

Importance of the Role of Flexible Spacers in Liquid Crystal Formation by Bent Dimesogenic and Star-Shaped Trimesogenic Compounds

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A series of compounds that contain varying numbers of the same mesogenic structure, biphenyl *p*-oxybenzoate unit, attached through a pentamethylene spacer to the central benzene ring were prepared and their liquid crystallinity was studied. The mesophase-forming ability of a dimesogenic compound was found to be greatly dependent on whether or not its geometric shape is linear and also on the existence of the pentamethylene spacer between the mesogen and the central core. The presence of the spacer enhanced the capacity of a compound to form a mesophase. In the trimesogenic compound the mesogens were linked to the 1,3,5-positions of the core benzene ring through the spacer. The compound was found to be enantiotropically nematic.

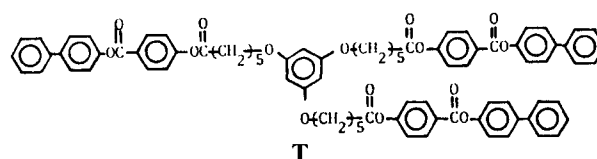
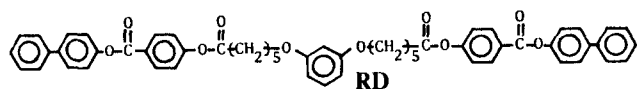
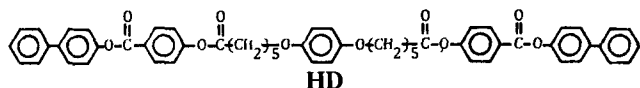
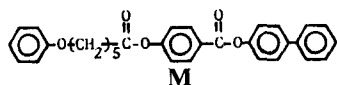
Introduction

In our previous communication¹ we have reported the synthesis and thermal properties of a series of compounds containing varying number of a mesogenic unit, 4-*n*-butylazobenzene structure, attached through ester bond to the central benzene ring. And it was concluded that the presence of mesogenic units in a multi-mesogenic compound does not guarantee for the compound to be mesomorphic. In fact, the linear molecular shape is conducive to form a liquid crystalline phase.

The properties of dimesogenic compound which contain two identical²⁻⁶ or different mesogenic units⁷ flanking a central polymethylene or oligosiloxyl spacer are very interesting. They appear to be excellent model compounds for the main chain liquid crystalline polymers with spacers.^{8,9} And when they contain two different mesogens, their liquid crystalline behavior is not a simple combination of the properties of the two separate, monomesogenic counterparts.⁷

Recently Matsunaga *et al.*¹⁰ and Huang *et al.*¹¹ reported that star-shaped benzene derivatives having long alkyl groups are able to form discotic columnar mesophases. Discotic phases were first reported by Chandrasekhar¹² in 1977.

Since a long polymethylene spacer is expected to give more conformational freedom for the mesogenic units to form an ordered structure in melt, we prepared the following series of compounds and their ability to form mesophases were studied. These compounds contain one, two or three mesogenic units, biphenyl 4-oxybenzoate structure, which are attached to the benzene ring through the pentamethylene spacer;



As one can see from the above formulas, the compounds **RD** and **T** are of bent structures, *i.e.*, the mesogen-containing structures are not colinearly attached to the central benzene ring.

Experimental

Synthesis of the Compounds

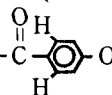
Biphenyl *p*-carbethoxybenzoate(1). *p*-Carbethoxybenzoyl chloride prepared from *p*-carbethoxybenzoic acid (6.0 g; 2.86×10^{-2} mole) and excess thionyl chloride was reacted with *p*-phenylphenol (4.6 g; 2.72×10^{-2} mole) in 15 ml of pyridine at room temperature for 12 hours. The precipitate was thoroughly washed with dil-NaOH solution and then with water. Biphenyl *p*-carbethoxybenzoate thus synthesized was recrystallized from acetone. The yield was 9.74 g (96.3%). This compound formed a nematic phase in melt (mp. 141°C) and its nematic-to-isotropic transition temperature, T_i , was 159°C.

