

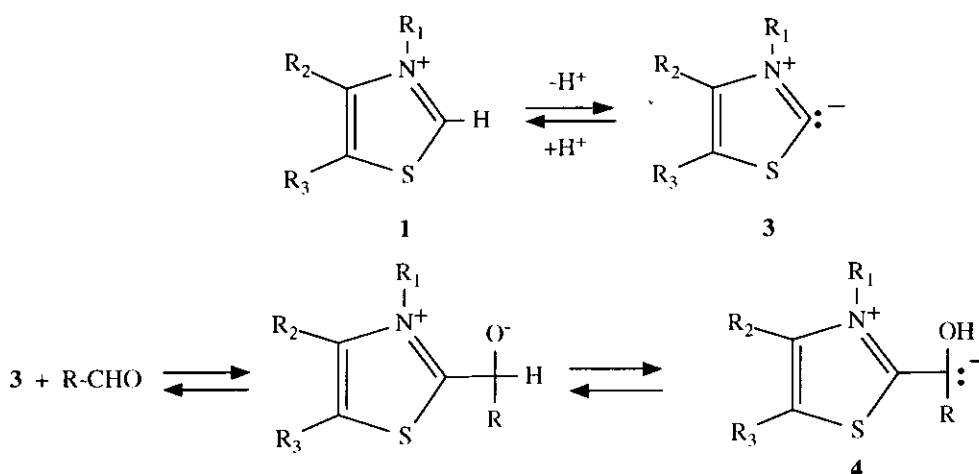
USE OF 3,3'-POLYMETHYLENE-BRIDGED THIAZOLIUM SALTS PLUS BASES AS CATALYSTS OF THE BENZOIN CONDENSATION AND ITS MECHANISTIC IMPLICATIONS: PROPOSAL OF A NEW MECHANISM IN APROTIC CONDITIONS

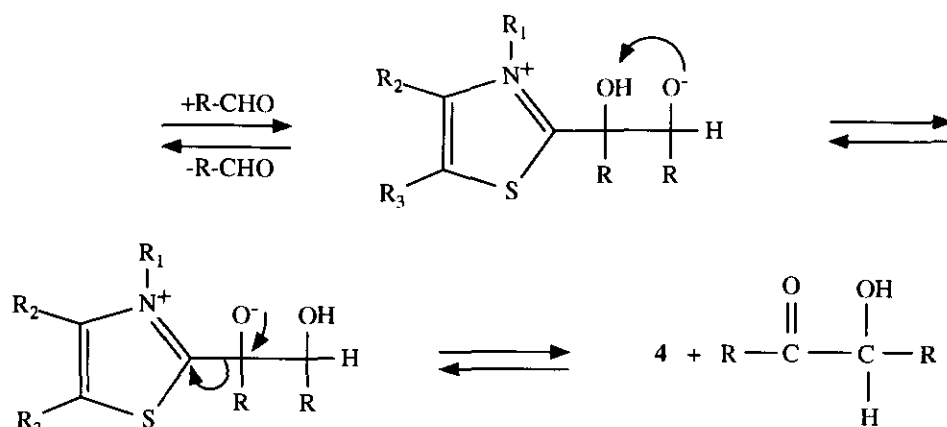
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Abstract- 3,3'-Polymethylene-bridged thiazolium and benzothiazolium salts are used as precatalysts for the benzoin condensation and it is found that catalytic activity depends strongly on the methylene bridge length. This result supports our previous postulation that, at least in strictly aprotic medium, bis(thiazolin-2-ylidene)s, and not thiazolin-2-ylidenes, are the catalytic species in the benzoin condensation catalyzed by thiazolium salts plus base. As a consequence, a new mechanism based in experimental data and AM1 calculations is proposed.

The benzoin condensation can be catalyzed by cyanide ion,^{1,3} thiazolium salts (1) plus bases,^{4,5} or bis(thiazolin-2-ylidene)s (2).^{6,7} Deprotonation of thiazolium ions affords thiazolin-2-ylidenes (3) which, according to the classical proposal of Breslow, would be the actual catalytic species in the benzoin condensation (Scheme I) and related reactions.



