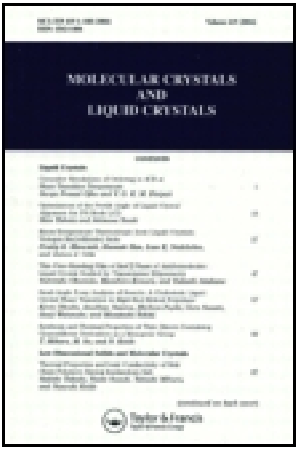

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Synthesis and Structure of 1,4-Diazabutadiene Liquid Crystals

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Synthesis and Structure of 1,4-Diazabutadiene Liquid Crystals

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Nine 1,4-diazabutadiene compounds, Ar-N=C(R)-C(R)=N-Ar, R=H, Me; Ar= $H_{2n+1}C_nO-C_6H_4$, 2,4-$(H_9C_4O)(Me)-C_6H_3$, were synthesized and their liquid crystal properties were studied through thermal polarizing microscopy. The X-ray single crystal structure of compound **9** (Ar-N=C(H)-C(H)=N-Ar, Ar=2,4-$(Me)(H_9C_4O)C_6H_3$) was tested. It is a monoclinic crystal system, space group $P2_1/C$ with the unit cell parameters: a=7.0703(3)Å, b=8.6741(4)Å, c=18.3115(8)Å, β =95.392(1)°. V=1114.57(9)Å^3, z=2, Dc=1.134 Mg/m^3, R=0.0490, Rw=0.1237.

Keywords: liquid crystal; 1,4-diazabutadiene derivatives; diimine; molecular structure

INTRODUCTION:

Designing and synthesis of new types of liquid crystalline materials is one of the most important jobs in this field, as it can supply target molecules for the mesophases behavior investigation and also can enrich the structure-property relationships of liquid crystalline. 1,4-

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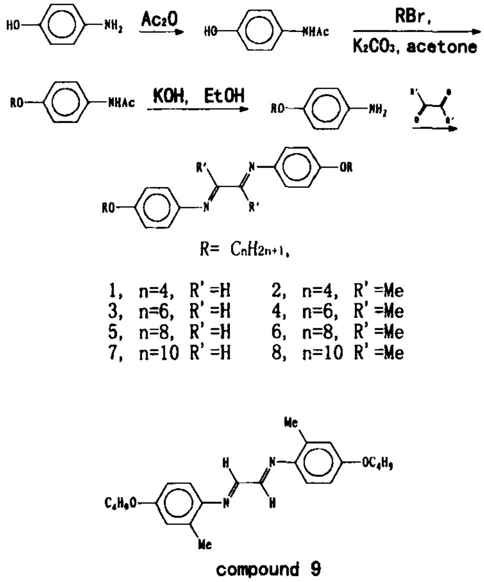
Diazabutadiene compounds have been used widely as ligands for the late-transition metal catalysts of olefin polymerization[1-4] and as intermediates for organic synthesis[5,6]. Here we reported first time this structure of 1,4-diazabutadiene using as building block in the liquid crystal materials. Nine Diimine compounds were synthesized and their mesophase behaviors were investigated through thermal polarizing microscopy. Single crystal structure of one compound was reported. Scheme 1 listed the synthetic route of the compounds.



SCHEME 1, Synthesis of the 1,4-Diazabutadiene Liquid Crystals

EXPERIMENTAL

Instruments:

The IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were measured on Brucker ACE-200 and ACE-300 spectrometers. The corresponding frequencies for ^{13}C NMR spectra were at 50.32, 75.47MHz for the respective spectrometers.

Synthesis of *p*-alkoxylaniline[7].

0.1 mol of aminophenol was dissolved into 30 ml of H_2O, 0.11 mol of acetic anhydride was slowly added with vigorous stirring and then heated in hot water for another 30 min. After reaction finished, the mixture was poured into 500g of ice. The precipitate was collected through filtration and washed by cold water and dried in the air.
The above acetanilide(0.1 mol), 0.1 mol of RBr, 0.15 mol of K_2CO_3 were added to 50 ml of acetone and refluxed 24h with stirring. After reaction finished, the solid was filtered out and the filtrate was concentrated to dryness. Then 0.20 mole of KOH and 50 ml of EtOH were added and refluxed 24h under N_2 gas. When reaction was complete, the cooled mixture was extracted 3 times with 100 ml ethyl ether, and dried with $MgSO_4$. The ether solution was concentrated to dryness and the residue was distilled under vacuum. About 0.04 mol of substituted aniline was collected and kept in cold. The overall yield from *p*-aminophenol is about 30-40 %.
From the above described method, 4-butyloxy aniline, 2-methyl-4-butyloxyaniline, 4-hexyloxyaniline, 4-octyloxyaniline and 4-decayloxyaniline were prepared.

p-$C_4H_9OC_6H_4NH_2$,
^{1}H NMR: 0.96(t, 3H);1.4-1.6(m, 2H), 1.7-1.9(m, 2H); 3.9(t, 2H); 3.4(w, 2H, NH_2), 6.6(d, 2H, Ar-H); 6.7(d, 2H, Ar-H). ^{13}C NMR: 13.6, 19.0, 31.2, 68.1, 115.3, 116.1, 139.8,151.9.