Anal. Found C 72.98, H 5.08; Calcd. C 72.93, H 4.97%. ¹H-NMR spectrum (acetone-*d*₆/TMS); δ 1.25(t, 3H, CH₃), δ 3.85(q, 2H, CH₂), δ 6.85-7.80(m, 11H, Ar), δ 8.25(d, 2H, $-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\text{C}_6\text{H}_4-\text{O}-$). IR-spectrum (KBr); $>\text{C}=\text{O}$ stretching at 1760 cm⁻¹, aromatic $>\text{C}=\text{C}<$ stretching at 1620 cm⁻¹ and C-O stretching at 1200 cm⁻¹.

Biphenyl *p*-hydroxybenzoate(2). Biphenyl *p*-carbethoxybenzoate (1.0 g; 2.76×10^{-3} mole) was suspended in 15 ml of ethanol. While this solution is being refluxed, an aqueous KOH solution (0.31 g in 5 ml of H₂O) was added dropwise. The whole solution was further refluxed for additional 2 hrs. The solution was filtered hot and its pH was adjusted to 3.5 with addition of CH₃COOH. The solution was mixed with cold water precipitating the product, biphenyl

p-hydroxybenzoate. The precipitate was thoroughly washed with distilled water. Yield was 0.50 g (62%) and its mp. was 237°C. The compound was found to be pure enough by TLC and spectroscopic analyses and, therefore, employed in the next step without further purification.

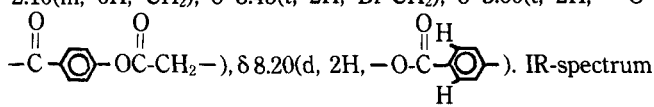
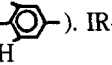
Anal. Found C 78.02, H 4.95; Calcd. C 78.62, H 4.83%. ¹H-NMR spectrum (acetone-*d*₆/TMS); δ 6.85-7.80(m, 11H, Ar),

δ 8.20(d, 2H, )-, δ 9.80(brs, 1H, OH). IR-spect-

rum (KBr); O-H stretching at 3500 cm⁻¹, >C=O stretching at 1760 cm⁻¹ and >C=C< stretching at 1620 cm⁻¹.

Biphenyl 4-(6-bromohexanoyl)oxybenzoate(3). 6-Bromohexanoyl chloride (0.55 g; 2.56×10⁻³ mole) was dissolved in 1.5 ml of pyridine and 1 ml of DMF, to which solution added was a pyridine (2 ml) solution of biphenyl *p*-hydroxybenzoate (0.6 g; 2.56×10⁻³ mole). The mixture was stirred overnight at room temperature. The whole mixture was poured into distilled water. The product was recrystallized from acetone (0.51 g, 54% yield). This compound was nematic (mp. 128°C) and isotropization (clearing) temperature was 138°C.

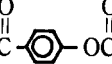
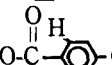
Anal. Found C 64.70, H 4.97, Br 17.20; Calcd. C 64.24, H 4.95, Br 17.11%. ¹H-NMR spectrum (CDCl₃/TMS); δ 1.40-2.10(m, 6H, CH₂), δ 3.45(t, 2H, Br-CH₂), δ 3.60(t, 2H, -O-

)-, δ 8.20(d, 2H, )-. IR-spectrum (KBr); aliphatic C-H stretching at 2950 cm⁻¹, >C=O stretching at 1760 cm⁻¹ and aromatic >C=C< stretching at 1620 cm⁻¹.

Biphenyl 4-(6-phenoxyhexanoyl)oxybenzoate(M).

