Journal of Molecular Structure, 317 (1994) 147–155
0022-2860/94/\$07.00

Conformational investigation of *N*-aralkylpyridinium ions by Cotton–Mouton effect method

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(Received 10 June 1993)

Abstract

Molar Cotton–Mouton constants and refractions are reported at 298 K for the following *N*-aralkylpyridinium cations as solutes in water or acetonitrile: $(C_6H_5)CH_2(^+NC_5H_5)$, $(4\text{-}ClC_6H_4)CH_2(^+NC_5H_5)$, $(3\text{-}ClC_6H_4)CH_2(^+NC_5H_5)$, $(3\text{-}ClC_6H_4)CH_2(2'\text{-}Me^+NC_5H_4)$, $(4\text{-}NO_2C_6H_4)CH_2(^+NC_5H_5)$, $(2,5\text{-}Me_2C_6H_3)CH_2(^+NC_5H_5)$, $(2,5\text{-}Me_2C_6H_3)CH_2(2'\text{-}Me^+NC_5H_4)$, $(2,4,6\text{-}Me_3C_6H_2)CH_2(^+NC_5H_5)$, $(2,3,5,6\text{-}Me_4C_6H)CH_2(^+NC_5H_5)$, $(2,3,5,6\text{-}Me_4C_6H)CH_2(2'\text{-}Me^+NC_5H_4)$, $(2,3,4,5,6\text{-}Me_5C_6)CH_2(^+NC_5H_5)$ and $(2,3,4,5,6\text{-}Me_5C_6)CH_2(2'\text{-}Me^+NC_5H_4)$. The data are analysed in terms of the preferred conformations adopted by such cations in solution. In most cases these data are consistent with the presence, in solution, of helical or near-helical conformations, where both aryl and pyridinium rings are twisted in the same direction with respect to the C_{Ar}–CH_2–N_{Ar} reference plane. In contrast, tri-ortho-substituted diaryl cations adopt an asymmetric form in which the ortho-substituted aromatic ring lies almost perpendicular to the reference plane, and the mono-ortho-pyridinium ring forms an acute angle with the reference plane.

Introduction

Conformations of diaryl compounds are of interest because the spatial orientation of the rings depend both on the nature of the connecting bridge and on the electronic and steric properties of the atomatic nuclei.

The ground state conformations of diaryl derivatives, such as diarylmethanes, diarylethers, diarylsulphides and sulphones, benzophenones and pyridinium ions have been extensively investigated by many techniques [1,2]. The evidence to date indicates that such molecules in most cases may adopt one of two conformations: either (i) both aromatic rings are twisted in the same direction to the C_{Ar}–Z–$C_{Ar}(N_{Ar})$ reference plane (form A in Fig. 1) so as to impart a helical arrangement on the molecule, which thus posesses a C_2 point group skeletal symmetry, or (ii) one ring lies parallel to the reference plane and the other is perpendicular to it (form B, hereafter called the planar–orthogonal conformation).

At the same time, especially in the case of strong π-conjugation between the aromatic rings and the *Z* connecting bridge, some molecules, such as diarylsulphones [3], can adopt a conformation where both aryl rings are perpendicular to the C_{Ar}–Z–C_{Ar} reference plane (form C, hereafter called the orthogonal conformation). For some molecules form A or forms B and C can be distorted [4] and the conformational preference

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SSDI 0022-2860(93)07862-Q

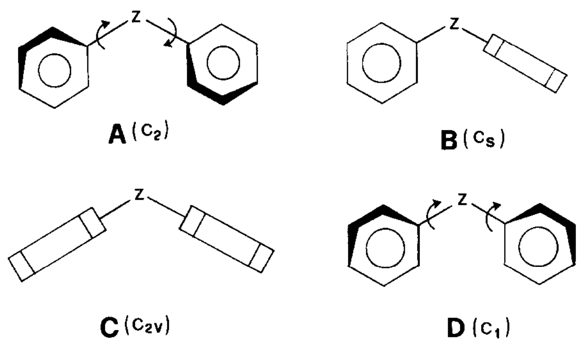


Fig. 1. Possible conformations for a diaryl compound. Point groups of symmetry are indicated.

can be interpreted in terms of form D (hereafter called the asymmetric conformation).