Syntheses of the 1,4-Diazabutadiene Compounds:

20 mmol of substituted aniline and 10 mmol of glyoxal (or 2,3-butanedione) was added to 10 ml of EtOH with stirring; several drops of formic acid was added and stirred overnight. The bright-yellow solid was got through filtration and crystallized from EtOH. The product was dried in high vacuum. Yield, 80-90%. From this method, nine 1,4-

diazabutadiene derivatives were synthesized. The physical data of compound **1**, **2** are listed.

$H_9C_4OC_6H_4$-N=C(H)-C(H)=N-$C_6H_4OC_4H_9$, (**1**)
IR (KBr, cm^{-1}): 2953, 2939, 2869, 1605, 1753, 1505, 1471, 1282, 1247, 1170. ^1H NMR($CDCl_3$): 0.99 (t, 6H), 1.4-1.6 (m, 4H), 1.7-1.9 (m, 4H), 4.0 (t, 4H), 6.94 (d, 4H, Ar-H), 7.33 (d, 4H, Ar-H), 8.42 (s, 2H, H-C=N). ^{13}C NMR($CDCl_3$): 13.8, 19.2, 31.2, 68.0, 115.1, 123.0, 142.8; 157.4,159.4. Analytical for $C_{22}H_{28}O_2N_2$, Found (calcd.): C, 74.77(74.96); H, 8.02(8.02); N, 7.75(7.95).

$H_9C_4OC_6H_4$-N=C(Me)-C(Me)=N-$C_6H_4OC_4H_9$ (**2**).
IR(KBr, cm^{-1}): 2956, 2934, 2872, 1637, 1604, 1503, 1475, 1244, 1207, 1121, 1108. ^1H NMR($CDCl_3$): 0.96 (t, 6H), 1.4-1.6 (m, 4H), 1.6-1.8 (m, 4H), 2.15 (s, 6H, CH_3-C=N), 3.95 (t, 4H), 6.72 (d, 4H, Ar-H), 6.88 (d, 4H, Ar-H). ^{13}C NMR($CDCl_3$):13.9, 15.4, 19.3, 31.4, 68.0,114.8, 120.6, 143.9, 156.0, 168.4. Analytical for $C_{24}H_{32}O_2N_2$, Found (Calcd.): C, 75.78 (75.75); H, 8.49 (8.49); N, 7.29 (7.36).

X-ray Crystallographic Analysis.

Diffraction data were measured at 298K on a Nonius CAD-4 diffractometer with graphite-monochromatized Mo Ka radiation. Cell parameters were determined by a least-squares fit on 25 reflections. Intensity data were corrected for absorption on the basis of an experimental Ψ rotation curve. The refinement procedure was by a full-matrix least-squares method, including all the non-hydrogen atoms anisotropically. Hydrogen atoms were fixed at the ideal geometry and a C-H distance of o.1nm; their isotopic thermal parameters were fixed to the values of the attached carbon atoms at the convergence of the isotropic refinement. Computing programmes are from the NRCC SDP VAX package. Crystallographic data of compound **9** are listed on Table 1.

TABLE 1, X-ray Single Crystal Parameters of Compound **9**:
Ar-N=C(H)-C(H)=N-Ar, Ar=2,4-(Me)($H_9C_4O)C_6H_3$.

Empirical formula	$C_{24}H_{32}N_2O_2$
Formula weight	380.25
Temperature	295(2)K
Wavelength	0.71073Å
Crystal system	Monoclinic
Space group	$P2_1/C$
Unit cell dimensions	a = 7.0703(3) Å
	b = 8.6471(4) Å beta = 95.329(1)°
	c = 18.3115(8)Å
Volume z	1114.57(9)$Å^3$, 2
Density(calculated)	1.134Mg/m^3
Absorption coefficient	0.072mm^{-1}
F(000)	412
Crystal size	0.40 X 0.17 X 0.16 mm
Θ range for data collection	2.23 to 27.49 °
Limiting indices	$-9 \leqslant h \leqslant 9$,
	$-10 \leqslant k \leqslant 11$,
	$-23 \leqslant l \leqslant 23$
Reflection collected	8224
Independent reflections	2563(R_{int} = 0.0280)
Absorption correction	Sadabs
Max. and min. Transmission	0.9280 to 0.6151
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2563/0/192
Goodness-of-fit on F2	1.023
Final R indices[I>2 δ (I)]	R1 = 0.0490, wR2 = 0.1237
R indices (all data)	R1 = 0.0652 wR2 = 0.1355
Extinction coefficient	0.023(4)
Largest diff. Peak and hole	0.190 and -0.176 $eÅ^{-3}$

RESULTS AND DISCUSSION.

