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Received (in Cambridge, UK) 2nd January 2001, Accepted 4th April 2001

First published as an Advance Article on the web 3rd May 2001

N-(Azulen-1-ylmethylene)arylamines, **5**, were obtained in a fast quantitative conversion and high yield from the condensation of the corresponding azulene-1-carbaldehydes with aromatic amines without solvent. The reactions of the Schiff bases obtained, **5**, were compared to those of the corresponding azo compounds **1a** which have already been studied. The lack of regioselectivity in the oxidation of **5** with anhydrous FeCl₃ at both the azulenyl and at the aryl moiety, in contrast with the oxidation of compounds **1a** which react mainly at the aryl, is in agreement with the differences of the calculated Fukui one electron reactivity index squared (I_R^2) for the reactive positions in these molecules. From the calculated net charge for different positions in the molecules, a regioselective course for the electrophilic halogenation with CuCl₂ for both compounds **1a** and **5** (at C3 in the azulene moiety) can be foreseen. However, the Schiff bases were chlorinated also at the aromatic ring; an explanation was proposed for this behaviour.

During our studies on the properties of compounds with homolytic and heterolytic double bonds 1,2-substituted with azulene-1-yl and other aryl, heteroaryl or azulene-1-yl groups, **1**, we have recently reported the halogenation of azulene-1-azoarenes derivatives, **1a**,¹ and also their chemical oxidation

Az-A=B-Ar Az = substituted or unsubstituted azulene-1-yl
Ar = substituted or unsubstituted aryl, heteroaryl or azulene-1-yl

1a-d

a: A = B = N
b: A = CH; B = N
c: A = N; B = CH
d: A = B = CH

with ferric chloride.² The substitution of azulene at the 1 position with an azo group increases its oxidation potential and therefore allows the halogenation even with molecular chlorine or mild chemical oxidation without the destruction of the azulene moiety.

For the regioselective halogenation of the azo compound **1a** A = B = N (Scheme 1), an electrophilic attack at the 3 position with the higher calculated net charge³ (Chart 1) has been proposed. In contrast, the oxidative coupling between two radical cations **1a**^{•+} formed by the oxidative single electron transfer (Scheme 1) takes place with a moderate regioselectivity. The coupling at C4' generates the main reaction product and the secondary product results from a mixed coupling of positions 4' and 3 (no 3,3-coupling takes place).

The proposed radical mechanism for the coupling of the radical cations is in good agreement with the Fukui one electron reactivity index squared,⁴ I_R^2 , presented in Chart 1, this indicates the considerable difference between the reactivity of the 4' and 3 positions.

As an extension of these studies it was interesting for us to explore the behaviour of the Schiff bases, **1b**, in order to establish how the replacement of the N=N double bond in **1a**

with C=N in **1b**⁵ is reflected in the chemical properties. Almost the same difference between the values of the net charges for the C4' and C3 in **1a** and **1b** results from the calculation (Chart 1) and this indicates a similar regioselectivity for the electrophilic reactions. At the same time, the differences between the values I_R^2 for the two series of compounds (Chart 1) must be reflected in different behaviour on oxidation.

In this paper a convenient synthesis of the azulene containing Schiff bases is disclosed together with the results of the chlorination and chemical oxidation of these compounds. Comparison with the results obtained for the corresponding azo compounds is also presented and appropriate mechanisms are discussed.

Results and discussion

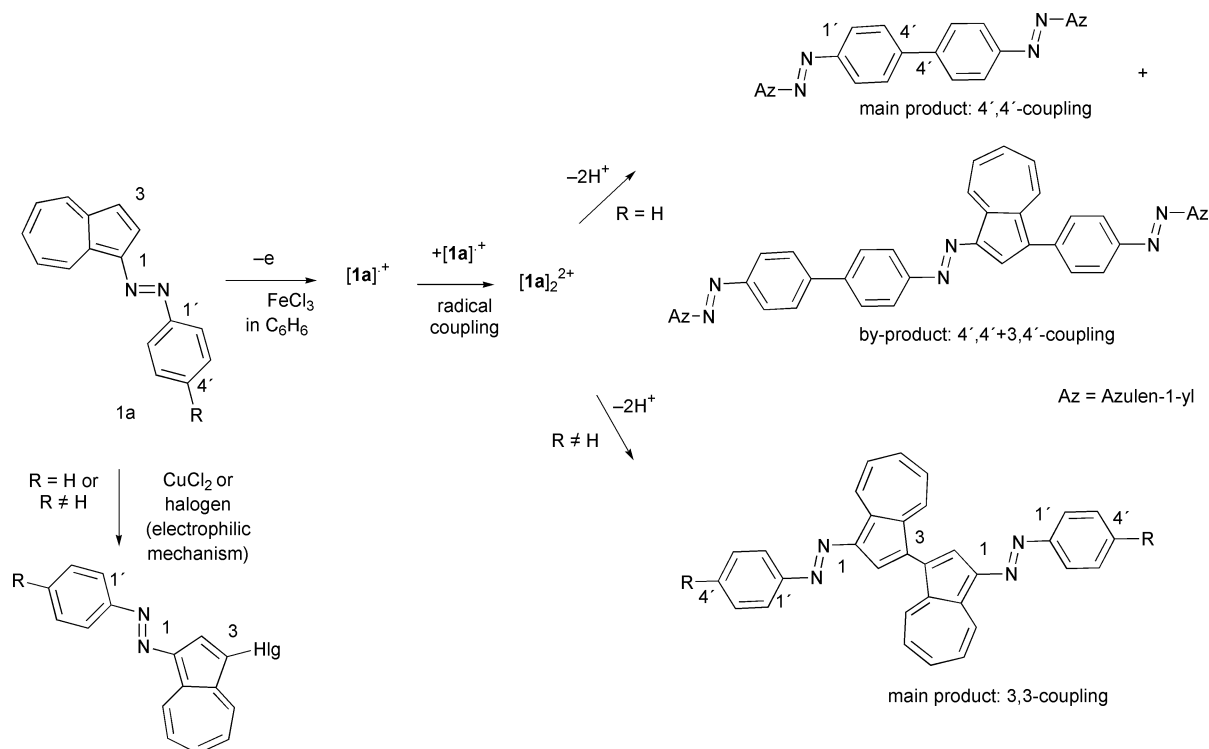
Synthesis of Schiff bases

The azulene-1-carbaldehydes, **2**, exhibit an increased contribution of the amphionic charge distribution due to its stable tropylium structure for the positive charge and, therefore, nucleophilic addition is expected to be difficult at the C=O bond. In spite of this limitation there are four references about the nucleophilic condensations of **2** with aromatic amines to generate Schiff bases: (a) in pyridine with amine in excess,^{6a} (b) in an excess of amine,^{6b} (c) in benzene with ZnCl₂ as a catalyst with the azeotropic removal of water^{6c} or (d) in DMF at 70–80 °C.^{6d} These protocols recommended the isolation of Schiff bases as pure products by separation on alumina and, eventually, by crystallization. Our attempts to obtain pure azulenic Schiff bases by chromatography on alumina (even with carefully dried eluents) failed because of the partial hydrolysis of these compounds and therefore the products were always contaminated with the corresponding azulene-1-carbaldehydes and aromatic amines.