NMR studies of the conformational properties of diphenylmethanes [5] and *N*-aralkylpyridinium ions [6] have shown that a number of tri-ortho-substituted systems exist predominantly in the type B conformation. In contrast, other types of ortho-substitution lead to skew forms with variable dihedral angles [6]. A type B conformation was also found for some tri-ortho-substituted diphenylmethanes by X-ray crystal analysis [7].

Continuing our investigations on diaryl compounds using their molecular properties such as anisotropy of polarizability we were interested in investigating in greater detail the static stereochemistry of different substituted *N*-aralkylpyridinium cations (listed in Scheme 1 and Table 1) with the aim of elucidating their preferred conformations (A, B, C or D, or an equilibrium between some of these conformations). In the present work we used the powerful technique of the Cotton-Mouton effect, which can be applied to charged organic molecules in polar media [8,9].

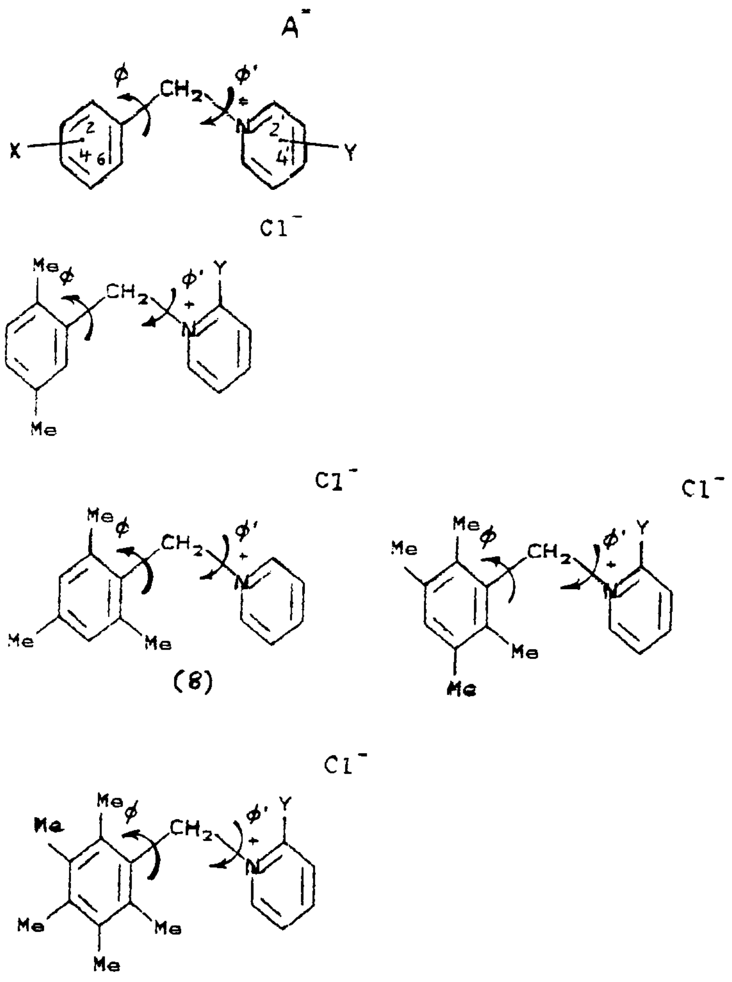
Experimental

General synthetic procedures

Pyridine and 2-methylpyridine were high purity commerical products (Aldrich). *N*-Aralkylpyridinium salts **1–12** were prepared in high yield ($\geqslant 85\%$) by reacting pyridine or picoline with the appropriate halobenzyl derivatives, in bulk, at room temperature. The crude products were washed several times with Et_2O and recrystallized from EtOH. Melting points and ^1H NMR chemical shifts of the synthesized samples are reported in Table 1.

