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X-ray Crystallography at 170 K of Racemic 2,2'-Dimethoxy-9,9'-biacridine and ^{1}H NMR Study of 2,2'-Diacetoxy-9,9'-biacridine

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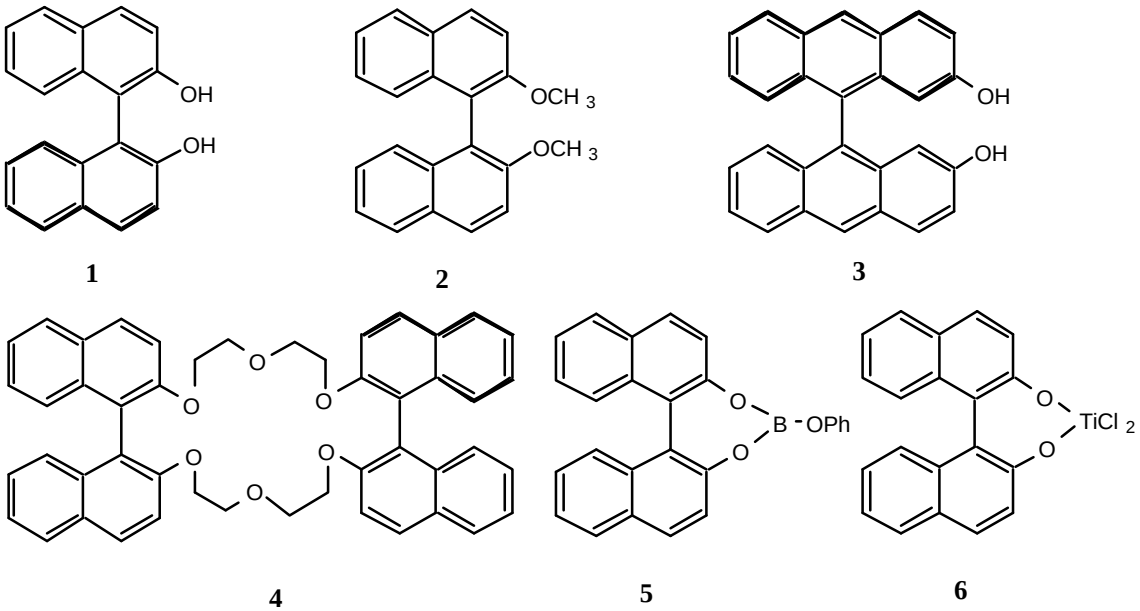
Abstract: Three derivatives of 9,9'-biacridine, 2,2'-dihydroxy, 2,2'-dimethoxy and 2,2'-diacetoxy have been prepared. The crystal structure of racemic 2,2'-dimethoxy-9,9'-biacridine $CHCl_3$ 1:1 complex has been determined and shows an almost perpendicular conformation of both acridine rings. ^{1}H NMR experiments using the diacetoxy derivative and both $Eu(tfc)_3$ and *R*-Pirkle's alcohol show the splitting of some signals characteristic of a racemic compound.

Keywords: Biacridines, X-Ray analysis, Lantanide shift reagents, Pirkle's alcohol.

Introduction

2,2'-Dihydroxy-9,9'-binaphthyl (**1**) (Scheme 1) has been used by Toda as a host [1,2]; the racemic compound can be resolved using a chiral amide guest [3] or a chiral ammonium salt [4] and afterwards can be used to prepare crystalline inclusion compounds with either ammonia or alkali metal hydroxides [5], while 2,2'-dimethoxy-1,1'-binaphthyl (**2**) is resolvable by entrainment [6]. 2,2'-Dihydroxy-9,9'-bianthryl (**3**) has also been used by Toda as a chiral host [1]. Chiral binaphthyl-22-crown (**4**) has been described by Cram and co-workers in the study of transport of racemic ammonium salts [7,8] (for a related macrocycle based on binaphthyls, see [9]). The chiral boron reagent **5** and the titanium derivative (BINOL-$TiCl_2$) **6** are useful reagents in asymmetric syntheses [10-13]. These series of possible applications prompted us to study compounds related to bianthryl **3** but using the 9,9'-bipyridyl skeleton **7** (Scheme 2) we have already described [14].



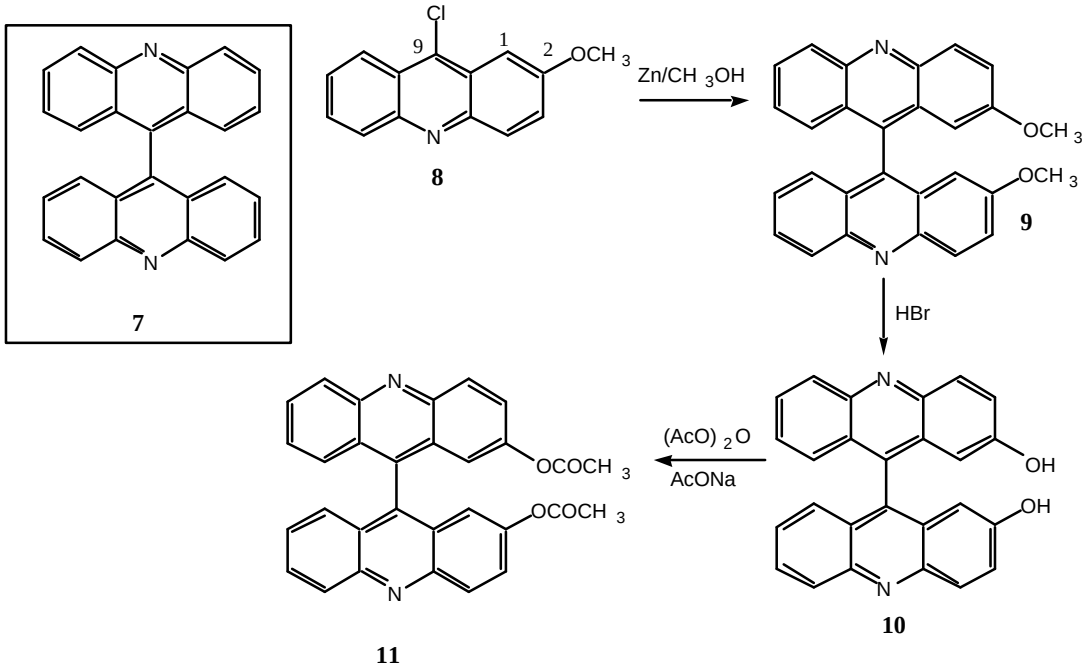
1 **2** **3** **4** **5** **6**

Scheme 1. Some important compounds related to binaphthyl and bianthryl.