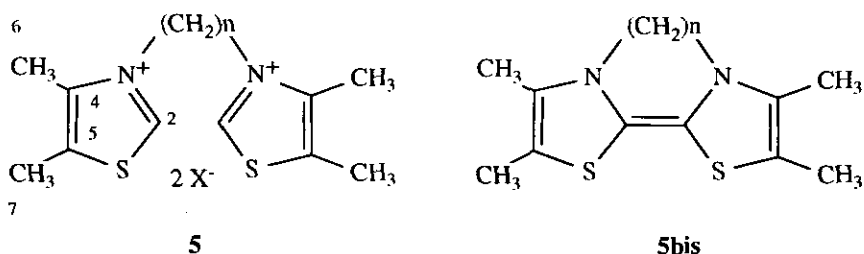


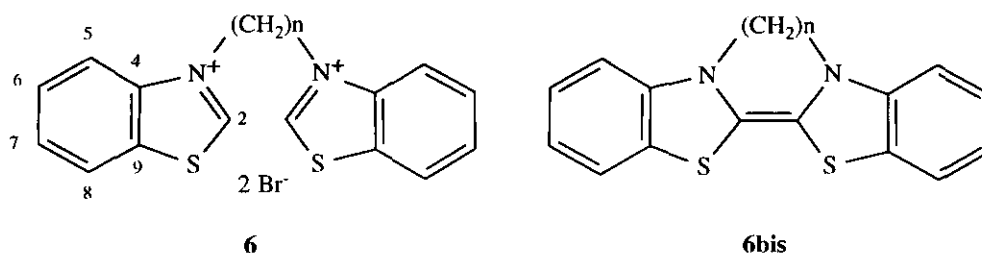
Scheme I

However, it is well known⁸⁻¹¹ that when adding a base to a solution of thiazolium salt, bis(thiazolin-2-ylidenes) (**2**) should be formed *in situ* by nucleophilic attack of the nascent thiazolin-2-ylidenes (**3**) on the surrounding thiazolium ions (see first part of Scheme IV); furthermore, it is also known that, in some cases, reaction of a bis(azolin-2-ylidene), for instance, tetraaminoalkenes, with an electrophile gives the same derivative that would be expected from direct reaction of the parent azolin-2-ylidene and the electrophile; in fact, bis(azolin-2-ylidene)s are compounds so closely related to the corresponding azolin-2-ylidenes that they are frequently referred to as their "dimers"; we will follow this practice here. The mechanism for this behaviour was proposed by Lemal¹², and it has been extrapolated, without positive evidences, to reactions of the analogous bis(thiazolin-2-ylidenes)s, including the benzoin condensation.

In a previous paper¹³ we reported the complete lack of catalytic activity of thiazolin-2-ylidenes generated by desilylation of 2-trimethylsilylthiazolium ions in strictly aprotic medium and, as a logical consequence, we have put forward the postulation of bis(thiazolin-2-ylidene)s as the relevant species when thiazolium salts plus bases are used as catalysts¹³⁻¹⁶ in such conditions.

We report here experimental work on 3,3'-polymethylene-bridged thiazolium bromides [α,ω -bis(4,5-dimethyl-3-thiazolio)alkane dibromides (**5**) and α,ω -bis(3-benzothiazolio)alkane dibromides, (**6**)], and also comparative results obtained by using pre-formed "dimers" (**5bis**) and (**6bis**), that shows *catalytic activity to depend strongly on the methylene bridge length*.





PREPARATION OF 3,3'-POLYMETHYLENE-BRIDGED THIAZOLIUM SALTS (5) AND (6) AND THEIR CORRESPONDING BIS(THIAZOLIN-2-YLIDENE)S.

After some rather unsuccessful attempts to preparing bridged thiazolium salts by using α,ω -dichloroalkanes, excellent results (in many cases almost quantitative yields) were systematically obtained by using α,ω -dibromoalkanes as the quaternizing agents in refluxing acetonitrile and an excess of thiazole to favour the desired double quaternization. Two series of bridged thiazolium bromides were prepared in this way, one starting from 4,5-dimethylthiazole (series 5) and the other from benzothiazole (series 6); in each series, the length of the bridge covered the range from $n=3$ to $n=8$ methylene units (compounds 5-3, 5-4, etc.; 6-3, 6-4, etc.). Attempts to use 1,2-dibromoethane as the quaternizing agent led only to the isolation *N*-(2-bromoethyl)thiazolium bromide; however, 1,2-bis(4,5-dimethyl-3-thiazolio)ethane dichloride (compound 5-2, Cl instead of Br) was prepared by condensation of 3-chloro-2-butanone with *N,N*-dithioformylethylenediamine (prepared from ethylenediamine).

The resulting salts were easily isolated and purified with the sole exception of compound (5-7) the high hygroscopicity of which made its manipulation difficult. All of them were soluble in methanol and insoluble in chloroform.

Preparative isolation of bis(thiazolin-2-ylidene)s formed by adding bases to thiazolium salts solutions is possible only if advantage can be taken of their eventual insolubility in the reaction medium. To avoid this important limitation an alternative general method was developed by us¹⁴ which consists in passing a methanolic solution of the thiazolium salt through a strongly basic ion exchange column, thermostated at 0 °C, in an inert atmosphere and collecting the eluted solutions over 3 Å molecular sieves. Solvent is then removed in high vacuum, low temperature and under an inert atmosphere. This methodology has been here applied to salts (5) and (6): halogen-free, oily, soluble in chloroform and in hot dioxane (in contrast to the insolubility of the parent thiazolium salts) and catalytically active products were obtained in all cases.

The main purpose in preparing "dimers" (5bis) and (6bis) was to compare their catalytic activities with those of the parent bridged thiazolium salts (plus base) but some new spectral information^{17,18} on these highly unstable species was also gathered. Thus, a regular peak series from fragmentation of the polymethylene chain is a very characteristic feature in the mass spectra of salts (5) and (6) (see Experimental) but these peaks are hardly observable in the mass spectra of "dimers".