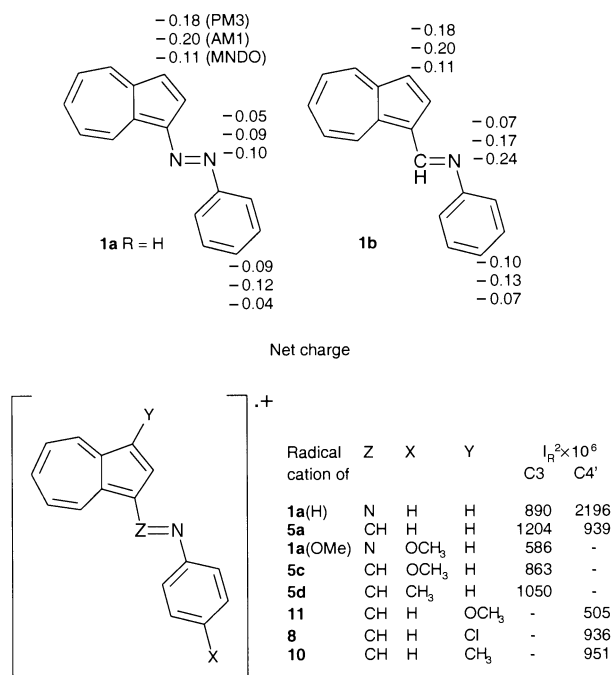
We have found that the condensation between the aldehydes, **2**, and aromatic amines, **3**, **4** (Scheme 2) without solvent proceeds smoothly and the yields are nearly quantitative.

As a rule, the equimolar mixture of aldehyde and amine that at the beginning was liquid at room temperature and under

† Electronic supplementary information (ESI) available: the elemental analyses and the detailed NMR, IR and UV-Vis spectra for the obtained Schiff bases. See <http://www.rsc.org/suppdata/p1/b1/b1000071/>



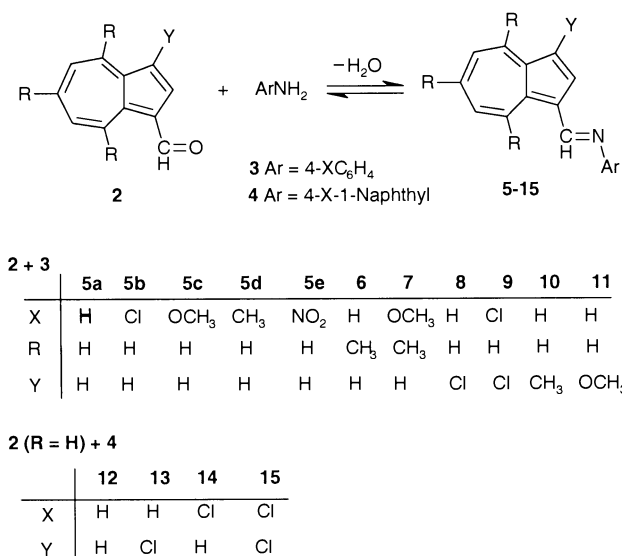
Scheme 1



Fukui one electron reactivity index squared for the radical cations, $I_R^2 \times 10^6$

Chart 1 Net charge and Fukui one electron reactivity index squared, $I_R^2 \times 10^6$, for the most reactive positions in the azo compounds, corresponding Schiff bases and their radical cations.

an inert atmosphere, after 12 to 24 h became solid and the condensation was complete. Before the crystallization from the absolute ethanol (or other solvents), the Schiff bases obtained in the reaction were contaminated with water.⁷ When both reactants were solid or one was scarcely soluble in the other, the mixture was heated to cause melting and then it was kept at room temperature. In some cases, the reaction was accomplished by heating *in vacuo* and thus the formed water was removed from the crystals. After the crystallization from a little amount of solvent and drying *in vacuo*, the analytically pure