Results and Discussion

Chemistry

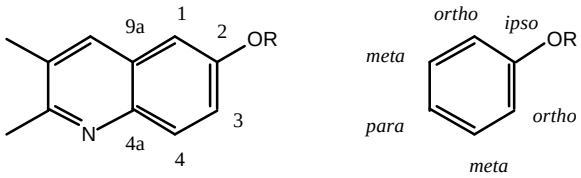
The dimethoxy derivative **9**, already known [15-17], was obtained from 2-methoxy-9-chloroacridine (**8**) according to Scheme 2. The diacetoxy derivative **11** was prepared to increase the poor solubility of biacridines [14].



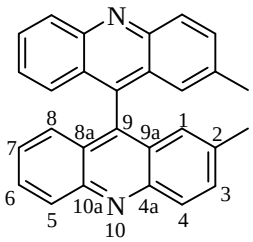
Scheme 2. Sequence of reactions used to prepare compounds **9-11**.

^{1}H and ^{13}C NMR spectroscopy

The chemical shifts of compounds **9-11** are reported in Tables 1 (^{1}H NMR) and 2 (^{13}C NMR). The assignments have been made by ^{1}H-^{1}H and ^{1}H-^{13}C bidimensional experiments. Although the spectrum of the parent biacridine **7** has been recorded in $CDCl_3$ [14], it is possible to calculate the Substituent Chemical Shifts (SCS) of compounds **9-11** and compare them with those reported by Ewing for monosubstituted benzenes [18].



Scheme 3.



Scheme 4. 9, R= OCH_3; **10**, R= OH, **11**, R= $OCOCH_3$.

Table 1. ^{1}H chemical shifts (in ppm) and ^{1}H-^{1}H coupling constants (in Hz) in DMSO-d_6.

No	**9**	**10**	**11**
H1	6.18, ^{4}J=2.5	6.17, ^{4}J=2.0	6.76
H3	7.59, ^{3}J=9.4, ^{4}J=2.5	7.49, ^{3}J=9.4, ^{4}J=2.0	7.73, ^{3}J=9.4
H4	8.29, ^{3}J=9.4	8.25, ^{3}J=9.4	8.40, ^{3}J=9.4
H5	8.31, ^{3}J=8.5	8.29, ^{3}J=8.8	8.36, ^{3}J=8.8
H6	7.79, ^{3}J=7.8, ^{3}J=8.5	7.76, ^{3}J=7.4, ^{3}J=8.8	7.83, ^{3}J=7.5, ^{3}J=8.8
H7	7.35, ^{3}J=7.8, ^{3}J=8.5	7.34, ^{3}J=7.4, ^{3}J=8.6	7.41, ^{3}J=7.5, ^{3}J=8.6
H8	6.92, ^{3}J=8.5	6.95, ^{3}J=8.6	7.00, ^{3}J=8.6
R	3.33 (OCH_3)	9.96 (OH)	2.07 ($OCOCH_3$)

Table 2. ^{13}C chemical shifts (in ppm) in DMSO-d_6.

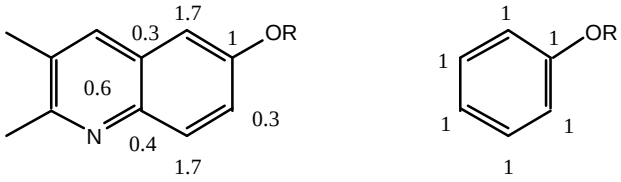
No	**9**	**10**	**11**
C1	101.13	103.93	115.56
C2	157.35	155.75	148.81
C3	125.14	125.88	127.72*
C4	131.76	131.76	131.56
C4a	145.19	145.27	147.15
C5	129.80	129.89	129.98
C6	129.40	129.10	130.81
C7	127.18	127.07	127.81*
C8	125.28	125.33	125.70
C8a	125.28	125.26	125.28
C9	137.52	137.04	139.50
C9a	125.87	126.56	125.28
C10a	146.61	146.38	146.55
R	56.02 (CH_3)	-----	169.21 (CO) 20.84 (CH_3)

*These signals can be inverted.

The *ortho* and *meta* positions of biacridines have to be treated separately. Even if the number of points (n = 3) is clearly insufficient, the following equations are obtained assuming that there is no intercept (SCS = 0 for the unsubstituted compounds):

SCS (C-2 biacridines) = (0.978±0.003) SCS (*ipso* benzene), r^2 = 1.000 (1)
SCS (C-1 biacridines) = (1.71±0.06) SCS (*ortho* benzene), r^2 = 0.997 (2)
SCS (C-3 biacridines) = (0.376±0.008) SCS (*ortho* benzene), r^2 = 0.999 (3)
SCS (C-4a biacridines) = (0.427±0.003) SCS (*para* benzene), r^2 = 1.000 (4)

The *meta* carbons (C-4 and C-9a) are not sensitive enough to SCS effects and the correlations are not good, nevertheless the effects on C-4 (slope 1.7) are larger than on C-9a (slope 0.3) and more similar to those observed in benzenes. If we make the assumption that in benzenes all the SCS effects correspond to a slope of 1 (total 6) and that in biacridines the overall effect is the same (total 6), then we can represent the two cases as follows:



Scheme 5.

The fusion to the heterocyclic moiety produces a localization of the π system in the sense indicated in the above resonance structure for **9**-**11** (the perturbation extends to this moiety which could account for the remaining 0.6).

^{1}H NMR experiments with lanthanide shifts reagents (LSR)

The synthesis used to prepare **9** must result in a racemic mixture and, since racemization of this kind of compounds is highly improbable, the same should happen to **10** and **11**. We carried out some experiments to find out if ^{1}H NMR in the presence of either LSR* or Pirkle's alcohol [19] could be used to determine the enantiomeric composition in the special case of axial chirality.