Phenol (0.081 g; 6.42×10⁻⁴ mole), the compound 3(0.3 g; 6.42×10⁻⁴ mole) and K₂CO₃(0.106 g; 6.42×10⁻⁴ mole) were dissolved in 1.5 ml of DMF and 1.5 ml of pyridine. The mixture was rigorously stirred at 60°C for 15 hours under a N₂ atmosphere. The mixture was poured into water. The precipitate was collected on a filter and recrystallized from acetone. The yield was 2.55 g (85%). This compound was nematic in melt, mp. 140°C, clearing point, 150°C.

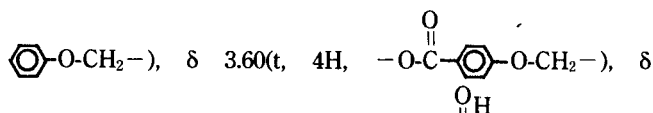
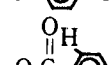
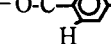
Anal. Found C 77.00, H 6.00; Calcd. C 77.50, H 5.90%. ¹H-NMR spectrum (CDCl₃/TMS); δ 1.40-2.50(m, 6H, CH₂),

δ 2.60(t, 2H, -O-CH₂-), δ 3.60(t, 2H, -O-C-)-, δ 6.80-8.10(m, 16H, Ar), δ 8.20(d, 2H, -O-C-)-).

IR-spectrum (KBr); >C=O stretching at 1760 cm⁻¹, C-H (-CH₂-) bending at 1460 cm⁻¹, C-O stretching at 1200 cm⁻¹.

1,4-Bis[6-{4-(biphenyloxycarbonyl)phenoxy}-6-oxohexyloxy]benzene(HD). This compound was prepared by the same procedure utilized for the synthesis of the above compound M. The only difference was in that hydroquinone was used instead of phenol. Two equivalent weight of 3 was used in the reaction. The compound was recrystallized from chloroform. The yield was 85%. This compound was nematic in melt, mp. 217°C, clearing temperature 241°C.

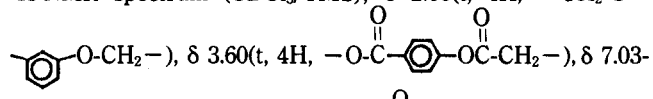
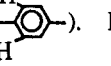
Anal. Found C 76.11, H 5.71; Calcd. C 76.16, H 5.72%. ¹H-NMR spectrum (CDCl₃/TMS); δ 2.60(t, 4H, -CH₂-O-

)-, δ 3.60(t, 4H, -O-C-)-, δ 7.02-8.54(m, 26H, Ar), δ 8.20(d, 4H, -O-C-)-. IR-spec-

trum (KBr); >C=O stretching at 1760 cm⁻¹, aromatic >C=C< stretching at 1620 cm⁻¹ and C-O stretching at 1200 cm⁻¹.

1,3-Bis[6-{4-(biphenyloxycarbonyl)phenoxy}-6-oxohexyloxy]benzene(RD). This compound was prepared from resorcinol and 3 using the exactly same synthetic method employed for the preparation of M and HD. The compound obtained was recrystallized from acetone. The yield was 75%, mp. 168°C.

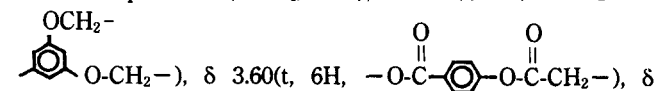
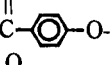
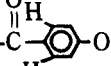
Anal. Found C 76.05, H 5.70; Calcd. C 76.16, H 5.72%. ¹H-NMR spectrum (CDCl₃/TMS); δ 2.60(t, 4H, -CH₂-O-

)-, δ 3.60(t, 4H, -O-C-)-, δ 7.03-8.50 (m, 26H, Ar), δ 8.20(d, 4H, -O-C-)-. IR-spectrum

(KBr); >C=O stretching at 1780 cm⁻¹, aromatic >C=C< stretching at 1620 cm⁻¹.

