# Conformational investigation of N-aralkyl-bispyridinium dications by the Cotton-Mouton effect method

S.B. Bulgarevich<sup>a</sup>, D.V. Bren<sup>a</sup>, D.Ya. Movshovich<sup>a</sup>, P. Finocchiaro<sup>b,\*</sup>, S. Failla<sup>b</sup>

<sup>a</sup>Institute of Physical and Organic Chemistry, Rostov University, 344711, Rostov on Don, Stachka 194/3, Russian Federation <sup>b</sup>Institute of Chemistry, Faculty of Engineering, University of Catania, Viale A. Doria 6, 95125 Catania, Italy

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### Abstract

Molar Cotton-Mouton constants and refractions are reported at 298 K for the following *N*-aralkyl-bispyridinium dications as solutes in water:  $1,3-(CH_2 + NC_5H_5)_2C_6H_4$ ,  $1,3-(CH_2 + NC_5H_4-2'-Me)_2C_6H_4$ ,  $1,3-(CH_2 + NC_5H_5)_2-4,6-Me_2C_6H_2$ ,  $1,3-(CH_2 + NC_5H_5)_2-2,4,6-Me_3C_6H_3)_2-4,6-Me_2C_6H_2$ ,  $1,3-(CH_2 + NC_5H_5)_2-2,4,6-Me_3C_6H_3)_2-4,6-Me_2C_6H_2$ . The data are analyzed in terms of the preferred conformations adopted by the cations in solution. The experimental data are consistent with the presence, in solution, of helical structures, where all pyridinium and aryl rings are twisted in the same direction with respect to the  $C_{Ar}-CH_2-N_{Ar}$  reference plane. In the case of the first four compounds listed above, the preferred conformers possess a spiral spatial arrangement of the three aryl rings along a screw line. For the last compound of this series, a mixture of different conformers seems to be populated in the ground state.

### Introduction

Recently, we investigated [1] the ground state solute conformations of a series of *N*-aralkylpyridinium ions in water and acetonitrile using the Cotton-Mouton technique and it was shown that in most cases the charged molecules adopt a conformation where both aromatic and pyridinium rings are twisted in the same direction with respect to the  $C_{Ar}$ -CH<sub>2</sub>-N<sub>Ar</sub> reference plane so as to impart a helical arrangement to the organic cations, which thus possess a  $C_2$  point group skeletal symmetry (Fig. 1).

On the contrary, triply ortho substituted cations (disubstituted in the phenyl ring and monosubstituted in the pyridinium ring) adopt an asymmetric form in which the di-ortho substituted aromatic ring lies almost perpendicular to the reference plane.

The evidence to date indicates that *N*-arylpyridinium cations, as well as many related diaryl derivatives such as diphenylmethanes, diphenyl ethers and diphenyl sulphides adopt a helical conformation in the ground state [2,3], whenever the substitutents on the two edges of the phenyl rings are not grossly different in steric requirement.

However, whenever a strong  $\pi$  conjugation between the aromatic rings and the bridging Z group (Fig. 1) arises, or whenever the steric hindrance in the ortho position is no longer balanced, the molecules can adopt twisted conformations different from the helical structures [3,4].

Continuing our investigation of the solute ground state conformations of N-aralkylpyridinium ions

<sup>\*</sup> Corresponding author.



Fig. 1. Helical conformation for a diaryl system. R and L conformations are mirror images of one another. The point group of symmetry is indicated.

using their molecular properties such as molecular polarizability and magnetizability, we were interested to investigate in detail the static stereochemistry of N-aralkyl-bispyridinium cations (compounds (1)-(6) as listed in Fig. 2 and Table 1) which are more complicated in comparison with the abovementioned diaryl systems. The cations under study possess three rings (one aryl and two pyridinium) and therefore the stereochemical problem is more complicated considering that in this case four torsional angles will define the conformation. In order to elucidate their preferred conformations, in this work we have used the powerful technique of the Cotton-Mouton effect which can be applied to charged organic molecules in polar media [5].

## Experimental

## General synthetic procedures

Pyridine and 2-methylpyridine were high purity commercial products (Aldrich). N-Aralkyl-bispyridinium salts (1)–(6) were prepared in high yield ( $\geq 80\%$ ) by reacting pyridine or picoline with the appropriate halobenzyl derivatives, in bulk, at room temperature. The crude products were washed several times with Et<sub>2</sub>O and recrystallized from EtOH. Melting points and <sup>1</sup>H NMR chemical shifts of the synthesized samples are reported in Table 1.

