic substances upon disubstitution), defined with respect to the results obtained from DRS techniques. For these compounds J values are near to 0.5.

Another group of rigid cores exists, which have J values near zero. There is no evidence in the literature that such cores give rise to mesomorphic phases, and it will be verified here that these form true "non-mesogenic" compounds; this requires (i) the preparation of different disubstituted derivatives and (ii) examining whether or not they give mesophases.

Rigid cores have J values between these two limits are for instance diphenyl ether and benzophenone, which exhibit some paratropic comportment; these species will be examined carefully.

Rigid cores with low J value

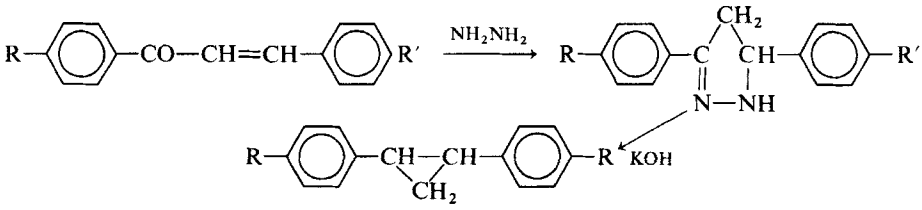
These rigid cores with low J value (Table I) have been studied:



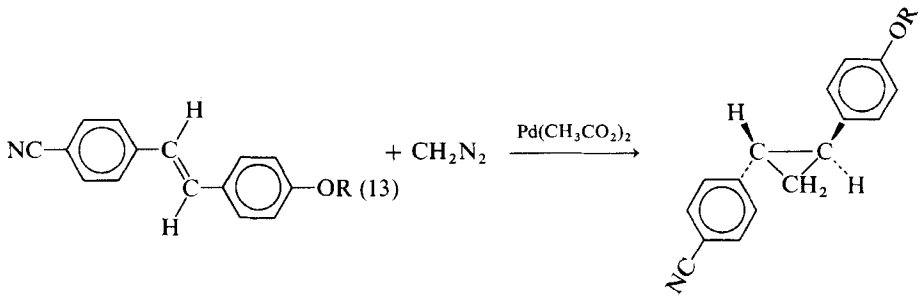
Firstly the general syntheses of their *p-p'*-derivatives is described.

Synthesis: 1,2-Diarylcyclopropanes: two methods were used in the preparation of these compounds:

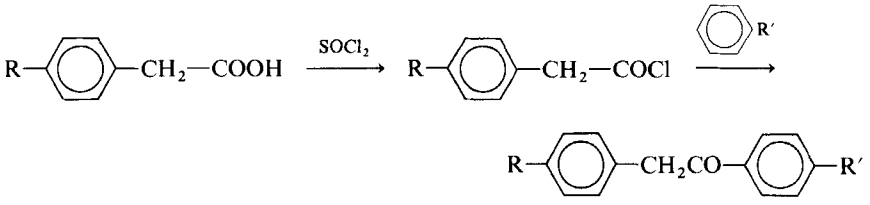
The modified Wolf–Kishner Reaction[11]



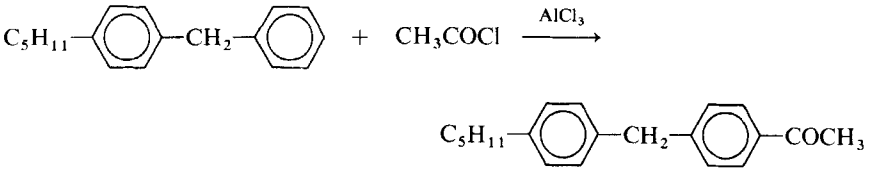
Addition Reaction—The diazomethane[12] derivative is obtained from N-Methyl-N-tosylnitrosamide, the reaction with the stilbene is a *cis* addition.



Deoxybenzoin Derivatives: They are obtained via the well-known Friedel–Crafts reaction from the para substituted phenylacetylchloride with an alkyl or alkoxy benzene.