Physical measurements

Solute magnetic birefringences (Cotton–Mouton effect) expressed as the molar Cotton–Mouton constant ${}_\infty(mC_2)$ were determined as 298 K. The apparatus was especially assembled for Cotton–Mouton measurements at the Institute of Physical and Organic Chemistry of Rostov University in Rostov on Don, Russian Federation and the apparatus scheme is similar to that described previously [10]. The techniques used for the measurements are already reported in the literature [10,11]. A He–Ne laser ($\lambda = 632.8\,\text{nm}$) was used as a light source. Benzene was used as a reference liquid. The benzene Cotton–Mouton constant (C) was taken as $C = 5.671 \times 10^{-15}$ emu. [12]. Densities were determined by a hydrostatic method and refractive indices were measured with the *ИРФ*-23 refractometer. For each compound relative densities, refractive indices, and Cotton–Mouton constants (d_{12}, n_{12} and C_{12}, respectively) were measured for a range of solutions having solute weight fractions w_2. Coefficients β, γ and D were derived using linear relations $d_{12} = d_1(1 + \beta w_2)$, $n_{12} = n_1(1 + \gamma w_2)$ and $C_{12} = C_1 + D w_2$ by least-squares analysis. The subscripts 1, 2 and 12 refer to the solvent, solute, and solution, respectively. Molar Cotton–Mouton constants ${}_\infty(mC_2)$ are given in cgs (emu) units, and ${}_\infty R_D$ is the experimental refraction at the sodium D-line (in $\text{cm}^3\,\text{mol}^{-1}$). The conversion factor from the electrostatic (cgs, emu) system is for the molar Cotton–Mouton constant ${}_\infty(mC)$ $1\,\text{m}^5\,\text{A}^{-2}\,\text{mol}^{-1} = 0.6333 \times 10^{10}\text{emu mol}^{-1}$. Experimental results are reported in Table 2.



	X	Y	A^-
(1)	H	H	ClO_4^-
(2)	4-Cl	H	Cl^-
(3)	3-Cl	H	Br^-
(4)	3-Cl	2'-Me	Br^-
(5)	$4\text{-}NO_2$	H	Cl^-

	Y
(6)	H
(7)	Me

	Y
(9)	H
(10)	Me

	Y
(11)	H
(12)	Me

Scheme I. The *N*-aralkylpyridinium cations examined in this work. In the starting conformation ($\phi = \phi' = 0$) the aryl and pyridinium rings are coplanar with the C_{Ar}–CH_2–N_{Ar} reference plane.

Results and discussion

Calculation of molar Cotton–Mouton constants

The experimental values of Cotton–Mouton constants $_{\infty}(mC_2)$ measured for salts **1**–**12** (Scheme 1) were ascribed only to the cations because the anions of these salts have isotropic polarizability and magnetizability due to their symmetry. Tensor additive schemes for molecular polarizability and magnetizability were employed to estimate theoretical Cotton–Mouton constants mC_{calc} as a function of the two internal rotation angles ϕ and ϕ' (see Scheme 1) for various cation conformations using molecular group and bond principal polarizabilities and magnetizabilities which are listed in Tables 3 and 4, respectively. Polarizabilities and magnetizabilities for the aryl rings of compounds **8**–**12** were taken from molecules such as mesitylene, durene, pentamethylbenzene, and hexamethylbenzene, considering isotropic properties of C–H bonds according to additive schemes [8,19]. It was supposed that the aromatic and pyridinium rings in *N*-aralkyl-