The LSR experiments were carried out on the diacetyl derivative **11**. First the achiral Eu(fod)$_3$ reagent was used in order to find which were the most sensitive signals. The result is represented graphically in Figure 1 (LIS, Δδ in ppm versus lanthanoid-substrate molar ratios) and the corresponding equations are in the Experimental part. The slopes are given below:

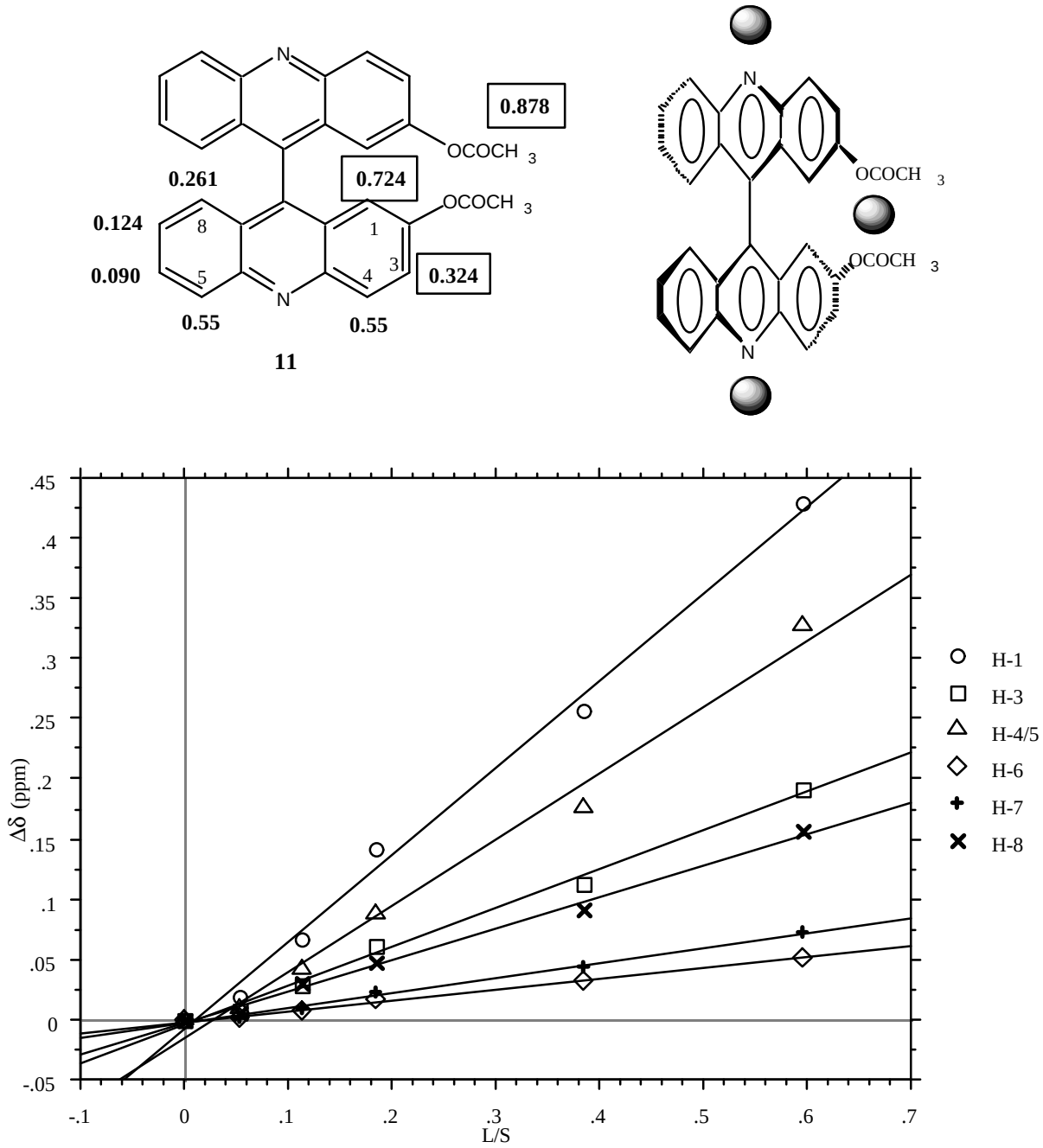


Figure 1. Plot of Δδ [δ(**11**)+Eu(fod)$_3$] - δ(**11**)] versus the molar ratio [Lanthanide Eu(fod)$_3$]/ [Substrate (**11**)] in 0.2 mL of $CDCl_3$ (the CH_3 signal of the acetoxy group is not shown).

In a first approximation (for quantitative analysis see ref. [20]), the LSR (grey spheres) occupies two positions, one near the acetoxy groups and the other near the pyridine nitrogen atoms.

The use of the chiral LSR reagent [LSR*] Eu(tfc)$_3$ (see experimental part) produces a splitting of two signals those corresponding to H1 and (using larger concentrations) to H3. As expected, the

intensities of both signals are the same. The fact that the phenomenon affects H1 and H3 but not H5 points out that it is the LSR* located near the acetoxy groups which is responsible for the diasterotopicity.

^{1}H NMR experiments with R-Pirkle's alcohol in $CDCl_3$

With *R*-Pirkle's alcohol [19], preliminary results (see Experimental Section) show that the methyl ($\Delta\delta$ = 0.105 ppm), H4 ($\Delta\delta$ = 0.024 ppm) and H6 ($\Delta\delta$ = 0.011 ppm) signals of compound **11** split ($\Delta\delta$ is the value of the splitting). For small amounts of the reagent, the two methyl group singlets are the most useful for determining possible enantiomeric excesses.

We decided to examine in detail the behaviour of **11**, chiral by virtue of a "chiral axis", in the presence of *R*-Pirkle's alcohol. In Figure 2 the aromatic part of the ^{1}H NMR spectra of compound **11** with and without *R*-Pirkle's alcohol are represented. The splitting affects the methyl group, H4, H6 and H7 aromatic protons. Since H4 and H5 almost overlapped, the analysis was carried out on the signals of H6 and H7 protons.

The signal of H6 at 7.792 ppm appeared as an overlapped double doublet that by deconvolution analysis showed a ^3J = 8.9 Hz (with H5) and ^3J = 6.65 Hz (with H7); in the same way, from the signal of H7 at 7.304 ppm it was possible to determine a ^3J = 8.4 Hz (with H8) and a $^3J \approx 6.65$ Hz (with H7). After addition of *R*-Pirkle's reagent, protons H6 and H7 gave rise to sixteen signals (Figures 3). Each signal was decomposed and simulated as the addition of **two** double double doublets ($^3J_{ortho}$+$^3J_{ortho}$+$^4J_{meta}$), with the same coupling constants that in absence of Pirkle's alcohol plus a $^4J_{meta}$ = 1.1 Hz (not observed in the free **11**), obtaining two chemical shifts for each one: H7 7.262 and 7.272 (Figure 3a); H6 7.686 and 7.704 (Figure 3b). A possible explanation of why the effect of Pirkle's alcohol is observed mainly on H6 and H7, is that these two "external" protons are the most accessible to the chiral reagent.

