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液晶材料研究

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計畫主持人：余良杰

執行單位：淡江大學化學系

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雙溴取代的奈環衍生物與對乙烯砒砒及對苯乙烯

經由黑克反應生成的高共軛分子

例用金屬鈀(Pd)之催化偶合反應對 1,6 與 2,6 溴化雙取代的環進行單一步驟與雙步驟的黑克反應(Heck reaction)，藉由溶劑的控制可獲得對稱或不對稱之雙取代化合物。在 1,6 雙溴系統中，在(o-tol)₃P/Et₃N 存在下，高產率的 6 位置單取代生成，且一定接在 6-的位置，不會有雙取代物；而在(o-tol)₃P/Et₃N/MeCN 系統中則有 1,6 雙取代一步生成，但有意想不到的 1-位置溴之脫去。我們嘗試了乙烯砒砒及乙烯苯衍生物，均得到類似的結果。然在 2,6 雙溴系統中，不論 Ph₃P 或 (o-tol)₃P，當 Et₃N/MeCN 溶劑量少時，產物均為雙取代，不會有單取代物。單取代物只有在 Et₃N/MeCN 溶劑量夠多時才會生成。這些高共軛分子產物之螢光強度約為 Stilbene 的一百至一千倍，且其中一些較像桿狀的分子具高溫液晶的特質。此外藉由核磁共振光譜追蹤此類分子之光化學反應，順式光產物明顯減少，我們認為此與其為高螢光強度有關。此系列分子均可做為非線性光學、螢光液晶質與光電的材料。

關鍵詞：黑克反應. 高共軛分子. 螢光

Highly Conjugated Molecules from Dibromonaphthyl Derivatives And 4-Vinylpyridine or 4-Acetoxy styrene by Heck Reaction

Palladium catalyzed coupling for 1,6- and 2,6-dibromonaphthyl derivatives with 4-vinylpyridine or 4-acetoxy styrene underwent mono- and bis-arylvinylation dependent on the choice of reaction conditions. For the 1,6-dibromoarenes, the monoarylvinylation derivative, shown to occur at position-6, was the sole product in the presence of (o-tol)₃P/Et₃N, and the bisarylvinylation derivative was the major product and accompanied by a minor product, arylvinylation at position-6 and reduced at position-1, in the presence of (o-tol)₃P/Et₃N/MeCN. For the 2,6-dibromoarenes, the bisarylvinylation derivative was the sole product in the presence of either Ph₃P or (o-tol)₃P, provided with a small volume of Et₃N/MeCN solvent, and the mono-arylvinylation derivative was the major product with larger solvent volume and higher haloarene ratio. Fluorescence intensities of 2,6-bisarylvinylation products were two to three orders of magnitude higher than that of stilbene. Nematic phases, at relative high temperatures, were observed for some of the rod-like molecules. Shown by ¹H NMR study that, at the photostationary state of isomerization, smaller fractions of cis-form were obtained for molecules exhibited larger fluorescence quantum yields. The results present here are beneficial to the pursuit of nonlinear optical materials, fluorescent mesogens, photo- and electro-active materials.

Keywords : Heck reaction. Highly Conjugated Molecules. Fluorescence.

苯乙醯基酯液晶

本研究的目的是探討以苯乙醯基酯(phenacyl ester, -ph-CO-CH₂-O-CO-)為條形分子之部份骨架時對液晶相的影響。其中包含兩個系列：系列一為 4'-(alkyloxyacetyl)phenyl 4-alkyloxybenzoate, C_mOAPC_n；系列二為 α, ω -bis[4-(4-alkyloxybenzoyloxy) benzoylmethylene]dioate, C_mOAPC_nDAPOC_m。

(1)系列一：m=4, n=1, 4 呈現雙向(enantropic)向列相(nematic phase)，n=1 和 n=4, 8, 10 分別呈現單向(monotropic)和雙向層相 A (smectic A)；m=8, n=1, 2 呈現雙向向列相，n=1~14 均呈現雙向層相 A，n=6~14 呈現雙向層相 C，n=3~14 呈現單向層相 E；m=12, n=1~9 呈現雙向層相 A，n=6~12 呈現雙向層相 C，n=3, 4 和 5~12 分別呈現單向和雙向層相 E。此系列的熔點在 65~75°C，澄清點(clearing point)在 110~130°C，液晶相溫度範圍約 50~70°C。(2)系列二中兩端相同的 C_mOAPC_nDAPOC_m：m=8, n=3~9 呈現雙向向列相，n=4, 6~13 和 n=5 分別呈現單向和雙向層相 A，n=9 呈現單向層相 C；m=12, n=9~11 呈現雙向向列相，n=11, 12, 14 呈現雙向層相 A，n=4~10, 12, 14 呈現雙向層相 C，n=9 呈現單向層相 x；n=9, m=1~10, 12 均呈現雙向向列相，m=4~9 呈現雙向層相 A，m=4 和 m=5~10, 12 分別呈現單向和雙向層相 C，m=9, 10, 12 呈現單向層相 X。兩端不同的 C_mOAPC_nDAPOC_p，m=8, p=12, n=8 呈現雙向向列相，n=8, 12 均呈現雙向層相 A 和單向層相 C。此系列的熔點在 120~165°C，澄清點在 140~200°C，液晶相溫度範圍約 10~40°C。