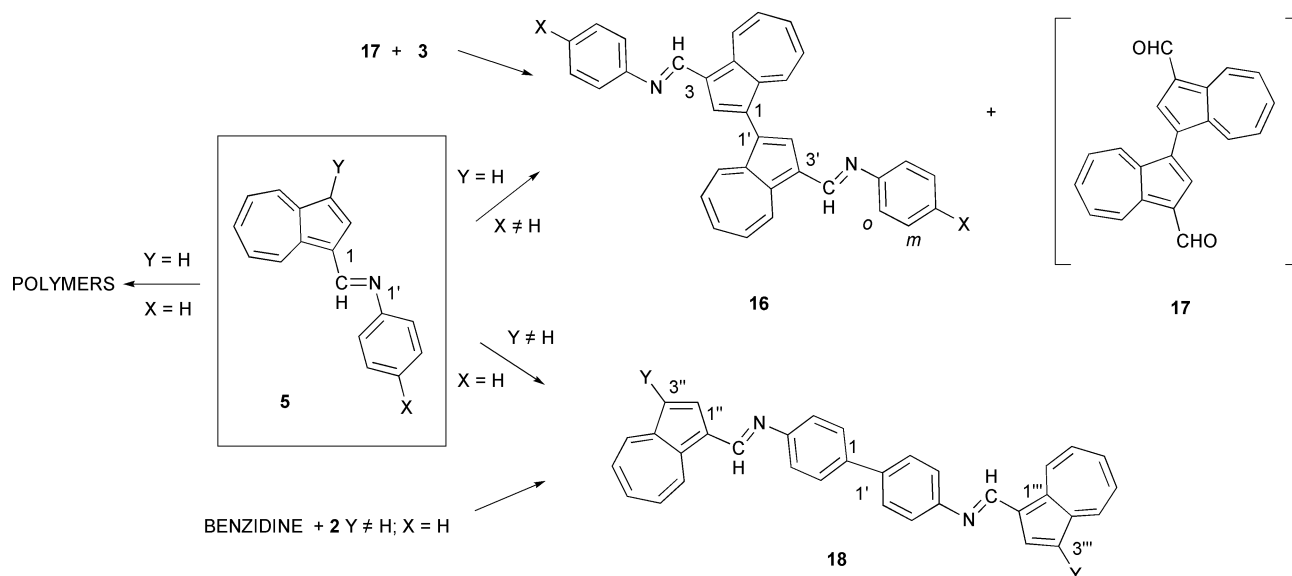
Scheme 2

Schiff bases were obtained. The specific reaction conditions and the results obtained are reported in Table 1. Compounds 5a–5e were reported in the literature^{6c} without characterization and the reported melting points are much lower than those found by us (Table 1), this indicates the difficulties associated with the Schiff bases' purification. The obtained Schiff bases were characterized completely. The NMR spectra of these compounds and of the corresponding azo derivatives^{1,8} present common general features for the azulene and aromatic moieties (the positions and the multiplicity of the proton or ¹³C signals); the characteristic signal for the proton in CH=N lies near 9 ppm and for carbon, near 155 ppm. The infrared absorption frequency of the CH=N group occurs at 1570–1610 cm⁻¹, under the same signal for the azomethyne group substituted with an aryl group at both C and N (1645–1650 cm⁻¹).⁹ The elemental analyses and the detailed NMR, IR and UV-Vis spectra for the obtained Schiff bases are reported in the electronic supplementary information (ESI).†

Table 1 Synthesis of the Schiff bases without solvent

Aldehyde, 2	Amine	Schiff base	Reaction conditions ^{a,b}	Found mp/°C (in lit.) ⁶
R = Y = H	3 X = H	5a	12 h, rt	132 ^c (125)
R = Y = H	3 X = Cl	5b	30 min, 80 °C, 12 h, rt ^d	114 ^c (95)
R = Y = H	3 X = OCH ₃	5c	30 min, 80 °C, 12 h, rt	83–84 ^c (oil)
R = Y = H	3 X = CH ₃	5d	12 h, rt ^d	84–85 ^c (79)
R = Y = H	3 X = NO ₂	5e	2 h, 100 °C, 12 h, rt ^d	143 ^c (128)
R = CH ₃ , Y = H	3 X = H	6	30 min, 100 °C, 12 h, rt and vacuum 6 h at 70 °C	103 ^c
R = CH ₃ , Y = H	3 X = OCH ₃	7	30 min, 100 °C, 12 h, rt ^d	101.5–102
R = H, Y = Cl	3 X = H	8	30 min, 100 °C	60 ^c
R = H, Y = Cl	3 X = Cl	9	30 min, 100 °C, 12 h, rt ^d	82–83 ^c
R = H, Y = CH ₃	3 X = H	10	24 h, rt and 12 h vacuum	Oil ^f
R = H, Y = OCH ₃	3 X = H	11	24 h, rt and 12 h vacuum at 70 °C	73–74
R = Y = H	4 X = H	12	3 h, 100 °C, 2 days, rt	111 ^e
R = H, Y = Cl	4 X = H	13	30 min, 80 °C, 24 h, rt ^d	133 ^g
R = Y = H	4 X = Cl	14	30 min, 80 °C, 24 h, rt	102 ^g
R = H, Y = Cl	4 X = Cl	15	30 min, 80 °C, 24 h, rt ^d	147 ^g
R = Y = H	2-Naphthylamine	20	1 h, 100 °C, 24 h, rt	79 ^h
R = H, Y = Cl	3 X = OCH ₃	3-Cl-5c	3 h, 100 °C, 2 days, rt	78–79
R = H, Y = Cl	3 X = CH ₃	3-Cl-5d	3 h, 100 °C, 2 days, rt	69–70
R = H, Y = Cl	3 X = NO ₂	3-Cl-5e	3 h, 100 °C, 2 days, rt	201–202
R = H, Y = OCH ₃	3 X = Cl	4'-Cl-11	3 h, 100 °C, 2 days, rt	118.5–119.5

^a Temperature in the oil bath. ^b Before the crystallization, the resulted reaction mixture contained the Schiff base, water (for the reaction without heating and vacuum) and traces of the starting aldehyde and amine. The amount of the mixture and their ¹H-NMR spectra showed that the condensation yields were nearly quantitative. ^c From ethanol. ^d Vacuum, 3 h, 70 °C. ^e From diethyl ether. ^f The Schiff bases substituted at C3 are viscous compounds or very difficult to crystallize. ^g Dissolved in DCM, precipitated with *n*-pentane. ^h Dissolved in ether, precipitated with *n*-pentane.

**Scheme 3** Schiff base oxidation with FeCl₃ in benzene.

Oxidation of Schiff bases

The conditions for the oxidation of the Schiff bases were the same as for the corresponding azo derivatives: anhydrous ferric chloride as oxidizing agent (molar ratio FeCl₃–Schiff base, 4 : 1) in benzene, with magnetic stirring, at room temperature, without protection from air.

The conversion of **5a** was complete in two hours. However, all attempts to separate the products from the tarry reaction mixture or to hydrolyse this mixture failed.

For the quantitative oxidation of the Schiff bases substituted at C4', **5c** and **5d**, two hours were sufficient (Scheme 3). The reaction mixture was quenched with a cold saturated aqueous solution of NaHCO₃ and the products were extracted with dichloromethane (DCM) (it is interesting that the dimers‡ hydrolysed much more slowly than the monomers). There are no significant differences between the phenyl proton signals in

‡ The terms dimerization and dimer are used for the coupling with the elimination of two hydrogen atoms and for the products resulting from these reactions, respectively.

the ¹H-NMR spectra of the products, **16**, and the starting materials. For the azulenyl the signal for the 3-H proton in **16** disappears and the signal for the 2-H proton (a doublet in **5c** and **5d**) becomes a singlet for two protons in **16**. The NMR spectra (COSY and HETCOR experiments were also undertaken) together with the mass spectra attest the dimeric structure resulting from the coupling at C3 for the compounds **16c** or **16d** (traces of the dialdehyde **17** were present in the reaction mixture with careless work-up, indicating the hydrolysis tendency of **16**). The assigned structure was also confirmed by the condensation of dialdehyde **17** with the corresponding anilines **3** X = OCH₃ or CH₃ (Scheme 3). The yield of **16c** or **16d** (together with **17**, when it was formed) was nearly quantitative. It is important to remark that the sequence of reactions: azulene → **2** Y = H → **5** X ≠ H → **16** → **17**, which occurs in very good overall conversion and yield, represents a possible easy route to the interesting dialdehyde **17**.¹⁰

In the 4,6,8-trimethylated compound **7** the unfavourable steric interaction of the 'peri' methyl group hindered the