Diarylmethanes: These have been prepared both by the Friedel–Crafts reaction (between diphenylmethane and different aliphatic acid chlorides) and the Wolf–Kishner reduction of the appropriate diaryl ketones, viz.:



RESULTS AND DISCUSSION

The fusion temperatures of the different compounds prepared here, are listed in Table II. None of the substances are mesomorphic. This result is to be compared with the very low J values (ca. 0.0) measured for these three central rigid cores. From a molecular point of view, the implication is simply that these molecules exhibit an "isotropic repartition" ($J \sim 0$ for the deoxybenzoin and diphenylcyclopropane cores) or a tendency to orientate themselves perpendicular to each other ($J < 0$). Thus we can understand

TABLE II

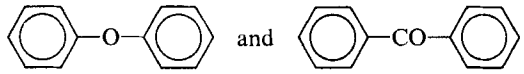
Formulas and fusion temperatures of the prepared compounds

Formule	T_F °C
trans NC–C$_6$H$_4$–CH(CH$_2$)–CH–C$_6$H$_4$–OC$_7$H$_{15}$	44
trans NC–C$_6$H$_4$–CH(CH$_2$)–CH–C$_6$H$_4$–OC$_8$H$_{17}$	41
CH$_3$O–C$_6$H$_4$–CH(CH$_2$)–CH–C$_6$H$_4$–OCH$_3$	70
CH$_3$O–C$_6$H$_4$–CH(CH$_2$)–CH–C$_6$H$_4$–OC$_7$H$_{15}$	34
CH$_3$O–C$_6$H$_4$–CH(CH$_2$)–CH–C$_6$H$_4$–CN	112
CH$_3$O–C$_6$H$_4$–CH$_2$–CO–C$_6$H$_4$–C$_5$H$_{11}$	62
Br–C$_6$H$_4$–CH$_2$–CO–C$_6$H$_4$–OCH$_3$	139
Br–C$_6$H$_4$–CH$_2$–CO–C$_6$H$_4$–C$_5$H$_{11}$	126
Br–C$_6$H$_4$–CH$_2$–CO–C$_6$H$_4$–C$_6$H$_{13}$	109
Br–C$_6$H$_4$–CH$_2$–CO–C$_6$H$_4$–C$_7$H$_{15}$	115
CH$_3$CO–C$_6$H$_4$–CH$_2$–C$_6$H$_4$–C$_5$H$_{11}$	Liquide

that it is difficult to obtain mesomorphic substances from these cores for which the strong tendency to lie parallel is well known. Thus we can conclude that if a central rigid core present a J value ~ 0 it is impossible, for the addition of any kind of substituent, to obtain mesomorphic substances; we term these "non-mesogenic central rigid" cores.