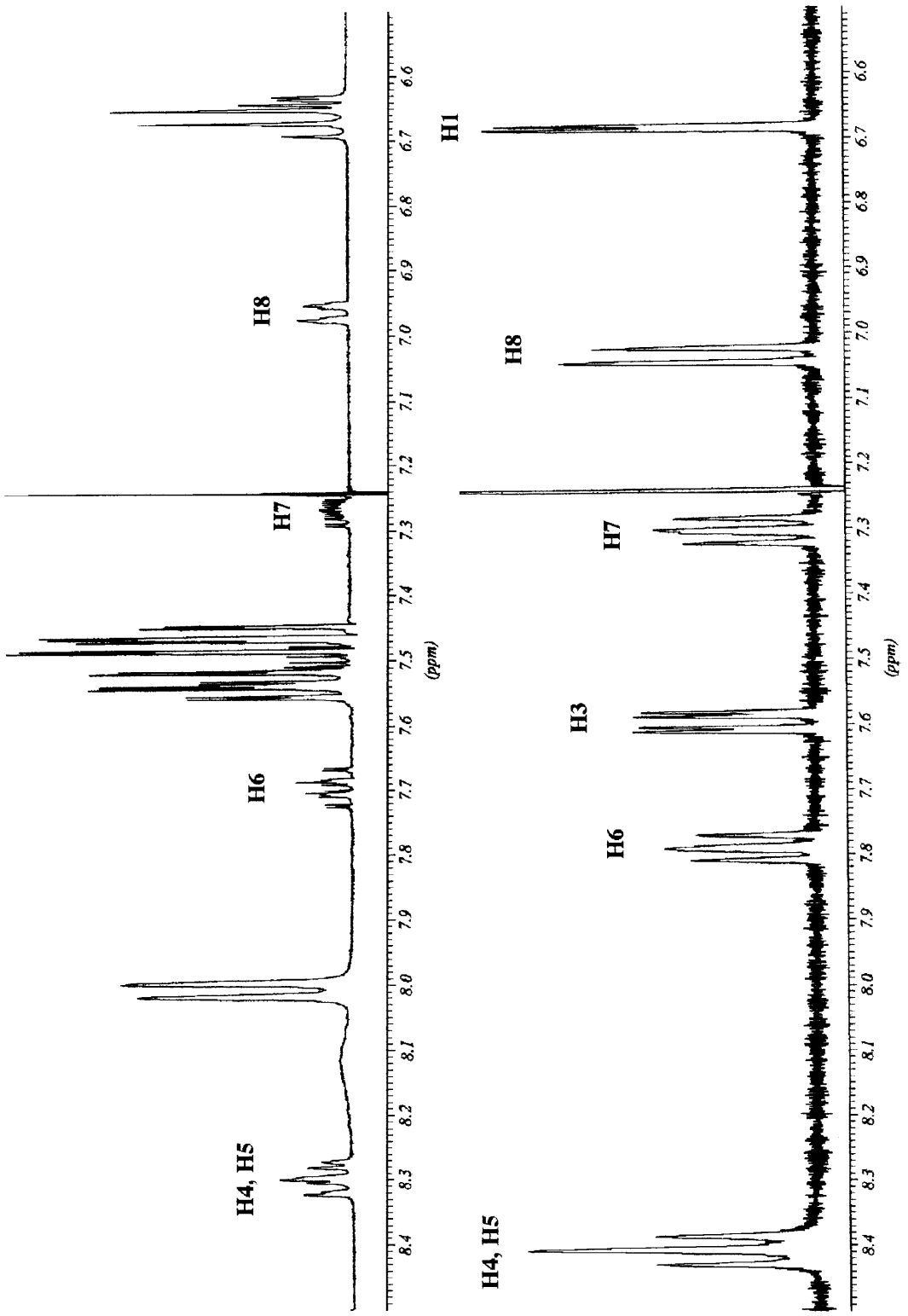


Figure 2. ^{1}H NMR spectra (400 MHz) of compound **11** before (bottom) and after addition of R-Pirkle`s alcohol (top).