## Physical measurements

Solute magnetic birefringences (Cotton-Mouton effect) expressed as molar Cotton-Mouton constants  $^{\infty}({}_{\rm m}C_2)$  were determined at 298 K. The measurement techniques have been described previously [1,6,7]. A He-Ne laser ( $\lambda = 632.8$  nm) was used as a light source. Benzene was used as a reference liquid. The benzene Cotton-Mouton constant (C) was taken as  $C = 5.671 \times 10^{-15}$  e.m.u. [8]. Densities were determined by a hydrostatic method and refractive indices were measured on a  $\text{MP}\Phi$ -23



Fig. 2. Structural formulae of the N-aralkyl-bispyridinium salts examined in this work as solutes in water.

No. <sup>a</sup>	M.p. (°C)	<sup>1</sup> H NMR (D <sub>2</sub> O) <sup>b</sup>
1	227-229	5.94(s,4H,CH <sub>2</sub> ), 7.64(s,4H,ArH), 8.17, 8.67 and 8.98(m,10H,PyH).
2	218-220	2.84(s,6H,CH <sub>3</sub> ), 5.94(s,4H,CH <sub>2</sub> ), 7.41(m,4H,ArH), 8.02, 8.57 and 8.88(m,8H,PyH).
3	153-155	2.29(s,6H,CH <sub>3</sub> ), 5.91(s,4H,CH <sub>2</sub> ), 7.34(s,2H,ArH), 8.12, 8.69 and 8.83(m,10H,PyH).
4	172-174	2.34(s,6H,CH <sub>3</sub> ), 2.88(s,6H,CH <sub>3</sub> ), 5.79(s,4H,CH <sub>2</sub> ), 7.35(s,2H,ArH), 8.03 and 8.55(m,8H,PyH).
5	245-247	2.24(s,3H,CH <sub>3</sub> ), 2.43(s,6H,CH <sub>3</sub> ), 6.08(s,4H,CH <sub>2</sub> ), 7.45(s,1H,ArH), 8.14 and 8.71(m,10H,PyH)
6	286-288	2.30(s,6H,CH <sub>3</sub> ), 5.94(s,4H,CH <sub>2</sub> ), 7.33(s,2H,ArH), 8.14, 8.60 and 8.88(m,10H,PyH).

Table 1 Physico-chemical data for the N-aralkyl-bispyridinium salts investigated

<sup>a</sup> See Fig. 2.

<sup>b</sup> Spectra were recorded on a Bruker WP-80 FT instrument at room temperature in  $D_2O$  as solvent and DSS as internal standard.

refractometer. For each compound, relative densities, refractive indices and Cotton-Mouton constants  $(d_{12}, n_{12} \text{ and } C_{12})$  were measured for a range of solutions having solute weight fractions w2. Coefficients  $\beta$ ,  $\gamma$  and D were derived using the linear relations  $d_{12} = d_1(1 + \beta w_2)$ ,  $n_{12} = n_1(1 + \gamma w_2)$  and  $C_{12} = C_1 + Dw_2$  by least-squares analysis. The subscripts 1, 2 and 12 refer to the solvent, solute and solution, respectively. Molar Cotton-Mouton constants  ${}^{\infty}({}_{m}C_{2})$  are given in c.g.s. (e.m.u.) units and  ${}^{\infty}R_{\rm D}$  is the experimental refraction at the sodium D line (in  $cm^3 mol^{-1}$ ). The conversion factor for the molar Cotton-Mouton constant  $({}^{\infty}({}_{m}C)$  from the electrostatic (c.g.s., e.m.u.) system is  $1 \text{ m}^5 \text{ Å}^{-2} \text{ mol}^{-1} = 0.6333 \times 10^{10} \text{ e.m.u. mol}^{-1}$ . Experimental results are reported in Table 2.