1,3,5-Tris[6-{4-(biphenyloxycarbonyl)phenoxy}-6-oxohexyloxy]benzene(T). Phloroglucinol(0.027 g; 2.14×10⁻⁴ mole), the compound 3(0.30 g; 6.42×10⁻⁴ mole) and Na₂CO₃ (0.07 g; 6.6×10⁻⁴ mole) were dissolved in 1.5 ml of DMF and 0.5 ml of pyridine. The mixture was maintained at 60°C for 15 hours under a N₂ atmosphere. The mixture was poured into water and the precipitate was collected on a filter and thoroughly washed with water. The recovered solid was found by TLC to be a mixture of three different compounds. The mixture was passed at room temperature through a styragel column in a Waters Associate Prep. 500 unit and only the desired fraction was collected. Eluent was 1,1,2,2-tetrachloroethane. After the solvent was evaporated, the final product was recrystallized from chloroform. The weight of the product thus obtained was 0.14 g (50% yield). Its IR and NMR spectra were consistent with the structure, mp. 207°C.

Anal. Found C 75.10, H 5.30; Calcd. C 75.70, H 5.70%. ¹H-NMR spectrum (CDCl₃/TMS); δ 2.60(t, 6H, -CH₂-O-

)-, δ 3.60(t, 6H, -O-C-)-, δ 7.02-8.54(m, 33, Ar), δ 8.20(d, 6H, -O-C-)-. IR-spec-

trum (KBr); >C=O stretching at 1780 cm⁻¹, aromatic >C=C< stretching at 1620 cm⁻¹, C-O stretching at 1200 cm⁻¹.

Thermal and Microscopic Characterization

Thermal behavior of the compounds was studied on a differential scanning calorimeter(DSC; Mettler TA 3000) and on a polarizing microscope(Leitz, Ortholux) equipped with a hot-stage(Mettler FP-2). Heating and cooling rates were maintained at 10°C/min. Thermodynamic parameters for thermal transitions were obtained from the area of the peaks that was calibrated against indium reference. Optical texture of the melts were observed with the polarizers cross-

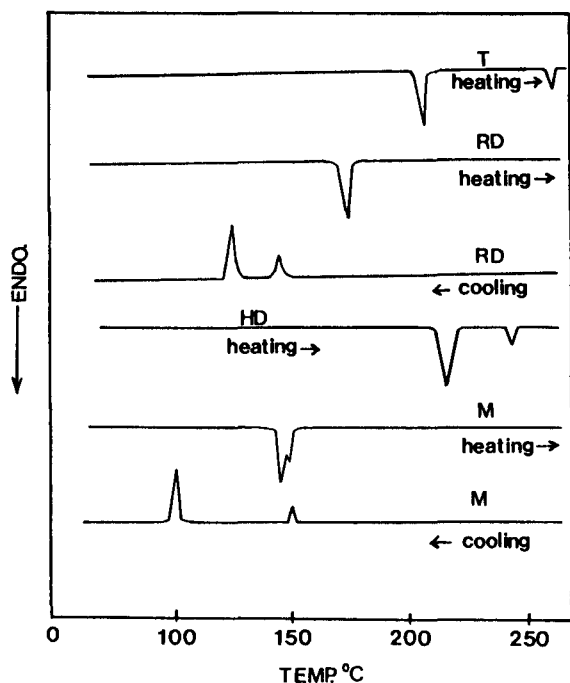
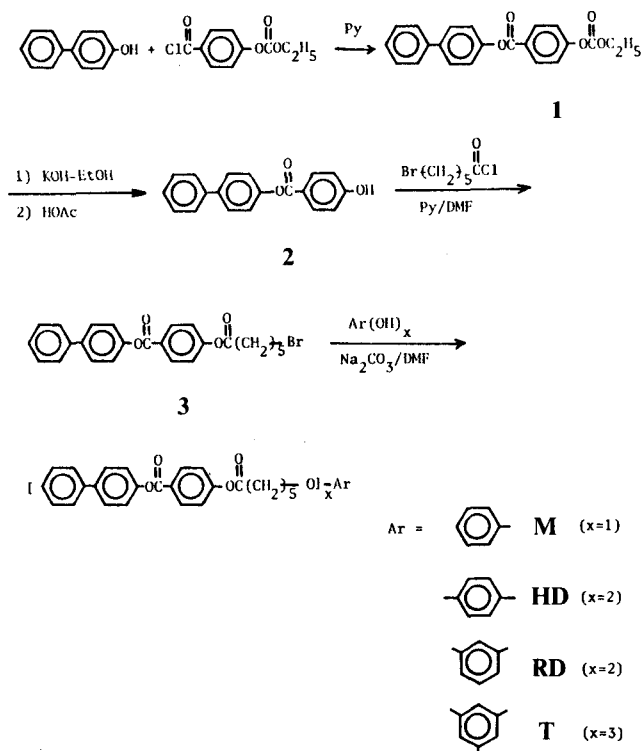


