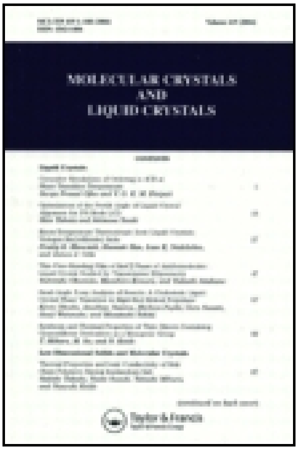

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Dipole Moments, ESCA, Theoretical Calculations and Gas-Liquid Chromatographic Studies on Some P-P′-Derivatives of Benzylidene Aniline

G. M. Janini [a] , G. H. Hovakeemian [a] , A. Katrib [a] , N. J. Fitzpatrick [a b] & S. Attari [a]
[a] Department of Chemistry, Kuwait University, Kuwait
[b] Chemistry Department, University College, Belfield, Dublin, Ireland

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Dipole Moments, ESCA, Theoretical Calculations and Gas-Liquid Chromatographic Studies on Some *P-P*'-Derivatives of Benzylidene Aniline

G. M. JANINI, G. H. HOVAKEEMIAN, A. KATRIB, N. J. FITZPATRICK† and S. ATTARI

Department of Chemistry, Kuwait University, Kuwait

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Pairs of nematic liquid crystals of the Schiff's base type that are identical in length-to-breadth ratios, but differ in the location of the atoms in the central linkage were synthesized. Combined ESCA and theoretical calculations revealed that the nature of the highest occupied molecular orbital is different being more localized on one atom in one of the pair but more delocalized in the other. The compound with the delocalized orbital has the higher nematic-isotropic transition temperature. Dipole moment measurements in support of the proposed electronic structures are presented. The polarity difference was revealed when these compounds were separated by gas-liquid chromatography on a polar column with elution in the order of solute polarity.

INTRODUCTION

Thermal stability of the nematic liquid crystal mesophase has generally been characterized in terms of the nematic-isotropic transition temperature (the clearing point). Comparison of the clearing points of analogous chemical structures with systematic variations have revealed considerable knowledge of the effect of molecular structure on the

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†Permanent Address: Chemistry Department, University College, Belfield, Dublin, Ireland

macroscopic behavior of liquid crystals, but has done little to advance our knowledge of liquid crystals on the molecular level.[1] It has been established that the thermal stability of the nematic state is mainly affected by the molecular shape (length-to-breadth ratio), the anisotropy of molecular polarizability and to a lesser extent by the molecular dipole moment. The contribution of each effect to thermal stability is, however, difficult to assess separately, because by changing the molecular structure, the molecular shape, polarizability and dipole moment are simultaneously changed.

In this work we undertook the synthesis of pairs of nematic liquid crystals that are identical in molecular shape but differ only in the location of the atoms in the central linkage. Such structural variations will only affect the electronic distribution and consequently the polarizability and dipole moments of the molecules but not their length-to-breadth ratios. We measured the dipole moments of these molecules and used Electron Spectroscopy for Chemical Analysis (ESCA), extended Hückel calculations and gas-liquid chromatography (GLC) to investigate their properties.

EXPERIMENTAL

Materials:

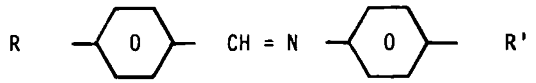
The compounds reported in Table I were prepared as illustrated for the liquid crystal *p*-methoxybenzylidene-*p*-cyanoaniline (CI). A 1 : 1 molar ratio mixture of *p*-methoxybenzaldehyde and *p*-cyanoaniline was refluxed in absolute ethanol for several hours. The product was collected by filtration of the hot suspension and recrystallized in ethanol. All other compounds were synthesized in a similar manner using the appropriate aldehyde and aniline. Chemicals were obtained from standard commercial sources. Structures for the products were deduced from the method of preparation. Spectroscopic structural verifications (IR, NMR, and MS) were carried out on selected compounds. The designation of the mesophases were made on the basis of Differential Scanning Calorimetry (Du Pont 990 Thermal Analyzer) and hot stage optical microscopy (Bock-Monoscop 'M'). Only six of the compounds reported in Table I were liquid crystals. Structures CVII–CXVII failed to yield liquid crystalline material.