#### **Results and discussion**

#### Calculation of molar Cotton-Mouton constants

The experimental values of the Cotton-Mouton constants  $^{\infty}({}_{m}C_{2})$  measured for salts (1)-(6) (Fig. 2) 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 polarizability and magnetizability were employed to estimate theoretical Cotton-Mouton constants  ${}_{\rm m}C_{\rm calc}$  as a function of the four internal rotation angles  $\phi_1$ ,  $\phi_2$ ,  $\phi_3$  and  $\phi_4$  (see Fig. 3 and Scheme 1) for different conformations using the principal molecular bond and group polarizabilities and magnetizabilities

Table 2				
Molar refractions and molar	Cotton-Mouton constants	s of N-aralkyl-bispyridinium	salts measured in water at 298	ĸ

Compound	$w_2^a$	β	$\gamma^{b}$	D	$\infty R_{\rm D}^{\rm b,c}$	$10^{15} \times \infty (_{\rm m}C_2)^{\rm c}$
1	0.03-0.11	0.351	0.154	50.10	105.6 ± 1.5	7.58 ± 0.75
2	0.03-0.12	0.315	0.153	45.56	$115.3 \pm 1.0$	$7.33 \pm 0.39$
3	0.03-0.12	0.189	0.167	51.43	$105.8 \pm 0.9$	$6.64 \pm 0.20$
4	0.03-0.12	0.187	0.167	57.39	$114.2 \pm 1.1$	$8.01 \pm 0.65$
5	0.04-0.12	0.195	0.171	52.22	$110.7 \pm 1.8$	$7.02 \pm 0.21$
6	0.03-0.12	0.197	0.175	71.16	$107.3 \pm 1.3$	$9.19\pm0.49$

<sup>a</sup> Range of concentrations used expressed in weight fractions.

<sup>b</sup> For the sodium D line.

<sup>c</sup> Mean-square deviations are indicated.



Fig. 3. Planar representation of one of the possible diastereomeric N-aralkyl-bispyridinium dications. The starting structure  $(\phi_1 = \phi_2 = \phi_3 = \phi_4 = 0)$  depicted here can be described as a down-up, endo-exo diastereomer. The dotted line indicates the reference line.

listed in Tables 3 and 4, respectively. Polarizabilities and magnetizabilities for the aryl rings of ions (1), (2), (3), (4), (6) and (5) listed in Fig. 2 were taken from molecules such as *m*-xylene, durene and pentamethylbenzene; whereas for the pyridinium ring they were taken from the  $C_5H_5^+NCH_3$  cation, considering isotropic properties of the C-H bond according to additive schemes [5,14]. It was assumed that the aromatic and pyridinium rings in *N*-aralkylbispyridinium ions are ideal hexagons and the geometry at the methylene bridge was also taken as ideal, according to sp<sup>3</sup> hybridization of the carbon atom.

In the calculation of  ${}_{m}C_{calc}$  for different conformers with the use of the tensor additive schemes, any increase in the average polarizability was not taken into account. In other words, as in the investigation of the *N*-arylpyridinium cations [1], it was assumed that this possible increase is distributed evenly among the principal molecular polarizability axes.

Before discussing the experimental results it is necessary to provide a deeper insight into the conformational aspects of the cations under investigation.

For the enumeration of the possible stereoisomers of the pyridinium cations (1)-(6), let us start from any planar arrangement of all aromatic and pyridinium rings, with an initial reference

structure  $(\phi_1 = \phi_2 = \phi_3 = \phi_4 = 0, \text{ Fig. 3})$ .<sup>a</sup> For cations (1)-(6), which originate from a meta or para disubstituted aryl moiety, in order to properly identify all possible planar structures, we shall consider the ideal line which passes through the two carbon atoms of the methylene bridges, denoted as a reference line. Such a reference line divides the plan in which the molecule is lying into two regions: one is up and the other down. Thus, in the most general case (i.e. the two pyridinium rings are constitutionally different and/or do not possess a local  $C_2$  axis of symmetry, and the central aryl ring lacks  $C_2$  symmetry), four different stereoisomeric structures are generated by the four possibilities of partitioning the two pyridinium rings into these two regions: up-up, up-down, down-up and down-down. Such an arrangement is analogous to the s-cis/s-trans nomenclature more conveniently used for describing geometrical isomerism, and arises by virtue of the two internal rotation angles  $\phi_2$  and  $\phi_3$ , which can assume only two possible values (zero or  $\pi$  radians) in order to maintain the planarity of the whole molecule. More-over, in the most general cases, by rotation of zero or  $n\pi$  radians around the other two

<sup>&</sup>lt;sup>a</sup> The analysis given here is general and in principle can be applied to all molecules possessing three aryl rings, free to rotate around four torsional angles.