Table 1
Physicochemical data for the *N*-aralkylpyridinium salts investigated

N[a]	X	Y	Anion	M.p.(°C)	^{1}H NMR (D_2O)[b]
1	H	H	ClO_4^-	95–97	5.8 (s, 2H, $-CH_2-$), 7.46 (m, 5H, ArH), 8.05, 8.50 and 8.85 (m, 5H, PyH)
2	4-Cl	H	Cl^-	161–163	5.83 (s, 2H, $-CH_2-$), 7.44 (s, 4H, ArH), 8.11, 8.6 and 8.96 (m, 5H, PyH)
3	3-Cl	H	Br^-	158–159	5.86 (s, 2H, $-CH_2-$), 7.5 (m, 4H, ArH), 8.22, 8.64 and 8.97 (m, 5H, PyH)
4	3-Cl	2-Me	Br^-	160–162	2.8 (s, 3H, CH_3), 5.85 (s, 2H, $-CH_2-$), 7.27 (m, 4H, ArH), 7.97, 8.55 and 8.84 (m, 4H, PyH)
5	4-NO_2	H	Cl^-	204–206	6.05 (s, 2H, $-CH_2-$), 7.64 (d, 2H, $J_{AB} = 9.1$ Hz, ArH), 8.36 (d, 2H, $J_{AB} = 9.1$ Hz, ArH), 8.2, 8.7, and 9.05 (m, 5H, PyH)
6	–	H	Cl^-	210–212	2.23 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 5.83 (s, 2H, $-CH_2-$), 7.22 (s, 1H, ArH), 7.27 (s, 2H, ArH), 8.1, 8.6 and 8.82 (m, 5H, PyH)
7	–	Me	Cl^-	146–148	2.3 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.87 (s, 3H, CH_3), 5.78 (s, 2H, $-CH_2-$), 6.69 (s, 1H, ArH), 7.32 (s, 2H, ArH), 8.03 and 8.55 (m, 4H, PyH)
8	–	–	Cl^-	221–223	2.24 (s, 6H, CH_3), 2.31 (s, 3H, CH_3), 5.87 (s, 2H, $-CH_2-$), 7.11(s, 2H, ArH), 8.05 and 8.63 (m, 5H, PyH)
9	–	H	Cl^-	228–230	2.13 (s, 6H, CH_3), 2.2 (s, 6H, CH_3), 5.94 (s, 2H, $-CH_2$), 7.11 (s, 1H, ArH), 8.05 and 8.6 (m, 5H, PyH)
10	–	Me	Cl^-	198–200	2.08 (s, 6H, CH_3), 2.3 (s, 6H, CH_3), 3.07 (s, 3H, CH_3), 5.58 (s, 2H, $-CH_2-$), 7.28 (s, 1H, ArH), 7.70, 8.01 and 8.42 (m, 4H, PyH)
11	–	H	Cl^-	227–228	2.17 (s, 15H, CH_3), 5.94 (s, 2H, $-CH_2-$), 8.03 and 8.6 (m, 5H, PyH)
12	–	Me	Cl^-	185–187	2.12 (s, 6H, CH_3), 2.28 (s, 6H, CH_3), 2.32 (s, 3H, CH_3), 3.04 (s, 3H, CH_3), 5.62 (s, 2H, $-CH_2-$), 7.68, 7.98 and 8.38 (m, 4H, PyH)

[a] See Scheme 1.

[b] Spectra were recorded on a Bruker WP-80 FT instrument at room temperature in D_2O as solvent and DSS as internal standard.

pyridinium ions are taken as ideal hexagons. The geometry of the methylene bridge was also taken as ideal according to sp^3 hybridization of the carbon atom. In calculations of mC_{calc} of different conformers with the use of the tensor additive schemes (Tables 3 and 4) any increase in average polarizability to the additive value was not taken into account. In other words it was supposed that this possible increase is distributed evenly among principal molecular polarizability axes. One of the reasons is the uncertainty connected with the calculation of the part of the molar refraction which refers to organic charged molecules since the contribution related to the anion generally cannot be defined with acceptable reliability [20]. Some part of refraction may also be due to solvation. In any case this increment is expected to be small.

First of all we checked the presence in solution of conformer A only (Fig. 1). The calculated values of ϕ, ϕ' were obtained by imposing the condition

$$mC_{\text{calc}}(\phi, \phi') = {}_{\infty}(mC_2) \tag{1}$$

It should be noted that the A conformer model for compounds under study can only be an idealization since the aromatic moieties bonded through the

Table 2
Molar refractions and molar Cotton–Mouton constants of *N*-aralkylpyridinium salts measured in water [a] at 298 K