Figure 1. DSC thermograms of the compounds (N_2 atmosphere, heating and cooling rate; $10^\circ\text{C}/\text{min}$).

sed and the magnification was 200X.

Results and Discussion

The compounds consist of biphenylbenzoate ester mesogenic unit and the pentamethylene spacer. These compounds were synthesized following the reaction steps shown below:



Depending on the functionality and substitution position of

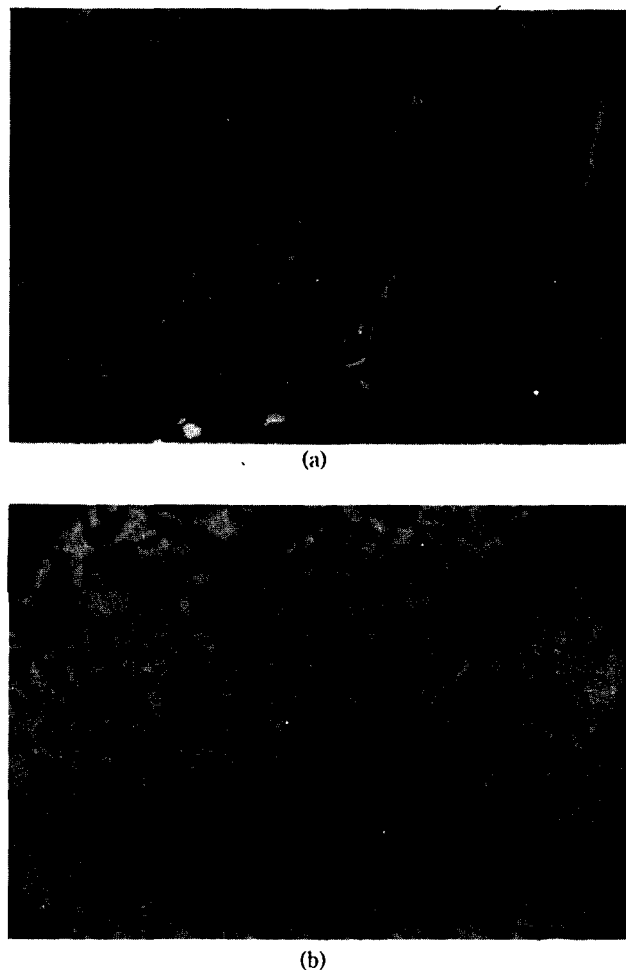


Figure 2. Photomicrographs of (a) **HD** taken at 231°C on heating and (b) of **RD** taken at 138°C on cooling (Magnification 200X).

the aromatic hydroxy compounds, we could obtain **M**, **HD**, **RD** or **T**. The structures of the final compounds were confirmed by elemental analyses, and IR and NMR spectra. Their purity was checked by TLC and liquid chromatography.