Table 2 Halogenation of Schiff bases, AzCH=NAr, with anhydrous CuCl₂ in CH₃CN at reflux (5 h)

Starting Schiff base	Molar ratio between the products ^a					
	Unreacted Schiff base	Az halogenated	Ar halogenated	Az and Ar halogenated	2 R = H; Y = Cl	2 R = H; Y = H
5a	3.1	10	1.2 ^b	4.5 ^d	1.6	0.6
5c	6.4	10	0.4 ^c	1.4 ^e	2.9	0.4
5d	5.2	10	0.5 ^c	1.0 ^f	1.9	1.9
5e ^g	3.0	10 ^h	0	0	0.5	2.5
12	11.5	10 ⁱ	2.5 ^j	5.0 ^k	17.2	2.5
8 ^g		1.4 ^l		1.4 ^d	0.9	—

^a Az and Ar = azulenyl and phenyl, respectively, substituted or non-substituted; for all compounds Az chlorination takes place at C3; for the signal assignments and the correctness of the integrals ratio, the chlorinated Schiff bases were obtained by a separate synthesis (the physical properties of these and other samples obtained by condensation of aldehydes **2** and amines **3** or **4** are reported in the Experimental or in the ESI). ^b Compound **5b**. ^c 3'-Chlorinated products, **3'-Cl-5c**, and **3'-Cl-5d**. ^d Compound **9**. ^e 3,3'-Dichlorinated product **3,3'-diCl-5c**. ^f The position of aromatic chlorination undetermined (probably in position 3'). ^g Reaction time 8 h. ^h Chlorinated product **3-Cl-5e**. ⁱ Product **13**. ^j Product **14**. ^k Product **15**. ^l Compound **8**.

access to C3 for the coupling. With **7** the reaction occurred slowly and only the chlorination at C3 took place. After the hydrolysis of the reaction mixture and filtration on alumina, the 3-halogenated and unhalogenated azulene-1-carbaldehydes, **2** R = CH₃, Y = Cl and **2** R = CH₃, Y = H, were obtained. The long reaction time produced a large amount of tarry products, which remained on the alumina.

The oxidation of the compound with a nitro group at C4', **5e** (even when prolonging the reaction time to 10 hours) resulted only in traces of Schiff base halogenated at C3, **3-Cl-5e**, identified as its hydrolysis product, aldehydes **2** Y = H and Y = Cl. The explanation of this behaviour could be the same as in the case of the inactivity of the corresponding azo compounds, namely, the reduced oxidation potential of the starting Schiff base by the substitution with the nitro group.

As a rule, substitution or steric hindrance of the 3 position in **8**, **10**, **11** and **6** decrease the reactivity of the starting Schiff bases. The compounds **8** or **11** reacted only partially. The reaction mixture contains the product of oxidation, **18**, traces of the aldehyde **2** Y = Cl or OCH₃ (from the work-up) together with the unreacted starting material (Scheme 3). After one day the compound **8** was oxidized in 50% and the product **18** Y = Cl was obtained in 100% yield. After 4 hours, the reaction of **11** took place in 64% conversion the yield of the dimer **18** Y = OCH₃ was, however, only 67%. A trace of the compound halogenated at C4', **4'-Cl-11**, was observed in the ¹H-NMR spectrum of the mixture; prolonging the reaction time increased the amount of **4'-Cl-11** and other uncharacterized secondary products. Due to hydrolysis on the chromatography column, the conversion of the starting material and the reaction yield were calculated from the amount of reaction mixture obtained and the integral ratio between the characteristic proton signals of the components in the ¹H-NMR spectrum of the mixture. The chosen proton signal for **8** and **11** was CH=N and for the aldehydes was CH=O. The presence of a second azomethyne proton signal in the reaction mixture showed the generation of a new Schiff base, namely the product **18**. The non-altered position of the proton signals for the azulenyl moiety in **18** in comparison with those in **8** and **11** and the presence of the AB group signal for 8 phenyl protons in **18** are consistent with the existence of a phenyl group *para* substituted in the molecule and confirm the coupling at the 4' position. The mass spectrum of the product shows the dimeric structure for **18**. For the unequivocal characterization of the products **18** the benzidine was condensed with the corresponding azulene-1-carbaldehydes **2** in the molar ratio 1 : 2 and the resulting compounds were compared with those obtained by oxidation (Scheme 3).

The compound substituted with methyl at C3, **10**, was oxidized with the generation of an insoluble resinous mixture of unidentified structure.

The behaviour of compound **6** was similar to that of compound **7**. After one day in the presence of FeCl₃ the halogenation at C3 took place; the amount of tarry compounds was, however, higher in comparison with **7**.

When the double bond N=N in the azo compounds is replaced by C=N in the Schiff bases, there is no reason for a change in the reaction mechanism of the oxidation (Scheme 1), namely a single electron transfer from the organic substrate with radical cation generation, then the coupling of two radical cations and the elimination of two protons from the dimeric dication. The experimental results seem to be in good agreement with this assumption.

As we discussed in the introduction, the values of I_R^2 for different positions in the radical cation of azulene-1-azoarenes, **1a**^{•+}, governed the tendency for the radical coupling. It transpires from Chart 1 that the difference between the I_R^2 values at C3 and C4' for the radical cation provided from the unsubstituted Schiff base, **5a**^{•+}, is not so marked in comparison to those for **1a**^{•+} and a marked decrease in the regioselectivity of the coupling is expected. The presence of two positions in the intermediate **5a**^{•+} with similar reactivity is reflected in the tendency towards oligomerization or polymerization in the oxidation of **5a** and confirms the calculations.

In contrast, dimerization can be observed for the Schiff bases substituted at the position 3 or 4'. The oxidation of the compounds substituted at C4' with OCH₃ or CH₃, **5c** or **5d**, occurred with 100% selectivity at C3 in comparison with the 53% coupling at C3 for the corresponding azo compounds (with 4'-OCH₃). Therefore the higher value for I_R^2 at C3 for Schiff bases (Chart 1) is consistent with the observed difference.