Rigid cores with medium J values: diphenylether and diphenyl-ketones

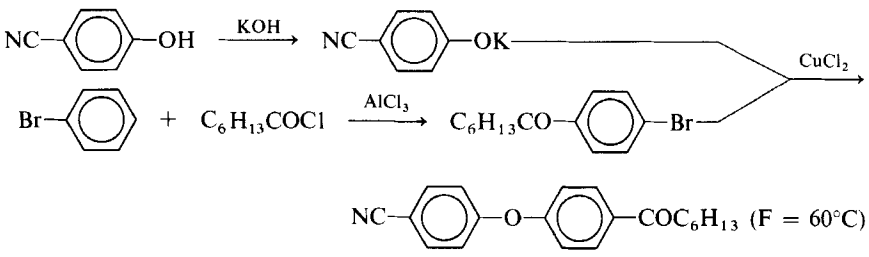
The two rigid cores



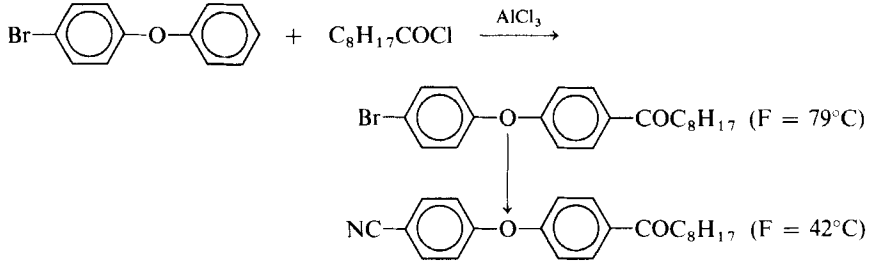
are paratropic, which means they possess J values which are positive and non-negligible. Furthermore, their fusion temperatures are very low, supporting the results obtained here for these.

Diarylethers: We have prepared three substances with substituents considered suitable for inducing mesomorphism. They were prepared via two different routes:

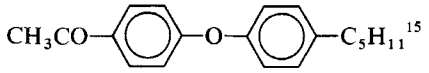
Ullman Reaction[14]



Friedel–Crafts Reaction



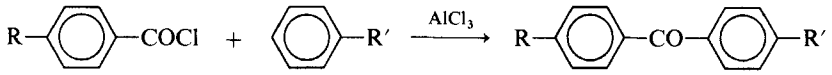
None of these are mesogenic; in fact we have also[15] recently measured the virtual nematic-isotropic transition for another derivative of this rigid core, i.e.:



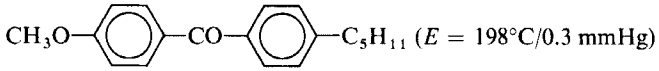
the transition temperature of this compound was determined to be $-150°C$, and this result indicates that the other similar substances will be far from mesomorphic.

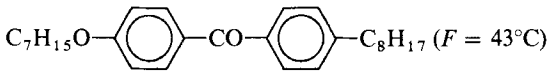
Diarylketones: Initially, when we measured the angular correlation parameter of pure benzophenone in the liquid phase, we thought it could possibly indicate a mesogenic core, since $J \sim 0.30$ which is close to the value measured for the tolane system ($J = 0.39$). As a result we tried different kinds of *p-p'*-substitutions with the aim of finding new liquid crystals.

Our first attempt made use of the Friedel–Crafts reaction,



Using this mechanism, we were able to prepare the two products: i.e.





The second of these compounds exhibits a virtual temperature (T_{NI}) equal to $-95°C$, which indicates that substances built from the diphenyl ketone core are also far from stable mesomorphism.

These results can be explained in terms of paratropism: i.e. the J value is too low for these rigid cores to be mesogenic in character. Thus we can conclude that lower is the J value of a central rigid core, lower is its mesogenic potentiality.

It is thus shown that there is a lower limit domain of J which a core must possess if mesomorphic substances are to be prepared from it. The question arises, is there an upper limit domain?

Using the chalcone rigid core we have prepared numerous para di-substituted compounds:

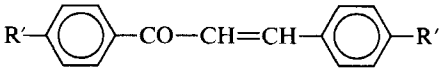
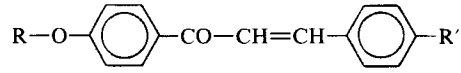


TABLE III

Formulas and fusion temperatures of the prepared chalcones



R	R′	T_F °C	T^*_{NI}
CH_3	$-OCH_3$	101	
CH_3—	$-OC_2H_5$	105	
CH_3—	$-OC_5H_{11}$	84	
CH_3—	$-OC_6H_{13}$	90	
CH_3—	$-OC_7H_{15}$	77	18
C_7H_{15}	—Br	120	
C_7H_{15}	—CN	96	

The fusion temperatures of these are listed in Table III. None of these substances are mesomorphic, but we observe that the virtual temperatures (T_{NI}) lie relatively close to the corresponding fusion temperatures (Table III).