Figure 1 compares thermal behavior of the compounds by their DSC thermograms obtained in heating cycles. The thermograms of the two linear compounds, **M** and **HD**, show two endothermic transitions. The lower temperature ones correspond to crystal-to-mesophase transitions and the higher temperature ones to mesophase-to-isotropic phase transitions. Although the cooling DSC curves are not included, these transitions occurred reversibly indicating that the two compounds are enantiotropically thermotropic. Their optical textures were of typical nematics meaning that they form nematic phases in melts (Figure 2).

In contrast to **M** and **HD**, the compound **RD** exhibited only one endothermic transition on heating (Figure 1). It, however, revealed two exothermic transitions when the isotropic melt was cooled to room temperature. Observation of optical textures of the melts during heating and cooling confirmed the DSC results and leads to the conclusion that **RD** is monotropic. In other words, the compound **RD** melts into isotropic melt at 168°C and is not able to form a liquid crystalline phase on heating cycle. It, however, forms a liquid crystalline phase before crystallization on cooling its isotropic

melt. It was found microscopically that **RD** forms nematic phase on cooling the melt (Figure 2). On the other hand, the trimesogenic compound **T** was enantiotropic. In other words, it formed mesophases on heating the solid as well as on cooling its isotropic melt.

All of the present compounds contain the same mesogenic units, but their number and the way by which they are interconnected are different. The compound **M** is monomesogenic and, as expected, enantiotropic. The dimesogenic compounds **HD** and **RD** differ in that in the former the two mesogens are connected through the linear *p*-hydroquinone moiety, whereas in the latter they are connected through the bent resorcinol moiety. Such a bent connection seems to be enough to make **RD** monotropic in spite of the presence of polymethylene spacers between the mesogen and the resorcinol moiety. Linear connection of the two mesogenic units in **HD** certainly favors the enantiotropic formation of the nematic phase.

On the other hand, in our previous article¹, we described that the dimesogenic compound could not form a mesophase where the two mesogens are directly attached meta to each other, to the central benzene ring. It did not contain any spacer between the mesogenic group and the connecting benzene ring. This is in a great contrast to the present observation that the compound **RD** is monotropic. Although the structure of the mesogens of **RD** and the previous compounds are different, it appears that the presence of the pentamethylene spacer in the former favors the formation of a mesophase. The presence of a long polymethylene spacer(s) may help to accommodate a certain degree of nonlinearity within a molecule, if it can take a variety of conformations by rotation around the C-C single bonds to compensate the nonlinear, structural orientation of the two mesogens. We reported earlier that the presence of flexible spacer favors the mesophase-forming capability of main chain, thermotropic polyesters.¹³⁻¹⁵

Attachment of three mesogenic units somehow improves the molecule's ability to form mesophases in melt and, therefore, the compound **T** is enantiotropic. Certainly the tri-branched shape of **T** allows the mesogens or the molecule to form ordered alignment in melt. Competitive attractive interactions among the three mesogens directioned angled should act unfavorably in the formation of mesophases. We¹ indeed reported earlier that the trimesogenic compound is not mesomorphic when the mesogens are directly bound at 1,3,5-positions of the central benzene ring. The fact that the compound **T** is enantiotropically mesomorphic again implies that the polymethylene spacer may be able to decouple the motions of the linked mesogens and give a higher level of freedom to form ordered domains in melt. The compound **T** is different in structure when compared with discotic compounds. The latter are usually made of a planar rigid core surrounded by long alkyl chains. This structural difference could be the reason why the compound **T** is not discotic, but nematic.