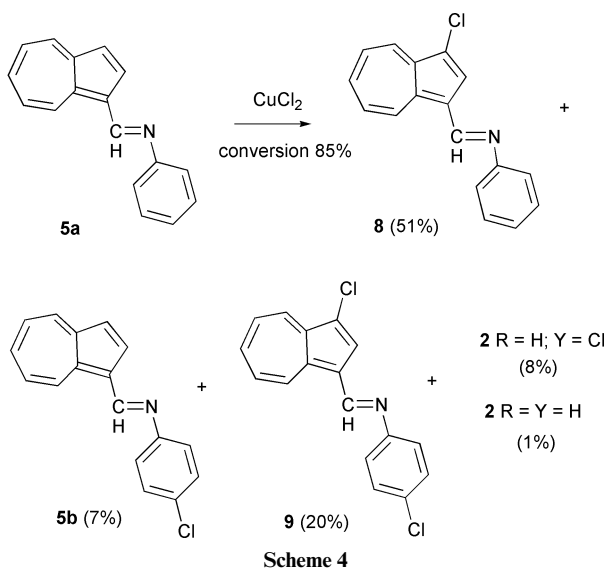
From the oxidation of **8** substituted at C3 with Cl the dimer **18** coupled at C4' resulted in a good yield, in accord with the high value for I_R^2 at this position. However, the starting material was recovered in 50% yield, probably because of the reversibility of the dimerization step. In spite of the similar value of I_R^2 at the same position in **10**, only tarry products resulted after the work-up. It is possible that the radical cation **10**^{•+} reacts in another unknown way. The lower value for I_R^2 at C4' for **11** is reflected in the moderate conversion and yield in the oxidation.

Chlorination of Schiff bases with cupric chloride

The halogenation of Schiff bases with cupric chloride was carried out under similar conditions to those for the reaction of the corresponding azo derivatives:¹ molar ratio of anhydrous CuCl₂-Schiff base, 3 : 1, in boiling acetonitrile with protection against the air humidity (the reaction time is reported in Table 2). The work-up was carefully carried out to minimize the hydrolysis of the starting material and halogenated Schiff bases, however, even in these conditions the Schiff bases were

partially hydrolysed. The separation of the compounds by column chromatography failed because of their advanced hydrolysis on the column. Therefore, the conversion of the starting Schiff base and the product yield were calculated from the $^1\text{H-NMR}$ spectra of the reaction mixture and the results are reported in Table 2.

The $^1\text{H-NMR}$ spectrum of the mixture from the chlorination of the unsubstituted Schiff base **5a** contains four singlet signals in the field of the azomethyne proton (8.80–9.00 ppm) indicating the possible presence of four Schiff bases. We propose that in addition to the corresponding proton signal for **5a** there are also the signals for three chlorinated compounds, at C3, C4' and at both these positions, the products **8**, **5b** and **9**, respectively (Scheme 4). The correct signal assignment for the



azomethyne proton was based on the comparison with samples of **5b**, **8** and **9** obtained separately from the corresponding aldehydes **2** and amines **3**; the same agreement was observed also for the singlets for 2-H proton. Two proton signals characteristic of aldehydes at 10.41 and 10.33 ppm, corresponding to **2** R = Y = H and **2** R = H; Y = Cl, respectively, are also present in the spectrum of the reaction mixture. Unfortunately, we cannot affirm without doubt which halogenated product (at C3, at C4' or at both positions) generated these aldehydes although the ratio between the non-hydrolysed products can provide some indications.¹¹ Despite these considerations, it is obvious that, in contrast to the regioselective halogenation of the azulene-1-azobenzene at C3, for **5a** the reaction takes place both at C3 and at C4' in benzene, although the halogenation favours the first position. The same behaviour can be observed for the chlorination of Schiff base substituted at the imino group with azulene-1-yl and 1-naphthyl, **12** (Table 2). The products obtained were also halogenated at C3, C4' and at both these positions (the compounds **13**, **14** and **15**, respectively).

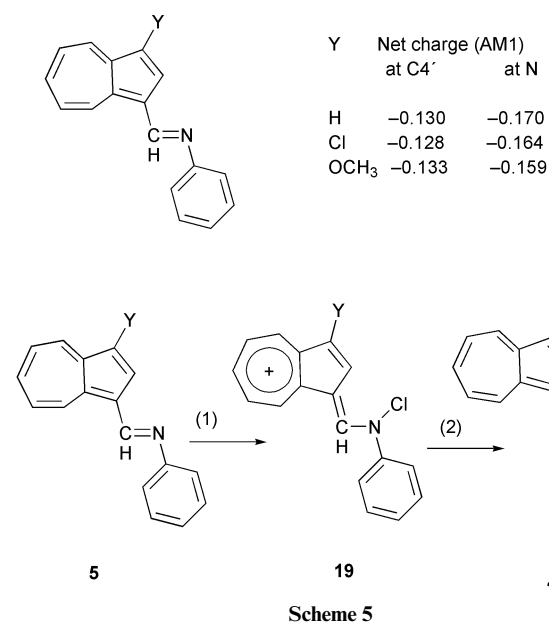
The chlorination of the Schiff bases substituted at C3, **8** and **11**, and at C4', **5c–5e** was interesting. Upon chlorination of **8**, a large amount of the starting material remained unreacted after 8 hours and the obtained mixture contained the product **9** substituted both at C3 and C4' with chlorine and the aldehyde **2** Y = Cl (Table 2) together with unreacted **8**. The halogenation of **11** (with OCH_3 at C3) occurred slower; after 8 hours only traces of chlorinated compound **4'-Cl-11** was observed in the reaction mixture.

The 4'-substituted Schiff bases are halogenated, as we expected, mainly at C3 with good conversions and yields (Table 2). The reaction was fast for the compounds with electron releasing substituents at C4', **5c–5d**, and a little slower for **5e** with NO_2 at C4', in agreement with the electrophilic mech-

anism. It is interesting to note that for the compounds with OCH_3 and CH_3 at C4', **5c** and **5d**, a small amount (*ca.* 10 mol%) of products chlorinated at the position 3' (*ortho* in respect to OCH_3 or CH_3) was also detected (Table 2).

Our previous studies on the halogenation of azulene-1-azoarenes with CuCl_2 prompted us to suggest an electrophilic attack at C3 in the azulene moiety,¹ the position with the maximum net charge in the neutral molecule. The results reported in Chart 1 indicate that the difference between the values for the net charge at C3 and C4' for the unsubstituted Schiff base is similar to that for the corresponding azo derivatives. Consequently, for the electrophile substitution the same regioselectivity for both compounds was expected.

In spite of the calculations, the experimental results indicate a marked difference between the poor selectivity for the Schiff bases' halogenation and the regioselectivity for the corresponding azo derivatives.¹² Our explanation for this behaviour is based on the observation that the calculated net charge at the nitrogen atom for Schiff bases (Chart 1) lies significantly over that for the nitrogen neighbour to the aryl group in azo compounds and is placed near the value for the position 3 of Schiff base. This means that an electrophilic attack, (1), can take place also at the nitrogen atom in HC=N (with reduced probability in comparison to that at C3) with the generation of the *N*-chloroamine cation **19** (Scheme 5).