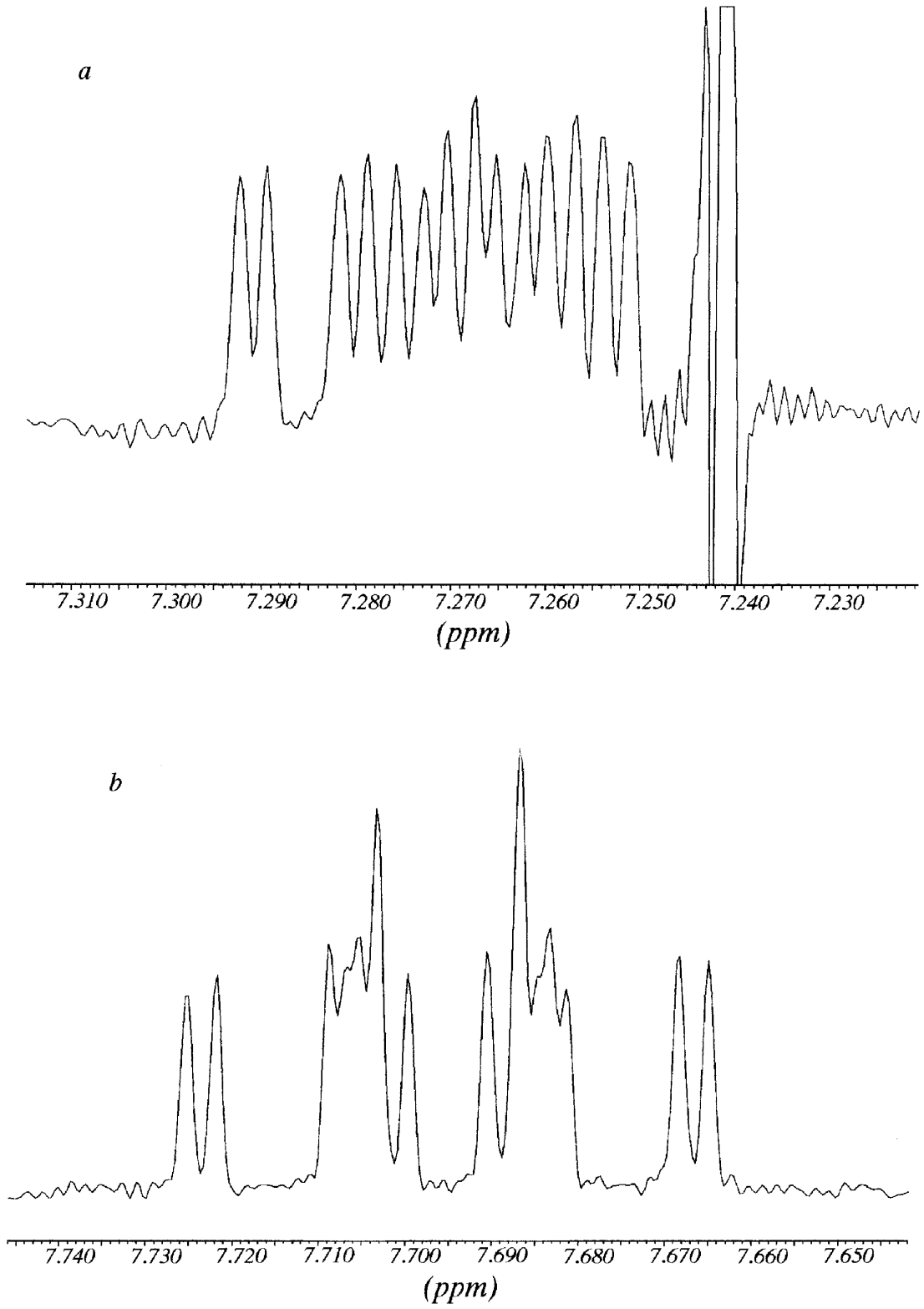


Figure 3. Multiplicity of the signals of H7 (Figure 3a) and H6 (Figure 3b) of compound **11** in the presence of R-Pirkle`s alcohol (corresspond to Figure 2 top).

Single Crystal X-Ray Analysis

Selected geometrical parameters are gathered in Table 3 according to the numbering scheme displayed in Figure 4a. The pattern of bond lengths and angles of the host molecule presents the same trends as the mean values obtained for seven acridine molecules (two polymorphic forms and several host-guest complexes) retrieved from the Cambridge Structural Database (CSD hereinafter, October 1997 Version) [22]. Both acridine moieties display a significant lack of planarity that is described by the angles between the mean least-squares planes of the central pyridine ring and each lateral phenyl ring, Table 3. The twist between both acridine planes is close to 90º, that is slightly bigger than the mean value of 83(6)º [in parentheses the estimated standard deviation of the sample] observed for six 9,9'-bianthryl derivatives not substituted in positions 1, 8, 1' and 8' and retrieved from CSD. There are no significant differences between both halves of the molecule, including the methoxy substituents, when they are overlapped according to a least-square procedure based on their atomic coordinates [23] [χ^2 values for x, y, z coordinates of 10.95, 15.31 and 17.91 versus a tabulated value of 26.30 at 95% probability level]. However, the host molecule is somehow distorted as can be seen in the Newman projection along the C(9)-C(9') bond shown in Figure 4b. One acridine moiety lacks its parallelism with the central C(9)-C(9') bond and is bent towards the $CHCl_3$ guest molecule, 6.0(2) versus 1.9(2)º, Table 3. This could be an indication of the strength of the intermolecular CH···N hydrogen bond.

Both methoxy groups are almost coplanar with regard to the phenyl rings they are attached to, Table 3, in agreement with the mean value of 5(5)º obtained after averaging 1797 hits retrieved from CSD. The search fragment was a methoxyphenyl moiety with no substitution at the *ortho* positions. Moreover, the C(Ph)-O and O-CH_3 distances and the C(Ph)-O-CH_3 angle do not differ significantly from the mean values 1.371(16), 1.419(25) Å and 117.8(12)º respectively, Table 3.

Table 3. Selected geometrical parameters and hydrogen bond interactions (Å, º).

C(2)-O(15)	1.356(6)		C(2')-O(15')	1.356(5)
O(15)-C(16)	1.426(7)		O(15')-C(16')	1.420(7)
C(9)-C(9')	1.501(6)			
C(1)-C(2)-C(3)	120.3(4)		C(1')-C(2')-C(3')	120.4(4)
C(6)-C(7)-C(8)	120.7(4)		C(6')-C(7')-C(8')	119.7(4)
C(12)-C(9)-C(13)	118.7(3)		C(12')-C(9')-C(13')	119.5(4)
C(11)-N(10)-C(14)	118.3(3)		C(11')-N(10')-C(14')	118.6(4)
C(2)-O(15)-C(16)	117.3(4)		C(2')-O(15')-C(16')	116.9(4)
C(1)-C(2)-O(15)-C(16)	-3.7(6)		C(1')-C(2')-O(15')-C(16')	1.8(7)
C(12)-C(9)-C(9')-C(12')	91.6(5)		C(12)-C(9)-C(9')-C(13')	-85.2(5)
C(13)-C(9)-C(9')-C(12')	-83.7(5)		C(13)-C(9)-C(9')-C(13')	99.5(5)
Angles between lines[a] and mean least-square planes[b]				
L1^L2	1.9(2)		L2^L3	6.0(2)
P1^P2	1.3(1)		P4^P5	1.8(1)
P2^P3	1.0(1)		P5^P6	3.3(1)
Hydrogen interactions	**D-H**	**H···A**	**D···A**	**D-H···A**
C(3)-H(3)···N(10')(x,y-1,z)	0.91(6)	2.89(7)	3.440(6)	120(5)
C(4)-H(4)···N(10')(x,y-1,z)	0.93(6)	2.68(6)	3.339(5)	129(4)
C(16')-H(16'1)···O(15)(-x,-y,-z+1)	1.06(7)	2.56(7)	3.583(6)	164(5)
C(17)-H(17)···N(10)(-x+1,-y,-z+1)	0.90(7)	2.45(7)	3.329(7)	168(5)
Cl_3C-H···N(acridine)[c]	1.00(11)	2.25(18)	3.228(97)	167(6)

[a] L1, L2 and L3 stand for the lines defined by the pairs of atoms [N(10'), C(9')], [C(9'), C(9)] and [C(9), N(10)] respectively. - [b] P2 and P5 stand for the mean least-square planes of the central rings and P1, P3, P4 and P6 for those containing the C(1), C(8), C(1') and C(8') atoms respectively. - [c] Mean values obtained from 4 hydrogen bonds retrieved from CSD [22]. The estimated standard deviation of the sample is in parentheses.