Mesophase behavior of the compounds.

The phase behaviors of the compounds were studied using polarizing microscopy with heating-plat. As the shape of molecular geometry is rod-like and these molecules are conjugated, the existences of liquid crystal behavior would be expected. Table 2 listed the phase transformation results. Compound **1**, **3**, **5** show liquid crystal phase, however, the temperature rage is narrow, about 10°C. Compound **2**,**4**,**6** have no liquid crystal properties. From the molecular structure of Ar-N=C(R)-C(R)=N-Ar, R=H, or Me, we know that these two groups of compounds have similarity in structure, except R group. When R=Me, the width of the compound is larger than that of R=H; such as compound **1** and compound **2**, the length of the two compounds is the same. So the conclusion is that the ratio of length/width of molecular is the key factor to the liquid crystal properties. Compound **9** which has no liquid crystal phase, is the same length with compound **1**, but has a methyl group on the benzene ring, which can also increase the width of molecule. From the X-ray crystal structure of compound **9** we got the results. The synthesis of new type of 1,4-diazabutadiene compounds and their metal complexes, their liquid crystal properties investigation will report soon.

TABLE 2, Mesophase and Transition Temperature(°C) Of the Synthesized 1,4-Diazabutadiene Molecules, $H_{2n+1}C_nO\text{-}C_6H_4\text{-}N{=}C(R')\text{-}C(R'){=}N\text{-}C_6H_4\text{-}OC_nH_{2n+1}$

Compound	Mesophase behavior[a]
1(n=4, R'=H)	C -130-S_B-140-Iso
2(n=4, R'=Me)	C-150-Iso
3(n=6, R'=H)	C-112-S_B-122-Iso
4(n=6, R'=Me)	C-132-Iso
5(n=8, R'=H)	C-112-S_B-122-Iso
6(n=8, R'=Me)	C-130-Iso
7(n=10, R'=H)	C-112-S_B-120-Iso
8(n=10, R'=Me)	C-126-Iso
9(n=4, R'=H, Ar=C_6H_3Me)	C-108-Iso

[a] C: crystal, Iso: isotropic, S_B: Smectic B.

X-ray crystal results.

Bond parameters of compound **9** are collected in Table 3. Figure 1 is the ORTEP drawing of this compound. The bond length and angel are comparable to classic data[9]. Bond length of N(1)-C(1) is 1.273Å, C(1)-C(1A), 1.457Å, and C(2)-N(1) , 1.420 Å. Bond angel of C(1)-N(1)-C(2) is 118.71 and that of N(1)-C(1)-C(1)#1 is 120.5.

Table 3, Bond Lengths[Å] and Angles[°] for Compound **9**.

O(1)-C(5)	1.372(2)	O(1)-C(9)	1.435(2)
N(1)-C(1)	1.273(2)	N(1)-C(2)	1.420(2)
C(1)-C(1)#1	1.457(3)	C(2)-C(3)	1.388(2)
C(2)-C(7)	1.411(2)	C(3)-C(4)	1.388(2)
C(4)-C(5)	1.391(2)	C(5)-C(6)	1.390(2)
C(6)-C(7)	1.398(2)	C(7)-C(8)	1.503(2)
C(9)-C(10)	1.516(2)	C(10)-C(11)	1.507(3)
C(11)-C(12)	1.520(3)		

C(5)-O(1)-C(9)	117.89(12)	C(1)-N(1)-C(2)	118.71(13)
N(1)-C(1)-C(1)#1	120.5(2)	C(2)-C(3)-C(7)	119.34(12)
C(3)-C(2)-N(1)	122.86(12)	C(7)-C(2)-N(1)	117.74(12)
C(2)-C(3)-C(4)	121.80(14)	C(3)-C(4)-C(5)	118.94(14)
O(1)-C(5)-C(6)	115.16(12)	O(1)-C(5)-C(4)	124.72(13)
C(6)-C(5)-C(4)	119.66(13)	C(7)-C(6)-C(5)	121.85(13)
C(6)-C(7)-C(2)	118.33(13)	C(6)-C(7)-C(8)	121.18(13)
C(2)-C(7)-C(8)	120.49(12)	O(1)-C(9)-C(10)	107.47(13)
C(11)-C(10)-C(9)	113.6(2)	C(10)-C(11)-C(12)	113.3(2)

The ORTEP drawing of compound **9** shows that 1,4-diazabutadiene moiety exists as Z,Z conformation, and the geometry of the molecule is rod-like shape. This result further proved our prediction.

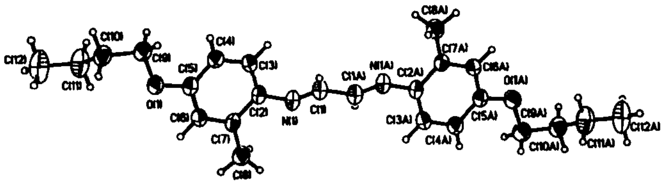


Figure 1, ORTEP drawing of compound 9

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