The second step, (2), could be the migration of chlorine from the nitrogen atom to position 4' (for **5a** and **12**) or, when C4' is substituted with CH_3 or OCH_3 , to the *ortho* position of these substituents (for **5c** and **5d**), similar to the displacement in the Orton rearrangement.¹³ The same mechanism can explain the difference between the reactivity of the compounds substituted at C3, **8** and **11**. Despite the similar net charge at C4' (Scheme 5) for these compounds and for the parent compound **5a**, the difference between this parameter at the nitrogen atoms can influence the reactivity of the Schiff bases that decreases in the order: **5a**, **8** and **11**. Certainly, further experimental evidence could consolidate the proposed mechanism.

The significant non-linear optical properties^{8,14} of the compounds with structure **1** have prompted us to continue our study on the synthesis and the properties of the compounds with the specific structures **1c** and **1d** and the research is in progress.

Experimental

Melting points were recorded on a Kofler apparatus (Reichert Austria). Elemental analyses were measured on a Perkin-Elmer

CHN 240B. UV spectra were recorded on a Beckman DK-2A, UV 5240. ^1H - and ^{13}C -NMR spectra were taken on Bruker Avance DRX4 (^1H : 400 MHz, ^{13}C : 100.62 MHz) and Gemini 300 (^1H : 300 MHz, ^{13}C : 75.47 MHz) spectrometers and, J values are given in Hz. TMS was used as an internal standard and when necessary, unequivocal signal assignment was confirmed by the analysis of the corresponding COSY and HETCOR spectra (the numbering for the exemplified compounds is indicated in the Schemes and is not always correlated with the IUPAC nomenclature). Mass spectra were recorded on a Finnigan MAT 311-A/100 MS and Carlo Erba QMD 1000. Dichloromethane (DCM) was distilled over calcium hydride.

General procedure for the synthesis of Schiff bases

An equimolar mixture of aldehyde¹⁵ and amine (without catalyst or solvent) was placed in a round-bottomed flask equipped with a reflux condenser, under an inert atmosphere. In most cases, mixing of the liquid reactants for a reaction time between 12 and 24 h, at room temperature, was enough for the complete conversion of the reactants, when the mixture became solid. When one or both reactants were solid, the mixture was heated until it became homogeneous and then it was kept at room temperature. In some experiments it was necessary to continue the heating of the reaction mixture at a lower pressure (about 0.1 atm). The reaction conditions are reported in Table 1. The crude Schiff bases obtained from anilines, **3**, were crystallized from the minimum amount of anhydrous ethanol; the crystallization solvents for other Schiff bases are described in Table 1. The products were thoroughly dried on P_2O_5 for a day and were stable over time. The pure Schiff bases obtained were, generally, dark-green coloured crystals. The melting points are reported in Table 1 and the elemental analysis, ^1H -, ^{13}C -NMR, IR and UV-Vis spectra are described in the ESI.† A typical example of the properties of the Schiff bases is described.

4'-Methoxy-*N*-(azulen-1-ylmethylene)aniline, 5c. Green crystals, mp 98 °C (from absolute ethanol) (Found: C, 83.02; H, 5.51; N, 5.36. $\text{C}_{18}\text{H}_{15}\text{NO}$ requires C, 82.73; H, 5.79; N, 5.36%); λ_{max} (dioxane)/nm, 236 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.4), 270 (4.2), 304 (4.4), 403 (4.2), 590 (2.6); ν_{max} (CCl_4)/ cm^{-1} 1610 (CH=N); δ_{H} (CDCl_3) 3.84 (3 H, s, CH_3), 6.96 (2 H, dd, J 7.0 and 2.0, 3'-, 5'-H), 7.29 (2 H, dd, J 7.0 and 2.0, 2'-, 6'-H), 7.32 (1 H, t, J 10.0, 5-H), 7.40 (1 H, d, J 4.0, 2-H), 7.40 (1 H, t, J 10.0, 7-H), 7.70 (2 H, J 10.0, 6-H), 8.35 (1 H, d, J 4.0, 2-H), 8.37 (1 H, d, J 10.0, 4-H), 9.00 (1 H, s, CH=N), 9.38 (1 H, d, J 10.0, 8-H); δ_{C} (CDCl_3) 55.6 (primary, CH_3), 119.1 (t, C-3), 122.0 (t, C-2', -6'), 125.7 (q), 125.9 (t, C-7), 126.3 (t, C-5), 136.1 (t, C-8), 137.9 (t, C-4), 138.7 (q), 138.9 (t, C-2 and C-6), 144.7 (q), 146.7 (t, C-4'), 153.6 (t, CH=N), 157.7 (q).

The chlorinated Schiff bases **5b**, **8**, **9**, **3-Cl-5c-e**, **3,3'-diCl-5c**, **3'-Cl-5c** and **4'-Cl-11** were obtained in the same way from the 3-chloroazulene-1-carbaldehyde, **2** ($\text{R} = \text{H}$; $\text{Y} = \text{Cl}$), or azulene-1-carbaldehyde and the corresponding amines **3** (the physical characteristics of the products are described in the ESI).†

The condensation of benzidine (one mole) with the corresponding aldehydes **2** (two moles) generated the dimers **16**. The dimers **18** were obtained from the dialdehyde **17** (one mole) and the corresponding amines **3** (two moles). Their physical properties are identical to those obtained by the Schiff base oxidation and are reported below.

General procedure for oxidation of Schiff bases

To a stirred solution of Schiff base (0.5 mmol), in benzene (12.5 cm^3), anhydrous ferric chloride (324 mg, 2 mmol) was added at room temperature. The reaction time was 2 h for **5a**, **5c** and **5d**, 10 h for **5e**, 4 h for **11**, 24 h for **6** and **8**, 48 h for **7**. The resulting mixture was quenched with a cold saturated solution of sodium hydrogen carbonate (50 cm^3). The organic solution was separ-

ated and the aqueous layer was extracted with DCM (3 \times 100 cm^3). The organic solution was washed with water and ice, dried (Na_2SO_4), filtered and the solvents were evaporated *in vacuo* to yield a solid residue.

Reaction of *N*-(azulen-1-ylmethylene)aniline substituted at C4' or at C3. The conversion of **5c** and **5d** and the yield of the products **16** ($\text{X} = \text{CH}_3$ or OCH_3) were nearly quantitative. For analytical purposes, the residue was crystallized from absolute ethanol. Chromatography of **16** on alumina with DCM as eluent (at a low flow), gave only 3,3'-dimer of azulene-1-carbaldehyde, **17**, in quantitative yield (after the elution of the corresponding aniline **3**).