Dielectric Measurements:

Solutions were prepared at 25.0 ± .5°C (the temperature of the experiment) by accurately weighing appropriate amounts of solute in 10 ml

TABLE 1

Transition temperatures for the compounds



			Transition Temperature °C		
Compound	R	R′	Solid-Nematic	Nematic-Isotropic	Solid Isotropic
CI	CH_3O	CN	105	117	
CII	CN	OCH_3	112	123	
CIII	$CH_3(CH_2)_2O$	CN	73	95	
CIV	CN	$CH_3(CH_2)_2O$	75	108	
CV[a]	$CH_3(CH_2)_2O$	OCH_3	90	96	
CVI[a]	OCH_3	$CH_3(CH_2)_2O$	88	95	
CVII	CH_3	CN			115
CVIII	CN	CH_3			140
CIX	NO_2	CN			187
CX	NO_2	$CH_3(CH_2)_2O$			101
CXI	$CH_3(CH_2)_3O$	NO_2			110
CXII	Cl	OCH_3			123
CXIII	CH_3O	Cl			90
CXIV	$CH_3(CH_2)_2O$	Cl			78
CXV	OH	OCH_3			209
CXVI	CH_3O	OH			187
CXVII	CN	CN			223

[a] monotropic liquid crystals.

volumetric flasks and, then, adding sufficient amount of benzene solvent to reach the 10 ml mark. The dielectric constants of the solutions were measured by a WTW DMO1 Dipole Meter using cylindrical gold-plated condenser cell, type DFL-2. The refractive indices were determined by the use of a Bausch and Lomb Abbe-3L Refractometer. The dipole meter scale readings were calibrated and converted to dielectric constants by the use of neat reference liquids for which the dielectric constants are known to within 0.1% at 25°C.[2] The reference liquids were: cyclohexane, $\epsilon = 2.015$; benzene, $\epsilon = 2.274$; *n*-hexane, $\epsilon = 1.882$ and toluene, $\epsilon = 2.379$. The temperature control for both the dipole meter and the refractometer was achieved by circulating water from a thermoregulator.

The dielectric constants and refractive indices were analyzed using the procedure of Guggenheim[3] and Smith,[4] in the solute concentration range of 6×10^{-5} to 2.0×10^{-4} mol cm^{-3}. The values of the constants and conversion factors used for the calculation of the dipole moments were: $k = 1.38066 \times 10^{-16}$ erg K^{-1}; Avogadro's number $= 6.022045 \times$

10^{23} mol^{-1}; and 1 Debye = 1 × 10^{-18} esu cm. When the appropriate data plots were made and analyzed, the correlation coefficients for the plots were all better than 0.999. The maximum error in the dipole moment values as determined from the slopes of the plots was 0.05 Debye.

ESCA:

A McPherson ESCA-36 spectrometer with a Mg Kα source (1253.6 eV) was used for measuring the X-ray photoelectron spectra. The samples were mounted on aluminium mesh at ambient temperatures. Spectral data were computer processed to reduce instrumental broadening of the peaks to ensure the resolution of peaks due to chemical shift and shake-up processes.

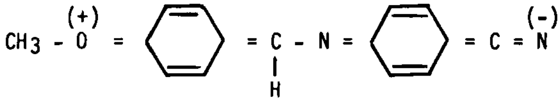
Gas-liquid chromatography:

A Perkin-Elmer Sigma I gas chromatograph equipped with a dual-column forced air oven, two flame ionization detectors, electronic carrier gas flow controllers and a Sigma 10 data station was employed. Retention data were directly recorded by the on-line data station. The polymeric stationary phase columns used were purchased from chromatographic suppliers. The liquid crystalline column packing was prepared by the solvent slurry technique with 100/120 mesh HP Chromosorb W, using chloroform solvent. Columns (2 mm i.d. × 6 ft. borosilicate glass) were conditioned at 20° above the highest operating temperature.