Scheme 1. Planar structures of the different possible stereoisomers for the cations (1)-(6).

torsional angles  $\phi_1$  and  $\phi_4$ , different planar diastereoisomers are generated. It is easy to deduce that, considering such an additional possibility of isomerism, each of the four above-mentioned s-cis/ s-trans structures will give rise to four different planar stereoisomers, which can be classified by the conventional exo/endo nomenclature, according to whether the ortho substituent in the pyridinium ring is opposite or is pointing towards the central phenyl ring.

Thus, it is apparent that for the most general substituted bispyridinium cations of formulae

Bond, group or reference molecule	$10^{23} b_1$	$10^{23} b_2$	$10^{23} b_3$	Ref.			
С–Н	0.065	0.065	0.065	9			
C <sub>Ar</sub> -CH <sub>3</sub> <sup>a</sup>	0.326	0.202	0.234	10			
$1,3-(CH_3)_2C_6H_4^{b}$	1.616	1.783	0.855	10			
1,2,4,5-(CH <sub>3</sub> ) <sub>4</sub> C <sub>6</sub> H <sub>2</sub> <sup>c</sup>	1.812	1.936	1.356	8			
$(CH_3)_5C_6H^c$	1.986	2.265	1.474	11			
C₅H₅ <sup>™</sup> CH <sub>3</sub> <sup>d</sup>	1.041	1.041	0.451	12			

Principal bond and group polarizabilities  $b_i$  (cm<sup>3</sup>) used in additive Cotton-Mouton constant calculations

<sup>a</sup> Polarizabilities  $b_1$  and  $b_2$  in the plane of the  $\pi$  system,  $b_1$  along the bond.

<sup>b</sup> Polarizabilities  $b_1$  and  $b_2$  in the plane of the  $\pi$  system,  $b_1$  along the  $C_2$  axis.

<sup>c</sup> Polarizabilities  $b_1$  and  $b_2$  in the plane of the  $\pi$  system,  $b_1$  along the C-H bond.

<sup>d</sup> Polarizabilities  $b_1$  and  $b_2$  in the plane of the  $\pi$  system.

depicted in Fig. 3,  $4 \times 4 = 16$  planar stereoisomeric structures are possible.<sup>a</sup>

Of course many of these diastereomers can be disregarded as feasible conformers on steric grounds: among planar structures in which the pyridinium ring bears a substituent in the 2'position, only diastereomers having such a group in the exo position will be considered ( $\phi_1 = \phi_4 = 0^\circ$ , in Scheme 1). Including the possible degeneracies which can arise whenever the two pyridinium rings are constitutionally identical and/or possess a local  $C_2$  axis of symmetry, or whenever the central aromatic ring possesses a  $C_2$  axis, the number of planar stereoisomers of cations (1)-(6) will be reduced to three, as indicated in Scheme 1. Deviation from coplanarity ( $\phi_1$ ,  $\phi_2$ ,  $\phi_3$  and  $\phi_4 \neq 0$ ), necessary in order to relieve steric strain, will generate an infinite number of possible conformers, which can be defined by the different values of any of the four torsional angles  $\phi_i$ .

However, there now exists a fairly impressive body of evidence [2,3] that supports the view that whenever two aryl rings are attached to a central atom, their sense of twist is the same. Thus, in order to simplify the calculations let us assume that for the cations under study, the values of all  $\phi_i$  angles

Table 4

Principal bond and group magnetizabilities  $k_i$  (cm<sup>3</sup>) used in additive Cotton-Mouton constant calculations

Bond, group or reference molecule	$-k_1 \times 10^{29}$	$-k_2 \times 10^{29}$	$-k_3 \times 10^{29}$	Ref	
C <sub>Ar</sub> -CH <sub>3</sub> <sup>a</sup>	1.54	2.32	2.32	13	
C <sub>6</sub> H <sub>5</sub> <sup>b</sup>	5.88	5.88	15.58	7	
1,2,4,5(CH <sub>3</sub> ) <sub>4</sub> C <sub>6</sub> H <sub>2</sub> <sup>b</sup>	13.04	13.04	24.32	8	
C₅H₅ <sup>↑</sup> NCH <sub>3</sub> <sup>b</sup>	5.2	5.2	14.4	12	

<sup>a</sup> Magnetizabilities  $k_1$  and  $k_2$  in the plane of the  $\pi$  system,  $k_1$  along the bond.