Comparison of melting points, T_m , and the values of heat of melting ΔH_m , leads to an interesting finding (Table 1). For the both quantities, the di- and trimesogenic compounds reveal higher values than the monomesogenic compound, **M**. Among the di- and trimesogenic compounds, the compound having a linear geometry, *i.e.*, **HD**, possesses the highest va-

Table 1. Thermal and Liquid Crystalline Properties of the Compounds

Compounds	T_m , °C ^a	ΔH_m , KJ/mole	T_i , °C ^b	ΔH_i , KJ/mole	LC ^c
M	140	16.8	150	8.9	nematic
HD	217	23.1	241	7.9	nematic
RD	168	17.4	144 ^d	0.38 ^d	monotropic (nematic)
T	207	18.7	263	1.97	nematic

^aMelting temperature. ^bIsotropization or clearing temperature.

^cLiquid crystallinity. ^dData obtained from the cooling DSC curve.

lues, which is a strong indication that the most efficient molecular packing in the solid state is achieved for this compound resulting in the highest lattice force and intermolecular attraction.

As far as the isotropization temperature, T_i , is concerned, T_i (241°C) of the linear dimesogenic compound, **HD**, is significantly higher than that(150°C) of the monomesogenic compound, **M**. This can be rephrased by the expression that thermal stability of the mesophase of **HD** is much better than that of **M**. The values of isotropization enthalpy, ΔH_i , of the two compounds, however, are not much different and are 8.9 and 7.9 KJ/mol, respectively. As expected, the ΔH_i value(0.38 KJ/mol) for monotropic **RD** obtained from the cooling DSC curve is significantly lower than those for **M** and **HD**. As mentioned above, this compound is able to form mesophase only in a supercooled state. The relative magnitudes of ΔH_i values for **M** and **HD** against their corresponding ΔH_m values are unusually high and are 53 and 34%, respectively. For monomesogenic compounds, ΔH_i value is usually in the range of 3-5% of ΔH_m value.¹⁶ On the other hand, it ranges 5-15% of ΔH_m for other dimesogenic compounds.^{2-4,7,17,18} The reasons for unusually high values for **M** and **HD** are not yet clear.

Conclusion

Following conclusions can be drawn from the results of the present study:

- 1) The presence of mesogenic unit in a molecule does not guarantee for the compound to become liquid crystalline.
- 2) When a compound is dimesogenic, *i.e.*, contains two mesogenic units, linear molecular shape is prerequisite to be mesomorphic. The flexible spacer, however, seems to improve capability of a bent compound to form a mesophase.
- 3) Even the trimesogenic and star-shaped compound is able to form a mesophase again indicating that the presence of a spacer helps mesophase-forming ability.

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References

1. J. -I. Jin, C. -S. Kang, and B. Y. Chung, *Bull. Korean*

- Chem. Soc., **11**, 245 (1990).
2. J. -I. Jin and J. -H. Park, *Mol. Cryst. Liq. Cryst.*, **110**, 293 (1984).
 3. J. -I. Jin, C. -M. Sung, and B. -W. Jo, *Bull. Korean. Chem. Soc.*, **6**, 40 (1985).
 4. J. -I. Jin, H. -T. Oh and J. -H. Park, *J. Chem. Soc., Perkin Trans. II*, 343 (1986).
 5. A. C. Griffin and T. R. Britt, *J. Amer. Chem. Soc.*, **103**, 4957 (1981).
 6. J. C. W. Chien, R. Zhou, and C. P. Lillya, *Macromolecules*, **20**, 2340 (1987).
 7. J. -I. Jin, H. -S. Kim, J. -W. Shin, B. Y. Chung, and B. -W. Jo, *Bull. Korean Chem. Soc.*, **11**, 209 (1990).
 8. J. -I. Jin, E. -J. Choi, S. -C. Ryu, and R. W. Lenz, *Polym. J. Jpn.*, **18**, 63 (1986).
 9. J. A. Buglione, A. Roviello, and A. Sirigu, *Mol. Cryst. Liq. Cryst.*, **106**, 169 (1984).
 10. Y. Harada and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **63**, 1691 (1990). and earlier papers.
 11. S. J. Huang, J. A. Feldman, and J. L. Cercena, *Polymer Preprints, Amer. Chem. Soc.*, **30(1)**, 348 (1989).
 12. S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, **9**, 471 (1977).
 13. W. Zhang, J. -I. Jin, and R. W. Lenz, *Makromol. Chem.*, **189**, 2219 (1988).
 14. A. K. Rao, J. -I. Jin, and R. W. Lenz, *Polymer Preprints, Amer. Chem. Soc.*, **28(2)**, 234 (1987).
 15. J. -I. Jin, E. -J. Choi, and S. -C. Ryu, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 241 (1987).
 16. G. W. Gray and P. A. Winsor, eds., 'Liquid Crystals & Plastic Crystals', Ellis Horwood Ltd., London, Vol. 2, Chapter 10 (1974).
 17. J. -I. Jin, J. -S. Kang, B. -W. Jo, and R. W. Lenz, *Bull. Korean Chem. Soc.*, **4**, 176 (1983).
 18. J. -I. Jin, Y. -S. Chung, R. W. Lenz, and C. Ober, *Bull. Korean Chem. Soc.*, **4**, 143 (1983).