Compound	w_2 [b]	β	γ [c]	D	$_\infty R_D$ [d]	$_\infty(mC_2) \times 10^{15}$ [d]
1	0.03–0.12	0.516	0.117	33.16	65.8 ± 0.9	3.60 ± 0.30
2	0.03–0.12	0.239	0.161	44.55	66.8 ± 0.9	3.80 ± 0.29
3	0.03–0.12	0.330	0.150	32.42	71.2 ± 0.8	3.27 ± 0.36
4	0.04–0.11	0.311	0.148	38.04	75.6 ± 0.9	4.03 ± 0.12
5	0.03–0.12	0.267	0.167	58.49	69.5 ± 0.6	5.20 ± 0.26
6	0.03–0.12	0.139	0.163	40.08	70.3 ± 0.6	3.34 ± 0.29
7	0.03–0.12	0.114	0.164	43.01	75.8 ± 0.8	3.80 ± 0.48
8	0.03–0.12	0.128	0.164	40.63	75.2 ± 0.7	3.61 ± 0.47
9	0.03–0.12	0.128	0.168	36.10	80.3 ± 0.9	3.36 ± 0.21
10	0.03–0.12	0.118	0.164	40.38	84.2 ± 0.9	3.96 ± 0.32
11	0.03–0.12	0.125	0.166	32.80	84.3 ± 1.2	3.23 ± 0.30
12	0.03–0.12	0.108	0.173	37.79	91.1 ± 0.9	3.92 ± 0.24

[a] Compound **1** was measured in acetonitrile.
[b] Range of concentrations used expressed as weight fractions.
[c] For the sodium D-line.
[d] Mean-square deviations are indicated.

methylene bridge are different. The starting conformation ($\phi = \phi' = 0$) for ions **1–12** is shown in Scheme 1. The relationship between ϕ and ϕ' is $\phi' = \phi$ for symmetric substitution and ϕ' is either equal to ϕ or $\phi \pm 180°$ in other cases. Examples of the $mC_{\text{calc}}(\phi, \phi')$ plots are shown in Fig. 2. The plots for other compounds are similar. In these plots we observed a maximum near 90°, and the difference between this maximum and the adjacent minimum is quite small. Thus a $mC_{\text{calc}}(\phi, \phi')$ plot can be divided into two regions: (I) the region with a steep slope, (II) the region with a gentle slope. Equation (1) in the case of symmetric substitution of the aromatic rings (cations **1**, **2**, **5**, **8**, **9** and **11**)

Table 3
Principal bond and group polarizabilities b_i (cm^3) employed in additive Cotton–Mouton constant calculations

Bond, group or reference molecule	$b_1 \times 10^{23}$	$b_2 \times 10^{23}$	$b_3 \times 10^{23}$	Reference
C–H	0.065	0.065	0.065	13
C_{Ar}–CH_3 [a]	0.326	0.202	0.234	14
C_6H_5 [b]	1.056	1.056	0.672	15
C_6H_5Cl [c]	1.478	1.255	0.821	12
$C_6H_5NO_2$ [c]	1.617	1.200	0.862	12
$(CH_3)_2C_6H_4$ [c]	1.613	1.402	1.075	12
$(CH_3)_3C_6H_3$ [b]	1.696	1.696	1.247	12
$(CH_3)_4C_6H_2$ [d]	1.812	1.936	1.356	12
$(CH_3)_5C_6H$ [d]	1.986	2.265	1.474	16
$(CH_3)_6C_6$ [b]	2.263	2.263	1.681	12
$C_5H_5\overset{+}{N}CH_3$ [b]	1.041	1.041	0.451	17

[a] Polarizabilities b_1 and b_2 in the plane of the π-system, b_1 along the bond.
[b] Polarizabilities b_1 and b_2 in the plane of the π-system.
[c] Polarizabilities b_1 and b_2 in the plane of the π-system, b_1 along the C–X bond.
[d] Polarizabilities b_1 and b_2 in the plane of π-system, b_1 along the C–H bond.