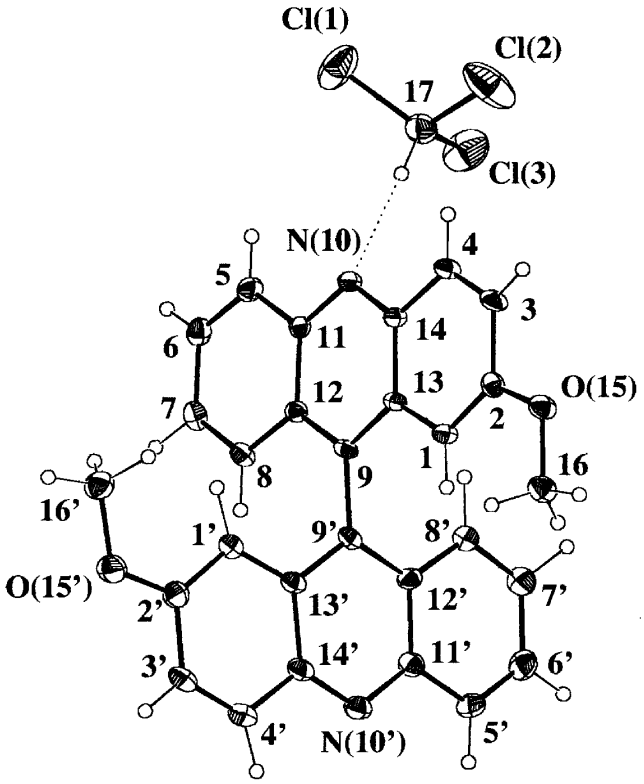


Figure 4a. Perspective view of the complex **9**·$HCCl_3$ displaying the numbering scheme and the host-guest intermolecular hydrogen bond (dotted line).

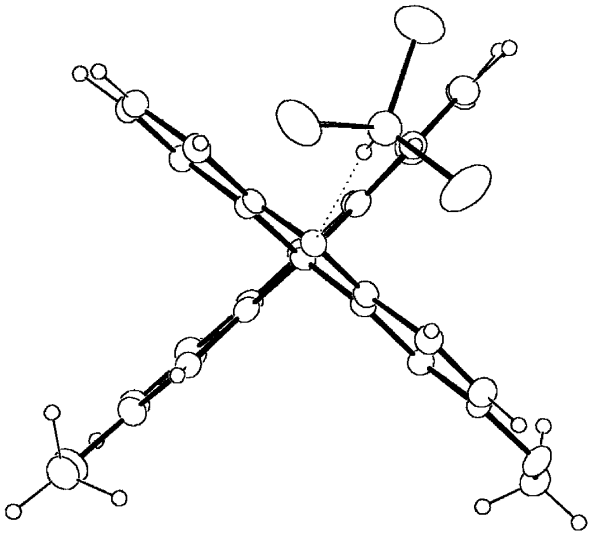


Figure 4b. Newman projection of **9**·$HCCl_3$ along the C(9)-C(9') bond, showing the molecular conformation of the biacridine moiety and the coplanarity of the metoxy substituents. Anisotropic displacement parameters are drawn at 30% probability level.