¹³C-NMR Study of the Application of the "Tools of Increasing Electron Demand" to the 8-Aryl-tricyclo[3.2.1.0^{2,7}]oct-8-yl Cations

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The ¹³C-NMR shifts of a series of para-substituted 8-aryl-tricyclo[3.2.1.0^{2,7}]oct-8-yl and 9-aryl-tricyclo[3.3.1.0^{2,8}]-non-9-yl cations were measured in FSO₃H/SO₂ClF at -90°C in order to examine whether the ρ^{C+} values can be used as a measure of the geometric influence on the charge delocalization resulting from σ conjugation in rigid tricyclopentylcarbiny cations. Plot of the Δδ^{C+} shifts against the σ^{C+} constants revealed excellent linear correlation. The 8-aryl tricyclooctyl systems yielded a ρ^{C+} value of -5.00 with r=0.9962. Previous investigation of the 9-aryl-tricyclononyl systems gave a correlation coefficient of r=0.9948 with a slope of ρ^{C+}=-4.95. A fair parallelism exists between the results of ¹⁹F-NMR studies and the change of ρ^{C+} value in these cations. Consequently, it is established that the ρ^{C+} value can be used to explain the mechanism of charge stabilization of the rigid cyclopropylcarbiny cation such as tricyclo[3.2.1.0^{2,7}] oct-8-yl cation.

Introduction

For many years solvolysis rates have been utilized to arrive at an understanding of the factors influencing the stability of carbonium ions. A remarkably consistent body of knowledge has been built up in this way. One possible difficulty has been the necessity of comparing the rate with a suitable model system. Occasionally this can lead to ambiguities. The tool of increasing electron demand appears to minimize such ambiguities.¹

Although this tool combined with the ¹³C-NMR method should give similar unambiguous answers about the structural effect on stability of the carbocation in superacid media, often conflicting interpretation has been made.² The ¹³C-NMR chemical shifts for the corresponding carbon in carbocation may be taken as a measure of the charge delocalization into the molecular structure.

Accordingly, numerous attempts seeking to correlate the ¹³C NMR chemical shifts for the cationic centers of the substituted benzylic carbocations with Hammett-Brown σ⁺ constants have been reported.³

Application of the tool of increasing electron demand to the study of fully formed cations in superacids requires the plotting of the ¹³C chemical shifts against some quantitative measure of electron demand. The use of electrophilic substituent constant σ^{C+} has been shown to be inappropriate for this purpose.

Therefore, Brown and coworkers developed the following modified Hammett-Brown equation of the form

$$\Delta\delta^{C+} = \rho^{C+} \cdot \sigma^{C+}$$

where Δδ^{C+} is the difference between the cationic carbon chemical shift for the unsubstituted benzylic carbocation and that for the substituted carbocationic species, i.e., Δδ^{C+}=