RESULTS AND DISCUSSION

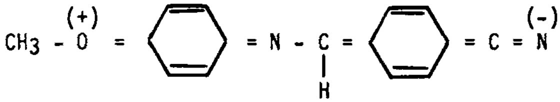
The results of the dipole moment measurements are presented in Table II. To explain the difference in the dipole moment of the first two compounds CI and CII, we compare their likely resonance structures. For CI a structural contribution from a resonance situation represented by **a** is very likely because at one end of the molecule the methoxy group is an electron releasing group and at the other end the cyano group is electron withdrawing. On the other hand CII is not likely to have a significant contribution from resonance structure **b**. This simple resonance argument explains the experimental finding that the dipole moment of CI is larger than CII.

A more concise and quantitative description of the electronic distribution is attempted using ESCA and theoretical calculations. Because of the very close 1s binding energies of the nitrogen atoms in the amino



(likely)

a



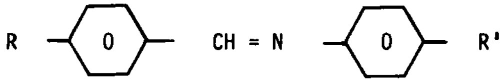
(not likely)

b

and the nitrile groups it was not possible to differentiate between them with ESCA. The main *N*(1s) line from both compounds was at 398.8 eV. However, careful examination of the X-ray photoelectron spectra (XPS) of compounds CI and CII reveal a significant difference. The XPS of compound CI shows a relatively small satellite line at 401.6 eV, while no such line is observed with compound CII (Figure 1). The satellite line is attributed to a positive shake-up process involving the outermost molecular orbital. Shake-up satellite lines have been reported in the X-ray photoelectron spectra of a wide variety of compounds.[5] A satellite line is formed when the emission of an inner photo-electron takes place parallel with an excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The position and relative intensity of the satellite line relative to the main spectral line serve to indicate the location of the HOMO. Shake-up transition at the high binding energy side of the main spec-

TABLE II

Dipole moments for the compounds



Compound	R	R'	Dipole Moment Debye ± .05
CI	CH_3O	CN	5.03
CII	CN	CH_3O	4.23
CIII	$CH_3(CH_2)_2O$	CN	5.34
CIV	CN	$CH_3(CH_2)_2O$	4.49
CV	$CH_3(CH_2)_2O$	OCH_3	2.36
CVI	OCH_3	$CH_3(CH_2)_2O$	2.40