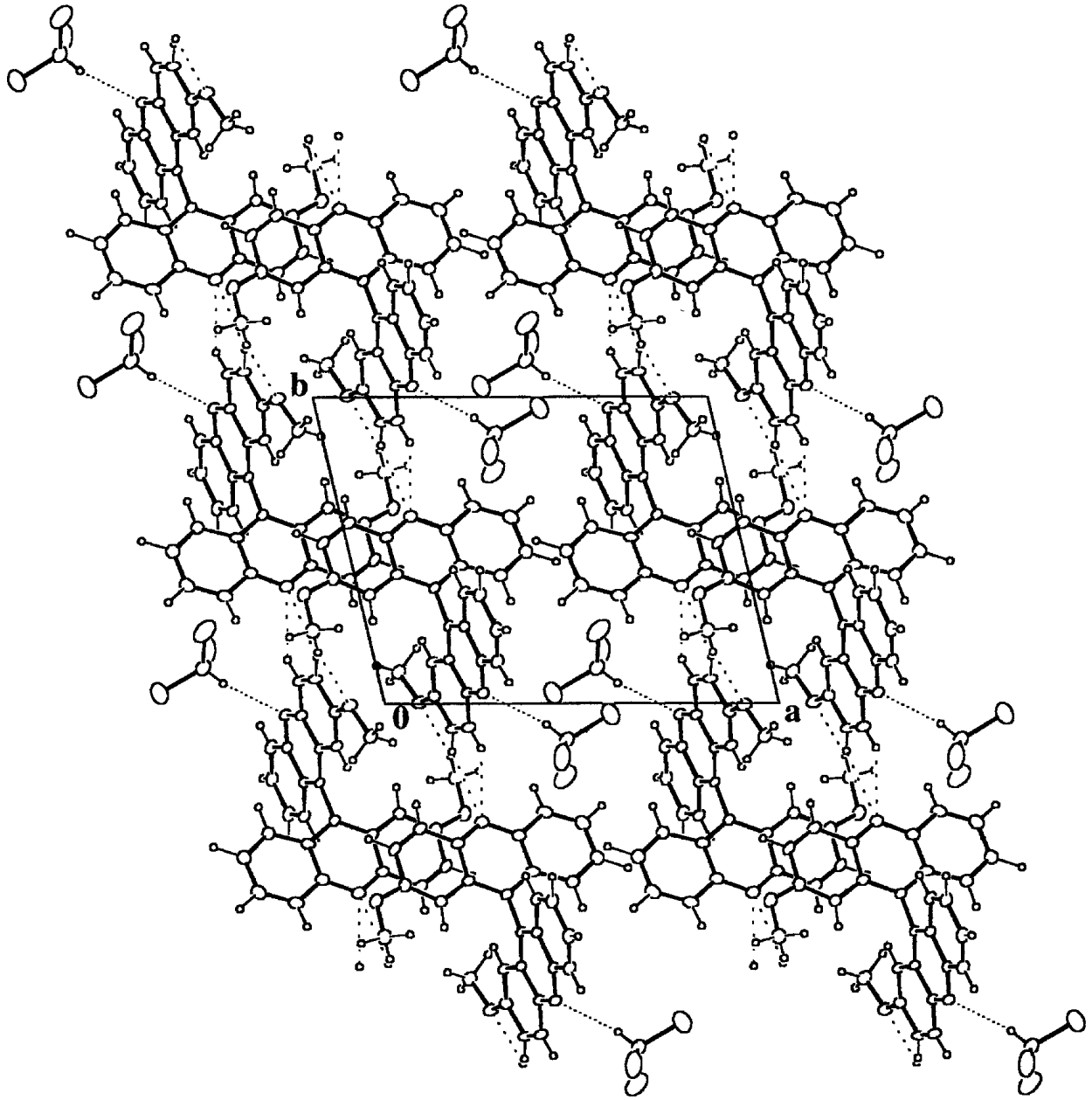


Figure 6. Packing diagram of **9**·$HCCl_3$ down the **c** axis. The most compact dotted lines mark the hydrogen bonds between the host and guest moieties. The remaining dotted lines stand for intermolecular hydrogen bonds between host molecules. The resulting structure is due to the packing of chains along **b** formed by centrosymmetric dimers around (0, 0, $^1/_2$) composed by host-guest pairs.

From fifty-one structures containing an acridine fragment (CSD), there are three that include $CHCl_3$ as guest, one of them with two crystallographically independent molecules, and in all cases, there is a strong and linear $Cl_3CH\cdots N$(acridine) hydrogen bond interaction, Table 3. The intermolecular hydrogen

bond is almost as strong as that reported for the $Cl_3CH\cdots O$ system [24], 2.22(3) and 3.16(2) Å for the H···O and C···O distances respectively. According to this observation, the title compound also presents this kind of host-guest interaction, which is the strongest one found in the crystal structure and that gives rise to pairs of host-guest bonded molecules, Table 3 and Figure 5. These pairs form dimers around inversion centers at (0, 0, 1/2) and symmetry related ones, by means of C-H···O hydrogen bonds. Finally, the dimers give rise to chains along the *b* axis through two contiguous C(Ph)-H···N hydrogen bonds, which constitute the final secondary structure motives that make up the whole crystal structure.

There are no voids left in the structure and the total packing coefficient [25] is 0.71 (C_k^{all} = $V_{molecules}$/Unit Cell Volume). However, the $CHCl_3$ molecules are packed together and enclosed in channels along the *c* axis left by the host matrix, Figure 5. In spite of the quite strong hydrogen bond interaction between the host and guest molecules, the local packing coefficient for this moiety is significantly lower than the overall one, $C_k^{local} = 0.56$.

Experimental

General

Melting points were determined on a Reichert Jung microscope instrument and are uncorrected. ^1H and ^{13}C FT-NMR spectra were recorded at 400 and 100.6 MHz on Bruker AMX400 spectrometer. The LSR experiments were carried out using a Varian Unity 500 (^1H at 499.84 MHz). In all cases, TMS was used as an internal standard.

2-Methoxy-9-chloroacridine (**8**)

1. Preparation of 4'-methoxy-*N*-phenylanthanilic acid. This compound was prepared according to the literature [20], from *p*-anisidine and *o*-bromobenzoic acid, with 97% yield, m.p. 187 ºC, Lit. 186 ºC [20].

2. Reaction of 4'-methoxy-*N*-phenylanthanilic acid with phosphorus oxychloride. In a 250 ml round bottom flask were placed 8.33 g (34 mmol) of 4'-methoxy-*N*-phenylanthanilic acid and 33 ml (0.36 mol) of phosphorus oxychloride. After 15 min at 90 ºC and then 2 h at 130 ºC, the reaction mixture was evaporated to dryness to eliminate the excess of phosphorus oxychloride. The residue was dissolved in 100 ml of chloroform and the chloroform solution washed carefully with aqueous ammonia than with water. After drying the solution with magnesium sulfate, the filtered solution was evaporated to dryness. The solid residue was crystallized in ethanol. Compound **1** was obtained pure as yellow needles (5.94 g, 71% yield), m. p. 152 ºC, Lit. m.p. 152-153 ºC [21].

2,2'-Dimethoxy-9,9'-biacridine (**9**)

In a 250 ml round bottom flask are mixed 2 g (8 mmol) of **8**, 0.6 g of powdered zinc (9 mmol) and

60 ml of anhydrous methanol. After 4 h reflux under nitrogen atmosphere, the mixture, still hot, was filtered off. The residue was partly dissolved in hot pyridine (50 ml) and the zinc eliminated by filtration. The addition of water resulted in the formation of a precipitate. After washing carefully with water, the residue was dried: a yellow powder was obtained (1.68 g, 49% yield), m.p. 264 ºC, Lit. 263-264 ºC [15].

2,2'-Dihydroxy-9,9'-biacridine (**10**)

In a 250 ml round bottom flask were mixed 1.3 g (3.12 mmol) of **9** and 80 ml of 48% hydrobromic acid (0.36 mol). After 48 h at reflux, the solution was poured into ice and neutralized with 5N ammonia (approx. 35 ml). A precipitate was formed, filtered, washed several times with water and dried: 750 mg (62% yield), m.p. > 400 ºC, Lit. 410-414 ºC [15].

2,2'-Diacetoxy-9,9'-biacridine (**11**)

In a 50 ml round bottom flask were mixed 0.5 g (1.28 mmol) of **10**, 0.66 g (8.1 mmol) of sodium acetate and 6 ml (0.6 mole) of acetic anhydride. After 2 h of stirring under reflux, the mixture was allowed to cool down and filtered. The precipitate was suspended in a little water, neutralized with NaOH 3N and filtered. The precipitate was washed with water several times. After drying, the green powder residue (0.44 g, 72% yield) is pure. M.p. 310 ºC. Anal. Calc. for $C_{30}H_{20}N_2O_6$, C 76.26, H 4.27, N 5.93%, Found: C 76.03, H 4.31, N 6.05%.