The reaction mixture from the oxidation of **8** and **11** contained mainly the starting Schiff base together with the dimers **18** ($\text{Y} = \text{Cl}$ and OCH_3 , respectively) and traces of aldehydes **2**. The amount of reaction mixture and the ratio between the integrals for the characteristic proton signals in the ^1H -NMR spectra showed that after the oxidation of **8** the starting material was recovered in 50% yield and the yield of **18** $\text{Y} = \text{Cl}$ was 100%. For **11**, 36% of the unreacted starting material was recovered and the yield of the oxidation product **18** $\text{Y} = \text{OCH}_3$ was 67% (in the ^1H -NMR spectrum of the mixture the signals of the compound halogenated at C4', **4'-Cl-11**, are present in trace amounts).

3,3'-Bis(*p*-tolyliminomethyl)-1,1'-biazulene 16 $\text{X} = \text{CH}_3$. Brown crystals, mp 129–131 °C (from absolute ethanol) (Found: C, 88.26; H, 5.74; N, 5.79. $\text{C}_{36}\text{H}_{28}\text{N}_2$ requires C, 88.49; H, 5.77; N, 5.73%); λ_{max} (dioxane)/nm 240 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.64), 303 (4.73), 406 (4.29); ν_{max} (CHCl_3)/ cm^{-1} 1120 s, 1450 m, 1500 m, 1580 s, 1640 s; δ_{H} (CDCl_3) 2.39 (6 H, s, CH_3), 7.15–7.30 (10 H, m, phenyl protons, 7-, 7'-H), 7.41 (2 H, t, J 9.6, 5-, 5'-H), 7.71 (2 H, t, J 9.6, 6-, 6'-H), 8.43 (2 H, d, J 9.2, 8, 8'-H), 8.55 (2 H, s, 2-, 2'-H), 9.09 (2 H, s, CH=N), 9.40 (2 H, d, J 9.6, 4-, 4'-H); δ_{C} (CDCl_3) 21.03 (CH_3), 120.86 (C-*meta*), 124.73 (q), 126.31 (C-5, -5'), 126.49 (C-7, -7'), 129.79 (C-*ortho*), 134.97 (q), 136.27 (C-4, -4'), 137.25 (C-8, -8'), 139.70 (C-2, -2'), 139.76 (C-6, -6'), 141.91 (q), 150.84 (q), 154.14 (CH=N); m/z (FD) 491 ($\text{M}^+ + 3$, 4.4%), 490 ($\text{M}^+ + 2$, 4.2), 489 ($\text{M}^+ + 1$, 88.8), 488 ($\text{M}^+ + 100$), 399 (25.0), 398 (12.5), 78 (19).

3,3'-Bis(*anisyliminomethyl*)-1,1'-biazulene 16 $\text{X} = \text{OCH}_3$. Green-brown, slightly soluble crystals mp 240–242 °C (from absolute ethanol) (Found: C, 83.28; H, 5.67; N, 5.63. $\text{C}_{36}\text{H}_{28}\text{N}_2\text{O}_2$ requires C, 83.05; H, 5.42; N, 5.38%); λ_{max} (dioxane)/nm 242 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.53), 294 (4.64), 400 (4.05), 555 (2.92); ν_{max} (CH_2Cl_2)/ cm^{-1} 1030 s, 1500 s, 1565 s, 1600 s; δ_{H} (CDCl_3) 3.86 (6 H, s, OCH_3), 6.97 (4 H, d, J 8.8, *meta*-H), 7.25 (2 H, t, J 10.0, 7-, 7'-H), 7.33 (4 H, d, J 8.8, *ortho*-H), 7.42 (2 H, t, J 9.6, 5-, 5'-H), 7.72 (2 H, t, J 9.6, 6-, 6'-H), 8.43 (2 H, d, J 9.6, 8-, 8'-H), 8.55 (2 H, s, 2-, 2'-H), 9.11 (2 H, s, CH=N), 9.42 (2 H, d, J 9.6, 4-, 4'-H); m/z (FD) 522 ($\text{M}^+ + 2$, 38.3%), 521 ($\text{M}^+ + 1$, 100), 78 (51.6).

1,1'-Biazulenyl-3,3'-dicarbaldehyde 17. Brown microcrystalline powder, mp 254–256 °C (from ethanol) (Found: C, 85.28; H, 4.37. $\text{C}_{22}\text{H}_{14}\text{O}_2$ requires C, 85.14; H, 4.55%); λ_{max} (dioxane)/nm 240 (log $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 4.48), 289 (4.69), 400 (3.98), 571 (2.84); ν_{max} (DCM)/ cm^{-1} 1120 s, 1360 w, 1410 m, 1500 w, 1640 vs, 3680 w; δ_{H} (CDCl_3) 7.50 (2 H, t, J 9.6, 5-, 5'-H), 7.69 (2 H, t, J 9.6, 7-, 7'-H), 7.91 (2 H, t, J 9.6, 6-, 6'-H), 8.45 (2 H, s, 2-, 2'-H), 8.49 (2 H, d, J 10.0, 4-, 4'-H), 9.68 (2 H, t, J 9.6, 8-, 8'-H), 10.49 (2 H, s, CHO); δ_{C} (CDCl_3) 125.22 (q, C-1, -1'), 125.85 (q, C-3, -3'), 128.66 (C-5, -5'), 129.93 (C-7, -7'), 138.02 (C-8, -8'), 138.13 (C-4, -4'), 140.83 (C-6, -6'), 141.27 (q, C-8a, -8'a), 142.72 (C-2, -2'), 143.46 (q, C-3a, C-3'a), 186.55 (CHO); m/z (70 eV) 310 (M^+ , 100%), 309 ($\text{M}^+ - 1$, 13), 281 ($\text{M}^+ - \text{CHO}$, 2), 252 ($\text{M}^+ - 2\text{CHO}$, 34), 226 (7), 155 (M^{2+} , 7), 154 (7), 126 (12), 125 (14).