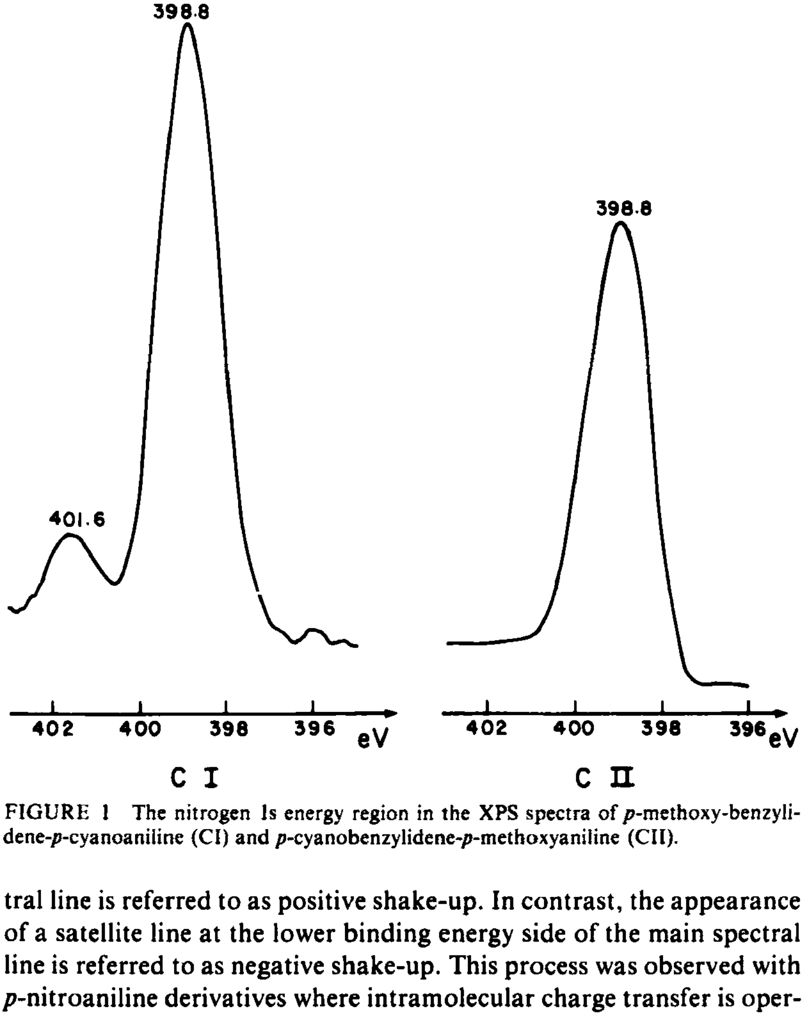


FIGURE 1 The nitrogen 1s energy region in the XPS spectra of *p*-methoxy-benzylidene-*p*-cyanoaniline (CI) and *p*-cyanobenzylidene-*p*-methoxyaniline (CII).

tral line is referred to as positive shake-up. In contrast, the appearance of a satellite line at the lower binding energy side of the main spectral line is referred to as negative shake-up. This process was observed with *p*-nitroaniline derivatives where intramolecular charge transfer is operative with the highest occupied molecular π orbital localized at the donor-ring moiety and the lowest unoccupied π^* orbital localized on the nitro group.[6,7] Thus the absence of shake-up in CII (Figure 1) indicate that the HOMO is mainly localized on the benzylidene *N* in CI and is delocalized in CII. Satellite lines due to π-π^* excitations are generally less intense and appear at higher binding energies relative to the main spectral line.

Extended Hückel calculations on CI and CII give supporting evidence for the ESCA results. Furthermore, both the ESCA results and the theoretical calculations are in agreement with the dipole moment measurements. Extended Hückel calculations were carried out with the program of R. Hoffmann and co-workers using standard bond lengths of Pople and Beveridge[8] and 120° and 109.467° angles. The molecules were considered planar. Charges, π-populations and total overlap populations were calculated for all atoms and bonds that constitute the two molecules, but the main discernable difference is observed in the trend in the total charge and π-populations presented in Table III. Examination of Table III clearly reveals that the oxygen of OCH_3 is more negative in CII and CN is more negative in CI which also has the more negative benzylidene *N*. The π-population support the conclusions based on the total charge. Thus CI shows electron drift towards CN (resonance structure **a**) while CII shows that the relative drift is towards the OCH_3 part of the molecule.

A non-bonding orbital resonance interaction between the lone pairs of the methoxy O and the benzylidene *N* in CII is largely responsible for keeping the charge dispersed in this part of the molecule with net flow of charge towards the methoxy O. In contrast the drift of charge in CI along the length of the molecule towards the cyano group is responsible for the polarization of the molecule leading to localized and separated charges and hence higher dipole moment. Furthermore, the HOMO in CI has its largest coefficient on the benzylidine *N*, supporting the ESCA evidence that the shake-up line at 401.6 eV in the XPS spectrum of CI corresponds to an n-π^* transition. In CII the HOMO is more delocalized over the benzylidene *N* and the adjacent ring and because of this delocalization a shake-up line is absent in the XPS spectrum of CII. Also in CI, the LUMO has its largest coefficient on the C of the HC=N double bond. In CII the corresponding coefficient is on the same moiety but is smaller. In both molecules the LUMO is delocalized but in CII the delocalization is greater.