Table 4
Principal bond and group magnetizabilities k_i (cm^3) employed in additive Cotton–Mouton constant calculations

Bond, group or reference molecule	$-k_1 \times 10^{29}$	$-k_2 \times 10^{29}$	$-k_3 \times 10^{29}$	Reference
$C_{Ar}-CH_3$[a]	1.54	2.32	2.32	18
C_6H_5[b]	5.88	5.88	15.58	10
C_6H_5Cl[c]	8.94	8.94	16.94	12
$C_6H_5NO_2$[c]	5.43	5.43	19.95	12
$(CH_3)_2C_6H_4$[c]	9.37	9.37	19.59	12
$(CH_3)_3C_6H_3$[b]	9.60	9.60	21.62	12
$(CH_3)_4C_6H_2$[d]	13.04	13.04	24.32	12
$(CH_3)_6C_6$[b]	16.26	16.26	28.50	12
$C_5H_5\overset{+}{N}CH_3$[b]	5.2	5.2	14.4	17

[a] Magnetizabilities k_1 and k_2 in the plane of the π-system, k_1 along the bond.
[b] Magnetizabilities k_1 and k_2 in the plane of π-system.
[c] Magnetizabilities k_1 and k_2 in the plane of π-system, k_1 along the C–X bond.
[d] Magnetizabilities k_1 and k_2 in the plane of π-system, k_1 along the C–H bond.

has only one solution in region I and this solution is reliable in connection with the steep slope of the plot. At the same time, Eq. (1) has two solutions in region II, but these solutions are not so reliable as in the case of region I due to the experimental errors and the gentle slope. If the Cotton-Mouton experimental value falls in region II and thus allows two solutions it can only be said that a broad range

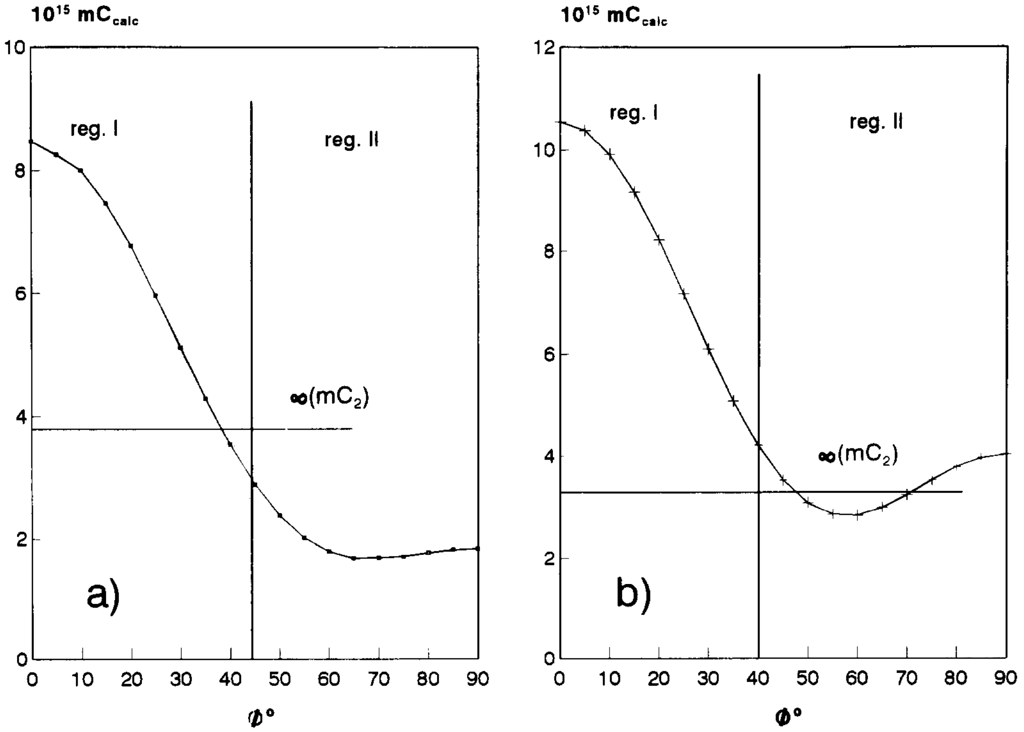


Fig. 2. Examples of plots of $mC_{calc}(\phi, \phi')$ for $\phi = \phi'$: (a) compound **2**; (b) compound **9**.