<sup>b</sup> Magnetizabilities  $k_1$  and  $k_2$  in the plane of the  $\pi$  system.

Table 3

<sup>&</sup>lt;sup>a</sup> This value can be easily deduced, in the most general case, by considering that the planar stereoisomers of the cations considered here are generated by four different torsional angles which can assume only two distinct values, zero or  $\pi$ radians; this means that (2)<sup>4</sup> = 16 isomers exist.

are also the same ( $\phi_1 = \phi_2 = \phi_3 = \phi_4 = \phi$ ) with  $\phi$ being equal to 41.4°, which is the average value obtained for N-aralkylpyridinium cations previously investigated by the Cotton-Mouton technique [1]. Inspection of Fig. 1 reveals that in diaryl molecules, twisting the two rings by the same magnitude will generate enantiomeric propeller shaped structures with either a right-handed (R) or left-handed (L) helicity, according to the sense of twisting, which can be counter-clockwise or clockwise, respectively. Now, analyzing our dications (1)-(6) as a system formed by two subsets of diaryl derivatives, the two rings AB or BC within each diaryl-methyl moiety can have an R or L helicity and thus four different conformations can be generated from any of the coplanar starting structures I-III listed in Scheme 1: they are named RR, LR, and LL, RL. The latter two conformations are mirror images of the first two and consequently are indistinguishable by Cotton-Mouton constants measured in an achiral medium.

Structures RR (or LL) are generated by twisting all the aryl rings in the same direction ( $\phi_1 = \phi_2 = \phi_3 = \phi_4 = 41.4^\circ$ ) and thus they are helical possessing the same sense of spiralization; however, conformers LR (or RL) possess  $\phi_1 = \phi_2 = 41.4^\circ$ and  $\phi_3 = \phi_4 = -41.4^\circ$  and thus they are no longer helical.

For all of the conformers generated in this way from the initial structures (I-III) of the cations (1)-(6) (Scheme 1) we calculated the  ${}_{\rm m}C$  values which are compared with the experimental  ${}^{\infty}({}_{\rm m}C_2)$  values in Table 5. Inspection of this table reveals that the various stereoisomers considered are clearly differentiated by their  ${}_{m}C_{calc}$  values. For the dications (1)–(5) the experimental Cotton– Mouton constant values are very close to those calculated for conformers of the type III(R,R), whereas for (6) the experimental data indicate a mixture of structures I(L,R) and III(L,R).

Of course, the hypothesis that in solution there is an equilibrium among all the possible conformers cannot be fully disregarded, considering that the experimental values for  ${}^{\infty}({}_{m}C_{2})$  fall in the range of the values for  ${}_{\rm m}C_{\rm calc}$  for the selected conformers (Table 5). However, for cations (1)-(5), the existence of other conformers besides III(R,R) should be small, considering the good agreement between calculated and experimental values. For such compounds, this statement can be demonstrated with the help of plots in cartesian coordinates of  ${}_{\rm m}C_{\rm calc}(i)$  vs.  ${}_{\rm m}C_{\rm calc}(j)$  if we consider the cations under the numbers (i) and (j) to be isoconformational. Such plots were proposed earlier by Exner and Jehlicka [14] using the square of dipole moments of isoconformational compounds and this idea was generalized for Kerr and Cotton-Mouton constants by Vereshchagin [5,15]. The points on this plot referring to different conformers are the vertices of the polygon, whereas the side segments of the polygon indicate an equilibrium between the conformers situated on the two vertices, while the points in the interior region of the polygon indicate an equilibrium among all the conformers. In other words, when an experimental

Table 5

Calculated  $({}_{m}C_{calc})$  and experimental  $({}^{\infty}({}_{m}C_{2}))$  values of Cotton-Mouton constants for the *N*-aralkyl-bispyridinium dications investigated. The calculated values are given for helical orientations of the aryl and pyridinium rings (see text)