Now let us consider several further aspects. If we examine the mesomorphic range of the different mesogenic cores, it becomes clear that, for a given core, the range depends drastically on the substituents used. Furthermore, for similar substituents placed on different central rigid cores, quite different mesomorphic domains have been observed. Nevertheless, let us attempt to define qualitatively, "mesomorphic power," as follows: the greater the number of mesomorphic phases possible for a particular mesogenic core, the greater the mesogenic power of that core. It is evident that tolane, benzoate, α-chloro, α-cyano or α-methyl stilbene exhibit a lower mesogenic power than the Shiff base and the stilbene. Now let us suppose that there exists a relationship between the J value and this mesogenic power; according to Table I, we observe just a relationship, although a rough one, which shows a maximum (of mesogenic power) corresponding to a J value near 0.55, above and below this maximum the mesogenic power is decreasing† and one can find a strictly non-mesogenic domain near $J \sim 0$.

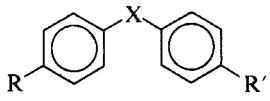
STRUCTURAL DISCUSSION

Until now, using the J value as a predictive element, we have attempted to order the different central rigid cores accordingly. We now try to explain our results from a structural point of view.

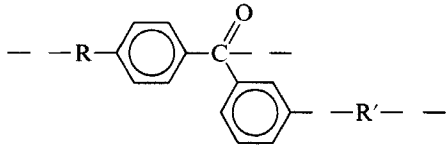
† It is noted that for α-methyl stilbene, only one stable mesogen has been found.

a Bent molecules

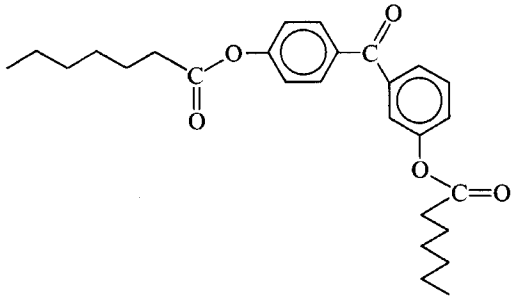
So-called "bent molecules" are those where there is an angle ($\neq 180°$) between the two benzene rings, e.g.



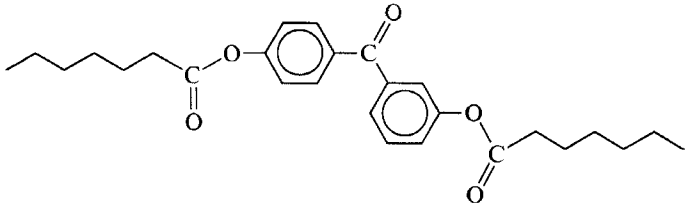
with X = CH_2, O, C = O. In fact we know that this geometry does not favour the formation of a mesophase. It was considered that meta substitution would provide a more favourable system; for example, in the benzophenone case



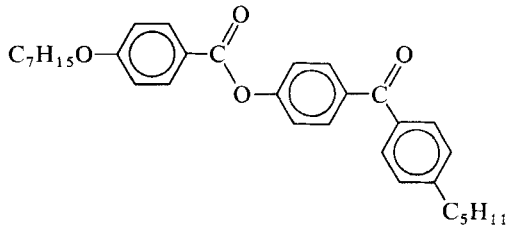
where now the R' substituent is parallel to the longer axis of the molecule. We have prepared:



or



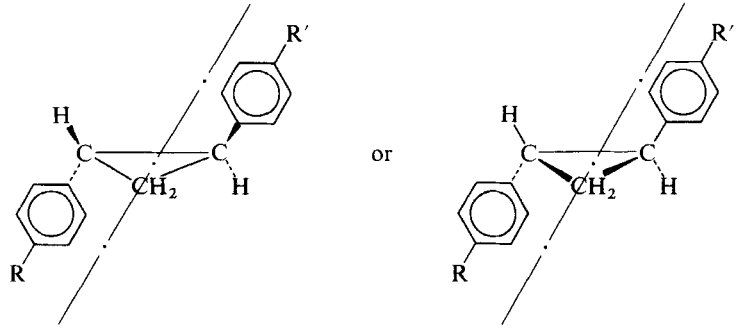
The first one of these is notably an unfavourable example. Finally, we have prepared a compound in which the length of the central rigid core has been increased, i.e.