TABLE III

Total charge and π-populations for the OCH_3, CN and HC=N fragments in CI and CII

		Total Charge		π-Population	
Fragment	Atom	CI	CII	CI	CII
OCH_3	O	−0.811	−0.822	1.903	1.914
	C	0.402	0.402	0.952	0.952
CN	C	0.783	0.791	0.699	0.692
	N	−1.046	−1.029	1.425	1.409
HC=N	N	−0.917	−0.886	1.459	1.429

The calculated energies also agree with the experimental UV results. For CII the HOMO is at −12.043 eV and the LUMO is at −10.127 eV with a ΔE of 1.916 eV, while for CI the HOMO is at −12.210 eV and the LUMO is at −9.932 eV with a ΔE of 2.278 eV. The UV spectra of these compounds in ethanol solvent show that the lowest energy absorption (HOMO → LUMO) in CI is at 316 nm (3.92 eV) while the corresponding absorption in CII is at 348 nm (3.56 eV). It is to be noted that the difference in energy between the main line and the shake-up line in the XPS spectrum of CI agrees to within 1.12 eV with the HOMO-LUMO transition of 3.92 eV as measured by UV spectroscopy.

What is quite clear from the foregoing is that there is a discernable difference in the electronic configuration of CI and CII, most notably is the relative delocalization of the HOMO in CII and its localization in CI. If delocalization of the HOMO would result in enhanced anisotropy of the molecular polarizability, then this perhaps explains the higher thermal stability of the nematic state of CII relative to CI. Our results also indicate that higher dipole moments do not intrinsically enhance the thermal stability of the nematic state as CI has the higher dipole moment while CII has the higher clearing point.

The same arguments with respect to dipole moment results, ESCA and theoretical calculations could be advanced to explain the difference between CIII and CIV. On the other hand CV and CVI are essentially very similar as seen from the results presented in Tables I and II.

In this part we attempt to use gas-liquid chromatography (GLC) to ascertain whether the difference in the polarity and clearing points of these compounds is manifested on the macroscopic level. GLC has been extensively used for the study of the solvent properties of liquid crystals, in particular, the aspects responsible for the unique selectivity of these phases.[9,10]

Chromatographic evaluation of these liquid crystals was attempted through examining their relative retention on columns of different polarity and retention mechanisms. Table IV gives a comparison of the relative retention of compounds CI through CVI on columns of OV-1 (non-polar methyl silicone), OV-225 (polar, 25% phenyl, 25% cyanopropyl, methyl silicone) and BPhBT (the liquid crystal, bis(*p*-phenylbenzylidene-α,α'-bi-*p*-toluidine). The compounds are listed in order of increasing retention on the OV-225 column. It is observed that each pair of solutes elute simultaneously on the non-polar OV-1 column indicating, as expected, identical vapor pressures and solute/stationary phase interactions for each pair at the temperature of the experiment. Similarly the solute pairs were not separated on the BPhBT liquid crys-

TABLE IV

Relative retention data of six liquid crystal solutes on different stationary phases

		Relative Retention ± 1%		
Compound	Dipole Moment	OV-1[a] at 240°C	OV-225[a] at 240°C	BPhBT[b] at 270°C
CV	2.30	1.00	1.00	1.00
CVI	2.40	1.00	1.01	1.01
CII	4.23	0.753	1.19	1.45
CI	5.03	0.758	1.36	1.46
CIV	4.49	1.17	1.61	1.88
CIII	5.34	1.18	1.84	1.89

[a] 3% on chromosorb WHP 100/120 mesh
[b] 6.2% on chromosorb WHP 100/120 mesh

tal column giving credence to the assumption that they are identical in length-to-breadth ratios. The use of high-melting liquid crystal stationary phases for the chromatographic analysis of low molar-mass mesogenic compounds may prove to be of analytical utility for the analysis of the purity and percent composition of liquid crystals used in display devices.

On the other hand, it is clear from Table IV that the elution of the solute pairs on the polar OV-225 column is in the order of solute polarity where the more polar compounds CI and CIII are retained longer than their less polar isomers CII and CIV respectively. Thus solute polarity is the only discernible difference that could be detected by gas-liquid chromatography.

Acknowledgment

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