Compound	$^{\infty}(_{\rm m}C_2) \times 10^{15}$ exp	$_{\rm m}C_{\rm calc} \times 10^{15}$ (see Scheme 1 and text)						
		I(R,R)	I(L,R)	II(R,R)	II(L,R)	III(R,R)	III(L,R)	
1	7.58	6.21	9.67	3.59	5.52	7.29	4.07	
2	7.33	5.62	9.60	3.17	5.57	7.36	3.04	
3	6.64	5.04	8.50	2.79	4.72	6.87	3.65	
4	8.01	4.55	8.53	2.46	4.86	7.01	2.68	
5	7.02	5.85	9.31	3.18	5.11	6.83	3.62	
6	9.19	5.73	9.59	2.52	2.77	4.70	8.59	



Fig. 4. Plots of  ${}_{m}C_{calc}(i)$  vs.  ${}_{m}C_{calc}(j)$  (see Table 5) for cations (a) (i = 1) and (j = 2); (b) (i = 5) and (j = 3). (c) calculated values; ( $\bullet$ ) experimental values.



Fig. 5. Most probable cis-cis(R,R) conformation of the cations (1)-(5). Both the pyridinium and central aryl rings are aligned along the spiral line and the arrangement of the rings with respect to the  $C_{Ar}-CH_2-N_{Ar}$  reference plane is helical.

point in the plot of  ${}^{\infty}({}_{\mathrm{m}}C_2)(i)$  vs.  ${}^{\infty}({}_{\mathrm{m}}C_2)(j)$  falls on a side line there is an equilibrium between the two forms, but when the point is inside the polygon, this implies that there is an equilibrium among all the conformers. Plots for pairs of cations (1)-(2) and (3)-(5) are shown in Fig. 4. For any other selected pairs of cations (1)-(5), the plots are similar. For the most probable conformation III(R,R), the plot also shows the range of  ${}_{\rm m}C_{\rm calc}$  values deduced according to the mean-squares deviation from the average value of  $\phi = 41.4^{\circ}$ , obtained from the data of the Cotton-Mouton investigation of N-aralkylpyridinium cations [1]. For the experimental points the range corresponding to the mean-squares deviation of the experimental values of  ${}^{\infty}({}_{\mathrm{m}}C_2)$  (Table 2) is also shown.

Inspection of Fig. 4 reveals that there is not only a close proximity between the experimental and the III(R,R) conformation points but also an overlap between their mean-square deviation ranges. Thus, it can be concluded that the most probable conformation for cations (1)–(5) is cis-cis(R,R) (as well as cis-cis(L,L)) and the contribution of other possible conformers should be negligible.

As far as cation (6) is concerned the conclusion cannot be so definite, since there is no isoconformational compound in the framework of our study. However, in all likelihood this cation exists predominantly either in the trans-trans(L,R) or the cis-cis(L,R) form, or as a mixture of them.

The conformation cis-cis(R,R) for cations (1)-(5) is quite interesting. As can be seen from Fig. 5 the helical arrangement of aryl and pyridinium rings in the cis-cis(R,R) conformer generates a spiral spatial arrangement of these three rings along a screw line. It is plausible that this conformation could be stabilized by the solvent used and originates from electrostatic factors influencing the structures of the cations examined. This spiral winding of the compounds investigated must lead to a decrease in the electrostatic interactions between the hydrophobic organic substrates, the cationic charges located inside the spiral and the water environment. At the same time, the positively charged pyridinium rings are moved far away from each other in order to decrease the repulsive electrostatic interactions between them. The same factors are involved in the spiral alignment of large, charged polymer molecules in water, as observed in proteins. However, when the substitution pattern in the central aryl ring of the cations examined is modified, as in the case of compound (6), different conformations can become more stable.

## Conclusions

The infinite dilution molar Cotton-Mouton constants of the N-aralkyl-bispyridinium cations examined are consistent with the presence in water of helical structures in which all the pyridinium and aryl rings are twisted in the same direction with respect to the  $C_{Ar}$ -CH<sub>2</sub>-N<sub>Ar</sub> reference plane. For the compounds (1)-(5), only one conformer is present in the ground state and it possesses a spiral spatial arrangement of these three rings along a screw line. For compound (6) the experimental data are better interpreted in terms of an equilibrium between two conformers still possessing a helical arrangement of the rings in each diaryl-methyl subunit.

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