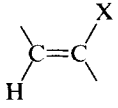
However, this substance is also non-mesomorphic.

b Quasi linear rigid cores

If molecular structure considerations can so easily explain why bent molecules are non-mesogenic (in the sense discussed) it is much more difficult to explain why quasi-linear cores such as diarylcyclopropane and deoxybenzoin are also non-mesogenic. Let us consider first the diarylcyclopropane case. The two benzene rings are not in the same plane but they are parallel to a general direction as is indicated below:

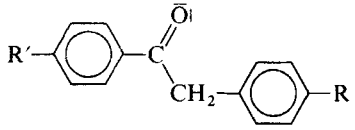


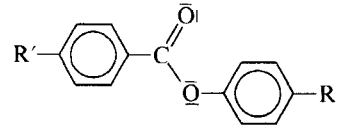
We observe the same features with α-chloro, α-methyl and α-cyano stilbenes and yet these cores are mesogenic! It is difficult to explain such behaviour, but it may be noted that the angle between the two benzene rings and the cyclopropane ring is bigger than that angle between the



plane and the benzene rings in the α-substituted stilbenes; this means that the transverse section of these compounds is less large than in the cyclopropane derivatives, and hence is more favourable for mesomorphism.

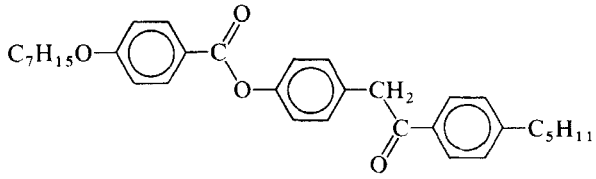
Finally we discuss the deoxybenzoin case. The molecular geometry of these compounds is very close to that of the benzoates, which are well-known mesogenic substances,





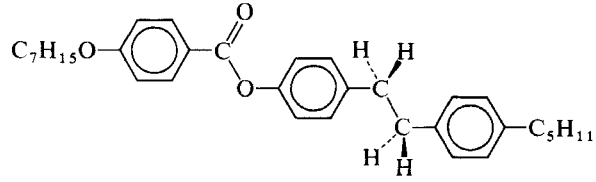
and here we have to find another "explanation"; for example, we might consider the possibility of a free rotation around the CH_2—CO bond which makes the deoxybenzoin molecule more flexible than the benzoate species in which the oxygen lone pair electrons are conjugated with double bonds enhancing the rigidity of this molecule.

It was thought that this flexibility could be compensated by increasing the length of the molecule by preparing the derivative.



This exhibited two monotropic mesophases K 130 I (113.5) N (111) S_B. Another homologous substance has also been prepared, i.e.

Two stable and one metastable phase were observed for this substance: K 59 $(S_B)'$ 69 S_C 81 N 128 I; however, the flexibility of the CH_2—CH_2 bond seems greater than the CH_2—CO bond.



CONCLUSION

We have shown first of all in this paper, that it is possible to order the "mesogenic power" of central rigid cores through the phenomenological parameter J. From this macroscopic viewpoint, we have described two types of cores, mesogenic and non-mesogenic kinds. The latter types are non-mesogenic

in the sense that for any reasonable disubstitution it is impossible to obtain a stable mesophase; moreover the virtual mesophase isotropic transition are far from room temperature but one cannot found a sharp limit between these two kind of cores, the evolution of the J values and mesogenic power is continuous. In the second part of the paper we have attempted to explain these results through simple geometrical or structural considerations, although after it is impossible (as in the case of deoxybenzoins) to explain anything of the non-mesogenic aspect. It may be thus concluded that the mesomorphic phenomena is still very mysterious! it may indeed be better to try to order the facts (J values can be used as predictive quantities), or to describe the nature rather than "explain" the origin, of the mesomorphic phenomenon by theoretical or experimental techniques.