NMR

The experiments with LSRs were carried out using $CDCl_3$ as solvent, compound **11** as substrate and a 500 MHz machine (Varian Unity 500, IQM, Madrid). In this solvent the chemical shifts are: H1 6.708 ppm (J = 2.3 Hz), H3 7.594 (J = 9.4, J = 2.3 Hz), H4 8.397 ($J \approx 9$ Hz), H5 8.397 ($J \approx 9$ Hz), H6 7.779 (J = 7.7 Hz), H7 7.295 (J = 7.7 Hz), H8 7.043 (J = 8.5 Hz), CH_3 2.112 ppm. For $Eu(fod)_3$, the equations corresponding to the lines of Fig. 1 are (ordered by slopes):

CH_3	$\Delta\delta = -12.00\times10^{-3} + 0.8776$ **L**/**S**, $r^2 = 0.991$
H1	$\Delta\delta = -8.067\times10^{-3} + 0.7238$ **L**/**S**, $r^2 = 0.994$
H4,5	$\Delta\delta = -15.16\times10^{-3} + 0.5504$ **L**/**S**, $r^2 = 0.987$
H3	$\Delta\delta = -4.925\times10^{-3} + 0.3240$ **L**/**S**, $r^2 = 0.995$
H8	$\Delta\delta = -2.293\times10^{-3} + 0.2610$ **L**/**S**, $r^2 = 0.994$
H7	$\Delta\delta = -2.269\times10^{-3} + 0.1236$ **L**/**S**, $r^2 = 0.994$
H6	$\Delta\delta = -0.179\times10^{-3} + 0.0897$ **L**/**S**, $r^2 = 0.994$

The accidental coincidence of H4 and H5 explains why the corresponding equation is of much lower quality (r^2 = 0.987 and intercept more different from 0).

The use of $Eu(tfc)_3$ yields the following equations, the first series corresponds to experiments up to 58.3 and the second one up to 99.0 lanthanoid-substrate molar ratios respectively (underlined are the signals that split; the methyl group evolution is not reported since for some **L**/**S** ratios its signal appeared under those of the LSR):

H4,5 $\Delta\delta = -18.09 \times 10^{-4} + 1.815$ **L**/**S**, $r^2 = 0.982$
<u>H1</u> $\Delta\delta = -2.142 \times 10^{-4} + 1.150$ **L**/**S**, $r^2 = 0.998$
H3 $\Delta\delta = -2.657 \times 10^{-4} + 0.7165$ **L**/**S**, $r^2 = 0.989$
H8 $\Delta\delta = -1.911 \times 10^{-4} + 0.5846$ **L**/**S**, $r^2 = 0.994$
H7 $\Delta\delta = -3.172 \times 10^{-4} + 0.2335$ **L**/**S**, $r^2 = 0.961$
H6 $\Delta\delta = -1.820 \times 10^{-4} + 0.0494$ **L**/**S**, $r^2 = 0.594$

H4,5 $\Delta\delta = 32.68 \times 10^{-4} + 1.196$ **L**/**S**, $r^2 = 0.993$
<u>H1</u> $\Delta\delta = 42.88 \times 10^{-4} + 0.6190$ **L**/**S**, $r^2 = 0.981$
<u>H3</u> $\Delta\delta = 23.98 \times 10^{-4} + 0.3927$ **L**/**S**, $r^2 = 0.984$
H8 $\Delta\delta = 22.61 \times 10^{-4} + 0.3049$ **L**/**S**, $r^2 = 0.975$
H7 $\Delta\delta = 6.749 \times 10^{-4} + 0.1221$ **L**/**S**, $r^2 = 0.967$
H6 $\Delta\delta = 0.626 \times 10^{-4} + 0.0094$ **L**/**S**, $r^2 = 0.873$

Preliminary results with R-Pirkle's alcohol at 400 MHz (^{1}H) show that the methyl signal (δ = 2.112) splits into two signals (δ = 2.103 and δ = 2.098 ppm). Repetition of the experiment starting with 7.5 mg of **11** in 1 ml of $CDCl_3$ and adding first 6 mg of R-Pirkle's alcohol and then 4 mg more shows the following changes in the 400 MHz ^{1}H NMR spectrum. In this experiment the chemical shifts of pure **11** are: H1 6.685 (J = 2.35 Hz), H3 7.597 (J = 9.4, J = 2.35 Hz), H4 8.408 ($J \approx 9$ Hz), H5 8.408 ($J \approx 9$ Hz), H6 7.792 (J = 7.8 Hz), H7 7.304 (J = 7.8 Hz), H8 7.035 (J = 8.4 Hz), CH_3 2.126 ppm. The spectrum containing 4 mg of Pirkle's alcohol and 7.5 mg of compound **11** in 1 ml of $CDCl_3$ shows the following chemical shifts: H1 6.685 (J = 2.35 Hz), H3 7.597 (J = 9.4, J = 2.35 Hz), H4 8.329 and 8.353 (d, J = 9.4 Hz), H5 8.342 (d, J = 9.1 Hz), H6 7.733 and 7.744 (J = 7.8 Hz), H7 7.304 (J = 7.8 Hz), H8 7.035 (J = 8.5 Hz), CH_3 2.098 and 2.103 ppm. The methyl group signals are singlets and thus are the most useful for determining possible enantiomeric excesses.

The spectral analyses were carried out on the spectrum of the pure compound **11** and on the spectrum obtained after the second addition of *R*-Pirkle's alcohol.

Crystal Data for **9**·*$CHCl_3$*

$C_{28}H_{20}O_2N_2^{\chi}$ $HCCl_3$, M_W = 535.86, T = 170 K, Cu-Kα radiation, triclinic, space group *P*-1, a =

13.8605(20) Å, *b* = 10.8710(12) Å, *c* = 8.6723(7) Å, α = 91.379(8)º, β = 75.991(7)º, γ = 103.003(13)º, *V* = 1234.7(3) Å^3, *Z* = 2, D_C = 1.441 Mg·m^{-3}, μ = 3.611 mm^{-1}, *F*(000) = 552, crystal size 0.07 x 0.20 x 0.30 mm, diffractometer Philips PW1100, $2 \leq \theta \leq 65º$, 4130 collected, 3000 independent refl. with $I > 2\sigma(I)$, 401 parameters. The structure was solved using the SIR92 [26] program and refined on *F* using XTAL3.2 [27] and PESOS [28] to $R(R_W)$ = 0.067(0.071) and *S* = 1.014. Semiempirical absorption correction (ψ-scan) [29] has been applied (Max-Min transmission factors: 1.000-0.756). The refined Zachariasen [30] extinction coefficient was 234(40). The non-hydrogen atoms were refined anisotropically and the hydrogen ones, found unambiguously in the Fourier difference synthesis, were included and refined as isotropic. The atomic scattering factors were taken from the *International Tables for X-Ray Crystallography*, Vol. IV [31]. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101042. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. code +(1223) 336-033, e-mail: teched@chemcrys.cam.ac.uk).

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