以 X-射線單晶繞射測量並解出 α, ω -bis[4-bromobenzoylmethylene]octa-nedioate 的晶體結構，得知苯乙醯基酯之乙醯基、氧原子和酯基、碳原子個別所構成面的夾角為 79.0°，證實其存在淨偶極矩(net dipole moment)，而此可能為乙醯基酯當連結基時比醚類或酯類有較寬的液晶相溫度範圍之原因。此官能基的氫譜為 5.35ppm(2H, s, -CO-CH₂-O-CO-)和紅外線光譜的 C=O 伸縮頻率分別為 1735cm⁻¹和 1701 cm⁻¹附近。

兩系列的澄清點轉移溫度出現奇偶效應(odd-even effect)，其中，含偶數碳分子的轉移溫度較含奇數碳高且改變 spacer 鏈長較改變尾鏈鏈長顯著，推測因改變 spacer 鏈長的碳氫鏈在全反態(all-trans form)時，其兩核心部份(cores)的關係是，偶數碳時約略平行而奇數碳時呈彎曲狀。

關鍵詞：苯乙醯基酯液晶

Phenacyl Ester Liquid Crystals

Mesophase behaviors of rod-like molecules with phenacyl ester were studied. Series I, namely the 4'-(alkanoyloxyacetyl)phenyl 4-alkoxybenzoate (C_mOAPC_n), C_4OAPC_n ($n=1,4,8$ and 10): exhibiting enantiotropic nematic (N) phase for $n=1$ and 4 , monotropic smectic A (S_A) phase for $n=1$, enantiotropic S_A for $n=4,8$ and 10 ; while C_8OAPC_n ($n=1\sim 14$): showing enantiotropic N for $n=1$ and 2 , enantiotropic S_A for $n=1\sim 14$, enantiotropic smectic C (S_C) phase for $n=6\sim 14$, monotropic smectic E (S_E) phase for $n=3\sim 14$; while $C_{12}OAPC_n$ ($n=1\sim 12$): presenting enantiotropic S_A for $n=1\sim 9$, enantiotropic S_C for $n=6\sim 12$, monotropic S_E for $n=3$ and 4 , and enantiotropic S_E for $n=5\sim 12$. The melting points were about $65\sim 75^\circ\text{C}$, clearing points were about $110\sim 130^\circ\text{C}$, and the temperature ranges of mesophase for this series were about $30\sim 50^\circ\text{C}$.

Series II, namely the α, ω -bis[4-(4-alkoxybenzoyloxy)benzoylmethylene]alkanedioate ($C_mOAPC_nDAPOC_m$), $C_8OAPC_nDAPOC_8$ ($n=3\sim 13$): exhibiting enantiotropic N for $n=3\sim 9$, enantiotropic S_A for $n=4$ and $n=6\sim 13$, monotropic S_A for $n=5$, and monotropic S_C for $n=9$; while $C_{12}OAPC_nDAPOC_{12}$ ($n=4\sim 12$ and 14): showing enantiotropic N for $n=9\sim 11$, enantiotropic S_A for $n=11,12$ and 14 , enantiotropic S_C for $n=4\sim 10,12$ and 14 , and monotropic smectic X (S_X) phase for $n=9$; while $C_mOAPC_nDAPOC_m$ ($m=1\sim 10$ and 12): All eleven members presented enantiotropic N, enantiotropic S_A for $m=4\sim 9$, monotropic S_C for $m=4$, enantiotropic S_C for $m=5\sim 10$ and 12 , and enantiotropic S_X for $m=9,10$ and 12 ; while $C_8OAPC_nDAPOC_{12}$ ($n=8$ and 12): exhibiting enantiotropic S_A and monotropic S_C for $n=8$ and 12 , and enantiotropic N for $n=8$. The melting points were about $120\sim 160^\circ\text{C}$, clearing points were about $140\sim 200^\circ\text{C}$, and the temperature ranges of mesophase for this series were about $10\sim 40^\circ\text{C}$. The crystal structure of α, ω -bis[4-bromobenzoylmethylene]octanedioate was confirmed by X-ray single diffraction measurements. The dihedral angle between the best least-square planes of $-(C=O)-C-O-$ group and $-C-O-(C=O)-$ group is 79.0° . It exhibited a net dipole moment, thus it maybe a reason which acetyl group ester as linking group represents the higher temperature ranges of mesophase than ether or ester one. $^1\text{H-NMR}$ spectrum of phenacyl ester (δ , ppm): 5.35 ($2\text{H}_s, -\text{CO}-\text{CH}_2-\text{O}-\text{CO}-$). IR spectrum of phenacyl ester, cm^{-1} : 1735 ($-\text{CO}-\text{O}-$), near 1701 ($-\text{CO}-\text{CH}_2-$).

The temperatures of cleaning points of series I and series II show a odd-even effect with even members have the higher than the odd members, varying the length of the spacer were more pronounced than varying the length of terminal chain. We assume the spacer exists in an all trans conformation. Thus for even membered spacers the two mesogenic moieties are almost parallel whereas for odd membered spacers they are bend.

Keyword : Phenacyl ester, Mesophase