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EXPERIMENTAL SECTION

I and J Measurements—We performed these measurements using the "gamma diffusiometre" previously described.[9,10]

MATERIAL PREPARATIONS

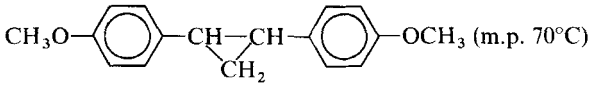
1 Diarylcyclopropanes

1-(4-heptyloxyphenyl) 2-(4'-methoxyphenyl)cyclopropane 7 g (~0.02 mole) of 4-heptyloxy-4'-methoxychalcone (prepared from *p*-methoxyacetophenone and heptyloxybenzaldehyde in a NaOH solution at room temperature), 25 ml of diethylene glycol and 5 ml of hydrazine was poured in an erlenmeyer. The mixture was heated under reflux near 190° C for 1.5 hour. The reaction mixture was allowed to cool to room temperature, then 3.2 g of KOH was added and heated at 200°C for 3 hours.

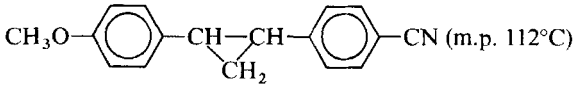
The mixture was then poured in a solution of concentrated sulfuric acid (4 ml) and glacial acetic acid (50 ml). The reaction mixture was stirred for half an hour and the organic layer was extracted with ether and washed with water, at last dried (anhydrous sodium sulfate). The solvent was removed by distillation and the product was purified by column chromatography on silicagel with a mixture of benzene (50%) and hexane as eluant. This procedure gives 4.7 g (67%) of pure material (m.p. 34°C).

IR: 1620, 1520 and 840 cm^{-1} (benzene ring), 1260, 1040 cm^{-1} (Ar—O—C).

With the same procedure we have obtained also the two products:



and



1-(4-cyanophenyl) 2-(4'-heptyloxyphenyl)cyclopropane 1.6 g (0.005 mole) of 4-cyano-4'-heptyloxystilbene, ethyl ether (120 ml) and 10 mg of Cd $(CH_3CO_2)_2$ were poured in a 200 ml erlermeyer. Heating is involved until all the stilbene is dissolved. The reaction mixture was cooled and a cold solution of CH_2N_2 in ether was added dropwise (prepared from 2.14 g of N-methyl-N-tosylnitrosamide). The mixture was stirred for 4 hours at room temperature. Benzene was added and after filtration the solvent is evaporated. The crude residue is crystallized in hexane. The precipitated product is the original material, and the second residue is a mixture of stilbene and cyclopropane. After 3 recrystallization in hexane, 100 mg of the desired compound was obtained (and 1.4 g of the original material) m.p. 44°C.

IR: 2250 cm^{-1} (C≡N), 1620, 1520 cm^{-1} (benzenic ring), 1255, 1040 cm^{-1} (A_r—O—C), 830 cm^{-1} (paradisubstituted benzene). Anal. Calcd. for $C_{23}H_{27}ON$: C, 82.88; H, 8.11; N, 4.20; Found: C, 82.77; H, 7.97; N, 4.37.

2 Deoxybenzoines

These compounds are obtained by the Friedel Crafts reaction. For the alcoxy derivatives we used the procedure previously described[17] with dichloromethane as solvent. In all other cases nitrobenzene was used.

3 Diarylmethanes

4-Acetylphenyl-4'-phenylpentylphenylmethane The Friedel Crafts reaction from 4-phenylpentylphenylmethane and acetylchloride give, the desired product (57%) b.p. 190°C (0.1 mm Hg).