Table 5
Calculated torsion angles ϕ, ϕ' (deg) which best fit the experimental data of *N*-aralkylpyridinium cations according to the helical structure model (form A)

<table>
<tr><th>Compound</th><th>ϕ</th><th>ϕ'</th></tr>
<tr><td>1</td><td colspan="2">38</td></tr>
<tr><td>2</td><td colspan="2">39</td></tr>
<tr><td>3</td><td colspan="2">45</td></tr>
<tr><td></td><td colspan="2">141</td></tr>
<tr><td>4</td><td>39</td><td>39</td></tr>
<tr><td></td><td>44</td><td>224</td></tr>
<tr><td></td><td>143</td><td>143</td></tr>
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<tr><td></td><td colspan="2">135</td></tr>
<tr><td>7</td><td>35</td><td>35</td></tr>
<tr><td></td><td>39</td><td>219</td></tr>
<tr><td></td><td>133</td><td>133</td></tr>
<tr><td>8</td><td colspan="2">42</td></tr>
<tr><td>9</td><td colspan="2">49</td></tr>
<tr><td></td><td colspan="2">71</td></tr>
<tr><td>10</td><td colspan="2">41</td></tr>
<tr><td></td><td colspan="2">81</td></tr>
<tr><td></td><td colspan="2">111</td></tr>
<tr><td></td><td colspan="2">130</td></tr>
<tr><td>11</td><td colspan="2">55</td></tr>
<tr><td></td><td colspan="2">70</td></tr>
<tr><td>12</td><td colspan="2">43</td></tr>
<tr><td></td><td colspan="2">84</td></tr>
<tr><td></td><td colspan="2">111</td></tr>
<tr><td></td><td colspan="2">124</td></tr>
</table>

of ϕ, ϕ' values will be possible. In the case of asymmetric substitution (cations **3**, **4**, **6**, **7**, **10** and **12**) the number of possible solutions is doubled. The results of such calculations (ϕ, ϕ' values) are listed in Table 5. As can be seen from the Table the compounds under study can be divided into two groups. Compounds **1**–**8** allow solution in region I of the mC_{calc} plot. The calculated ϕ,ϕ' values for different cations show small dihedral angles between ring planes and the C_{Ar}–CH_2–N_{Ar} reference plane. (This means that the angle between the ring planes and the C_{Ar}–CH_2–N_{Ar} reference plane is acute.) These angles are similar to those which have already been reported for a number of structurally related diaryl systems, such as diarylmethanes which were found to adopt helical conformations ($\phi = 43$–$71°$ by X-ray crystal structure analysis [7] and 41–44° by Kerr effect analysis [21,22]). Among these possible conformers, structures in which the ortho-substituent in the pyridinium ring lies in the external region of the C_{Ar}–CH_2–N_{Ar} valency angle are more probable because this arrangement reduces steric congestion.

Experimental Cotton–Mouton values for compounds **9**–**12** fall into region II of the mC_{calc} plot. Thus the ϕ,ϕ' values for these compounds are much closer to 90° than those for compounds **1**–**8**. However it is plausible that on increasing the number of substituents in the phenyl rings, the A conformation model is an approximation for the compounds examined and can only be applied to systems bearing aryl rings with similar electron and steric properties. Therefore for compounds **9**–**12** the experimental data were also used to examine the possibility of an equilibrium between planar–orthogonal (B) and orthogonal (C) forms (Fig. 1). (It should be noted that a similar analysis for compounds **1**–**8** leads to the conclusion that this possibility is not acceptable for them since the mC_{calc} values for conformers B and C are always less than the experimental values.) It was assumed that in form B, ϕ is 90° and $\phi' = 0°$ (compounds **9**–**12** with high steric congestion). The values of mC_{calc}, together with the weight fraction of form B, are listed in Table 6. Using such an analysis, it can be seen from the Table that the B form weight fractions for compounds **9**, **10** and **12** are small and close to each other (form C dominates). The opposite trend was found for compound **11**.