4,4'-Bis(3'-chloroazulen-1''-ylmethylene)benzidine 18 $\text{Y} = \text{Cl}$. Brown, slightly soluble, microcrystalline powder, mp 253–255 °C (ethanol and DCM) (Found: C, 77.01; H, 4.37; N, 5.09;

Cl, 13.53. C₃₄H₂₂Cl₂N₂ requires C, 77.13; H, 4.19; N, 5.29; Cl, 13.39%; λ_{\max} (dioxane)/nm 244 (log ϵ /dm³ mol⁻¹ cm⁻¹ 4.7), 310 (4.7), 429 (4.7); ν_{\max} (DCM)/cm⁻¹ 1120 w, 1140 w, 1390 m, 1480 w, 1580 s, 1605 m, 3060 w; δ_{H} (CDCl₃) 7.39 (4 H, dd, *J* 8.4, 1.5, 2-, 2'-, 6-, 6'-H), 7.42 (2 H, t, *J* 10, 5"-, 5'''-H), 7.45 (2 H, t, *J* 10, 7"-, 7'''-H), 7.71 (4 H, dd, *J* 8.4, 1.5, 3-, 3'-, 5-, 5'-H), 7.79 (2 H, t, *J* 9.8, 6"-, 6'''-H), 8.28 (2 H, s, 2"-, 2'''-H), 8.44 (2 H, d, *J* 10, 4"-, 4'''-H), 9.00 (2 H, s, HC=N), 9.40 (2 H, d, *J* 10, 8"-, 8'''-H).

4,4'-Bis(3"-methoxyazulen-1"-ylmethylene)benzidine 18 *Y* = OCH₃. Brown, very slightly soluble, microcrystalline powder, mp 225–227 °C (ethanol + DCM) (Found: C, 82.90; H, 5.51; N, 5.30. C₃₆H₂₈N₂O₂ requires C, 83.05; H, 5.42; N, 5.38%); δ_{H} (CDCl₃) 4.11 (6 H, s, OCH₃), 7.06 (2 H, t, *J* 10, 5"-, 5'''-H), 7.08 (2 H, t, *J* 10, 7"-, 7'''-H), 7.39 (4 H, dd, *J* 8.4, 1.5, 2-, 2'-, 6-, 6'-H), 7.56 (2 H, t, *J* 9.8, 6"-, 6'''-H), 7.70 (4 H, dd, *J* 8.4, 1.5, 3-, 3'-, 5-, 5'-H), 7.95 (2 H, s, 2"-, 2'''-H), 8.32 (2 H, d, *J* 10, 4"-, 4'''-H), 8.78 (2 H, d, *J* 10, 8"-, 8'''-H), 9.08 (2 H, s, HC=N); *m/z* (FD) 523 (M⁺ + 3, 4.4%), 522 (M⁺ + 2, 70.0), 521 (M⁺ + 1, 100), 520 (M⁺, 38), 78 (4.8).

Reaction of 4'-methoxy- and *N*-(4,6,8-trimethylazulen-1-ylmethylene)aniline, 7 and 6. The general oxidation protocol was followed and the same ratio between the reactants was used. After the work-up, the resulting residue was hydrolysed at reflux 24 h in 50% aqueous ethanol (30 cm³) in the presence of copper acetate (100 mg). The ethanol was evaporated *in vacuo* and the resulted suspension was extracted with DCM. After the filtration on alumina, the organic solution was washed with a dilute solution of HCl and with aqueous NaHCO₃ and was dried (Na₂SO₄). The solvent was removed under reduced pressure and the products were separated by chromatography on alumina with DCM.

The mixture from **6** was separated into two coloured fractions: the first contained the chlorinated aldehyde, **2** *Y* = Cl, R = CH₃, 30 mg (0.129 mmol) and the second contained the aldehyde **2** *Y* = H, R = CH₃, 22 mg (0.111 mmol). A significant amount of the material was insoluble and remained on the alumina after filtration.

From **7** were separated the aldehyde **2** *Y* = Cl, R = CH₃, 57 mg (0.288 mmol) and the aldehyde **2** *Y* = H, R = CH₃, 35 mg (0.151 mmol). In this case, tarry compounds were also separated by filtration.

General procedure for chlorination of Schiff bases

Anhydrous copper chloride (0.121 g, 0.9 mmol) was dissolved in boiling MeCN (distilled on CaH₂) (10 cm³) and a yellow solution was obtained. Then the Schiff base (0.3 mmol) was added and the colour of the solution turned to red. The solution was strongly refluxed (the reaction time is reported in Table 2) then MeCN was allowed to evaporate to *ca.* 5 cm³. After cooling at room temperature, benzene (50 cm³) and a saturated solution of NaHCO₃ (50 cm³) were added and the colour of the organic layer turned to green. The benzene solution was washed with water and then dried (Na₂SO₄). The work-up had to be quick in order to avoid extensive hydrolysis. The solvent was evaporated *in vacuo* and the reaction mixture was analysed by ¹H-NMR spectroscopy. The results are reported in Table 2. The physical properties, which enabled us to assign the structure of the products, are described in the ESI.† A typical example for the properties of the chlorinated Schiff bases is described:

4'-Methoxy-*N*-(3-chloroazulen-1-ylmethylene)aniline, 3-Cl-5c. Green crystals, mp 78–79 °C (from absolute ethanol) (Found: C, 73.00; H, 4.70; N, 4.68; Cl, 12.03. C₁₈H₁₄NOCl requires C, 73.09; H, 4.77; N, 4.73; Cl, 11.99%); λ_{\max} (dioxane)/nm, 242 (log ϵ /dm³ mol⁻¹ cm⁻¹ 4.4), 275 (4.2), 305 (4.4), 408

(4.2); ν_{\max} (CCl₄)/cm⁻¹ 1610 (CH=N); δ_{H} (CDCl₃) 3.85 (3 H, s, OCH₃), 6.96 (2 H, dd, *J* 8.8 and 2.2, 3'-, 5'-H), 7.29 (2 H, dd, *J* 8.8 and 2.2, 2'-, 6'-H), 7.36 (1 H, t, *J* 10.0, 5-H), 7.39 (1 H, t, *J* 10.0, 7-H), 7.75 (2 H, t, *J* 10.0, 6-H), 8.23 (1 H, s, 2-H), 8.44 (1 H, d, *J* 10.0, 4-H), 8.93 (1 H, s, CH=N), 9.34 (1 H, d, *J* 10.0, 8-H); δ_{C} (CDCl₃) 55.5 (4'-OCH₃), 114.4 (t), 118.4 (q), 122.0 (t), 123.5 (q), 125.8 (q), 126.6 (t), 135.6 (t), 136.2 (t), 136.9 (t), 137.3 (q), 137.8 (t), 146.0 (q), 152.1 (t, CH=N), 157.9 (q).

Acknowledgements

A. C. R. thanks the A. v. Humboldt Foundation for a research fellowship. The authors gratefully acknowledge the financial support of the Foundation and at the same time express their gratitude to Professor Klaus Hafner from Technical University Darmstadt for helpful suggestions and discussions. This investigation was partly supported by the National Agency for Science, Technology and Innovation—Bucharest.

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