4 Diarylethers

4-Bromophenyl-4'-nonanoylphenylether To 4-bromodiphenylether (24.8 g 0.1 mole) and nitrobenzene (100 ml). In a 250 ml Vessel anhydrous Al Cl_3 (14.8 g, 0.11 mole) was added in small fractions. The reaction mixture was maintained between −5°C and 0°C. Then nonanoic acid chloride (19.4 g, 0.11 mole) was added dropwise during one hour. The temperature of the mixture was allowed to rise to room temperature and the stirring was continued overnight. The reaction mixture was then poured in a solution of concentrated HCl (60 ml) and ice (150 g). Stirring and a gentle heating is performed to break emulsion of the mixture. The organic layer was extracted with nitrobenzene (100 ml) washed with an aqueous solution of Na_2CO_3 (5%) then with water up to neutralization at last dried over anhydrous sodium sulfate. Nitrobenzene is distillate under reduced pressure and the solid residue (35.5 g) was twice crystallized in benzene. 32 g (80.6%) of pure material was obtained, m.p. 79°C.

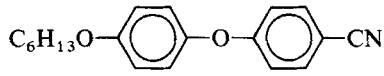
4-Cyanophenyl-4'-nonanoylphenylether Cu CN (1.1 g, 0.012 mole), dimethyl formamide (DMF) (8 ml) and 4-bromophenyl-4'-nonanoylphenylether (3.9 g) were successively added and heated to 160°C for 6 hours with a vigorous stirring. The mixture was then allowed to cool to room temperature. The mixture is poured in a solution of ethylene diamine (3 ml) in water (40 ml). A one hour more stirring is performed and benzene was added to dissolve the nitrile compound. The filtration was made over diatomeceous earth.

After decantation the organic layer was dried over anhydrous sodium sulfate. The solvent was removed and the product was purified by column

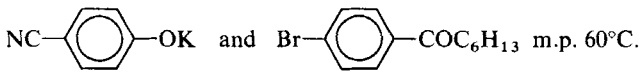
chromatography on silicagel with benzene (50%) and hexane (50%) as solvent. 2.7 g of the original material and 0.3 g of the desired compound (m.p. 42°C) were obtained (50% yield considering the reacting material).

I.R.: 2250 cm^{-1} (—C≡N), 1690 cm^{-1} (>C=O), 870 and 840 cm^{-1} (para-disubstituted benzene). Anal. Calcd. for $C_{22}H_{25}NO_2$: C, 78.80; H, 7.46; N, 4.18. Found C, 78.42; H, 7.44; N, 4.30.

The compound



was obtained by the Ullmann method from



m.p. 60°C.

5 Diarylketones

4-Methoxy-4'-pentylbenzophenone. This material is prepared from pentylbenzene and *p*-methoxybenzoylchloride by the Friedel Crafts reaction dichloromethane as solvent), b.p. 198°C, 0.3 mm Hg, yield 40%.

4-Hydroxy-4'-pentylbenzophenone. **4-methoxy-4-pentylbenzophenone.** (10 g, 0.035 mole) was dissolved in acetic acid (100 ml), then HB_r 48% (150 ml) was added and the mixture was stirred for 7 hours. The reaction mixture was then cooled to room temperature and poured in water (100 g) and ice (100 g). The filtration was performed after stirring and purification made by chromatography on silicagel. We have obtained 6 g of pure material m.p. 88°C, yield 69%.

4-Heptyloxybenzoyloxy-4'-pentylbenzophenone. The reaction of 4-hydroxy-4'-pentylbenzophenone (1 g, 0.039 mole) and heptyloxybenzoic acid chloride (1 g, 0.039 mole) in pyridin (5 ml) at room temperature for 24 hours give 1.3 g of pure material m.p. 73°C, yield 76.5%.

3,4'-Dioctanoyloxybenzophenone. Is obtained from 3,4'-dihydroxybenzophenone and octanoylchloride, m.p. = 59.5°C. Anal. Calcd. $C_{29}H_{38}O_5$: C, 74.68; H, 8.15. Found: C, 74.56; H, 8.05.

Acknowledgements

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