In order to interpret the experimental results an equilibrium between forms C and B can also be envisioned. However this possible interpretation is less plausible because the presence of form C is highly sterically demanding, especially for compounds such as **9**–**12** which bear ortho-methyl groups.

Furthermore, in diaryl systems form C was found to be appreciably populated only in molecules where a strong conjugative interaction exists

Table 6
Versions of equilibria between forms B and C and the presence of form D

Compound	$_{\infty}(mC_2) \times 10^{15}$	$mC_{\text{calc}} \times 10^{15}$		Weight fraction of form B	Form D ($\phi = 90°$) ϕ' (deg)
		Form B $\phi = 90°$ $\phi' = 0°$	Form C $\phi = \phi' = 90°$		
9	3.86	1.98	4.04	0.33	55
10	3.96	2.00	4.50	0.22	65 124
11	3.23	2.93	3.81	0.66	35
12	3.92	2.95	4.25	0.25	64 142

between the Z bridging group and the π-electrons of the aryl rings, such as in diarylsulphones [3]. This is certainly not the case for our *N*-aralkylpyridinium ions, considering the non-conjugative nature of the $-CH_2-$ bridge. Thus the hypothesis of an equilibrium between conformers B and C for the compounds investigated is not a realistic one.

Considering that previous NMR studies on some tri-ortho-substituted *N*-aralkylpyridinium ions [6] have provided evidence that such molecules exist predominantly in form B, we decided to explore the possibility that compounds **9**–**12** can adopt a distorted B conformation, hereafter called the asymmetric form D.

In such a form, where the aromatic ring is perpendicular with respect to the $C_{Ar}-CH_2-N_{Ar}$ reference plane or near to it, and the pyridinium ring is rotated by an angle ϕ' less than 90°, the diamagnetic shielding of the ortho-aromatic hydrogen atom would still be experienced [6]. The calculated values of ϕ' for cations **9**–**12** were obtained by imposing the condition $mC_{\text{calc}}(\phi = 90°, \phi') = {}_{\infty}(mC_2)$ and are listed in Table 6. For the other cations investigated the solution to this equation is absent. For systems **9**–**12** the values of the angles ϕ' are close to those calculated in the hypothesis of helical arrangement of the aromatic rings and this is quite realistic considering the large steric hindrances.

The results obtained under the two approximations are now compared: existence of a helical form A or existence of an asymmetric form D. The distinctive peculiarity of form A is that it can explain the conformational problems for all examined cations, (**1**–**12**). Furthermore, the degree of twisting of both rings for cations **1**–**8** is near to that found for structurally similar diarylmethanes [5,21,22]. However, the solution to the conformational problem in terms of asymmetric form D possessing orthogonal orientation of the aryl rings is achieved for cations **9**–**12** only. Comparing these results we are willing to conclude that for cations **1**–**8** a helical form A (or close to it) is the preferred conformation, but for cations **9**–**12** the conclusion about their preferred conformation is more difficult. Apparently, when considering the diamagnetic shielding experienced by the ortho-aromatic hydrogen for tri-ortho-substituted systems, cations **10** and **12** are predicted to exist in conformation D where ϕ is equal to 90° (or near to it, and $\phi > \phi'$) and the ortho-substituent in the pyridinium ring lies in the external part of the $C_{Ar}-CH_2-N_{Ar}$ valency angle. For cations **9** and **11** the ϕ and ϕ' angles are also large, and their values can still be consistent with form D.

Conclusions

From the above it can be concluded that the infinite-dilution molar Cotton–Mouton constants of the examined *N*-aralkylpyridinium cations are consistent, in most cases, with the presence in solution of helical (or near helical) conformers, where both aryl and pyridinium rings are approximately equally twisted in the same direction with respect to the C_{Ar}–CH_2–N_{Ar} reference plane. An exception to this rule are the tri-ortho-substituted derivatives which exist in an asymmetric form where the aromatic ring is nearly perpendicular to the reference plane and the pyridinium moiety is rotated by a value $0 \leq \phi \leq 90°$ with respect to the same plane.

Acknowledgements

We thank C.N.R. and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST) for financial support.

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