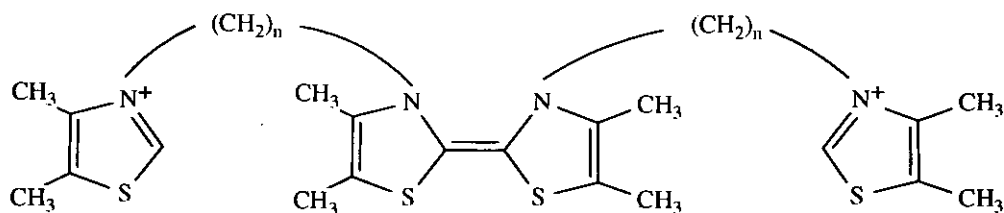
The ¹³C nmr spectrum of "dimer" (5bis-3) (a neutral species) showed, relative to that of the organic moiety of (5-3) (a dipositive ion), the expected upfield shift of tertiary aromatic carbon signals. Thus, the salt shows, in DMSO solution, a peak at 156.1 ppm, corresponding to the two equivalent carbon atoms 2 and 2' (see Figure), and two more signals at 142.0 and 133.2 ppm due to the two groups of equivalent carbon atoms 4-4'

and 5-5'. When sodium hydride is added such peaks disappear and appears a new set of signals at 136.0 and 128.4 ppm corresponding to quaternary carbon atoms 4-4' and 5-5', displaced at higher field because the disappearance of the charge in the formation of the bis(thiazolin-2-ylidene) system (type **2** structure), and a clear signal appears (carbon 2 and 2') at 114.0 ppm, in excellent concordance with the value described by Jordan¹⁹ for the, so called, "symmetric dimer" or bis(thiazolin-2-ylidene)s; this is the demonstration of the formation of the bis(thiazolin-2-ylidene) in basic conditions from bridged thiazolium salts as the sole product observed.

CATALYTIC ACTIVITY IN THE BENZOIN CONDENSATION OF 3,3'-POLYMETHYLENE-BRIDGED THIAZOLIUM SALTS (PLUS BASES) AND OF THE CORRESPONDING BIS(THIAZOLIN-2-YLIDENE)S.

Benzoïn condensation catalytic activity was measured by the yield in benzoïn obtained under the strictly controlled working conditions already employed in the desilylation study of 3-methyl-2-trimethylsilylbenzothiazolium trifluoromethanesulphonate.^{13,20} Yields are collected in the Table together with those from control experiments using the simple salts (**7**) [3,4,5-trimethylthiazolium (**1**, R₁=R₂=R₃= CH₃) iodide] and (**8**) [3-methylbenzothiazolium (**1**, R₁= CH₃, R₂-R₃= CH=CH-CH=CH) iodide] and their respective "dimers" (**7bis** and **8bis**).

Even at 100 °C, all thiazolium salts (**5**) and (**6**) were insoluble in dioxane but they went into solution after addition of the base (see experimental section). This points clearly to *in situ* formation of "dimers" (**5bis**) and (**6bis**), the solubility of which has been mentioned already; on the other hand, it is difficult to imagine that solubilisation could be due to formation of linear "dimers" such as **9**. At the end of the runs, after cooling, a crystalline precipitate of diisopropylethylamine hydrobromide was isolated. In experiments **6-3/A** and **6-4/A** very insoluble, high melting (> 260 °C) materials were isolated which according to their ms (peak at m/z = 149, C₈H₇NS⁺) were formed from the thiazolium salt; most probably, they are polymeric structures (no such materials were isolated in experiments **6bis-3/C** and **6bis-4/C**).



9

The nuclear experimental results are those of series **5/A** and **6/A**. As expected⁶ benzothiazolium salts afford much poorer benzoïn yields than simpler thiazolium salts but in both series the behaviour is very similar, showing an activity maximum for n= 7 (series **5**) or 6 (series **6**), it is to say that *the catalytic activity depends on the methylene bridge length*.

Table. Benzoin condensation catalytic activity of 3,3'-polymethylene-bridged thiazolium salts plus bases and the corresponding bis(thiazolin-2-ylidene)s.

	A	B	C	D
<u>7</u>	<u>69.2</u>	<u>27.5</u>		
<u>5</u>				
5-2	37.0			
5-3	59.2	35.4		
5-4	13.8	0		
5-5	39.7	7.6		
5-6	44.2	6.5		
5-7	64.9	7.9		
5-8	2.3	1.4		
<u>7bis</u>			<u>54.0</u>	
<u>5bis</u>				
5bis-2			34.0	
5bis-3			33.9	
5bis-4			44.7	
5bis-5			54.0	
5bis-6			69.4	
5bis-7			64.1	
5bis-8			53.9	
<u>8</u>	<u>4.0</u>			<u>4.4</u>
<u>6</u>				
6-3	0.8			1.8
6-4	1.3			0.9
6-5	15.4			11.0
6-6	26.8			14.7
6-7	11.7			2.1
6-8	1.4			4.3
<u>8bis</u>			<u>5.7</u>	
<u>6bis</u>				
6bis-3			1.9	
6bis-4			14.3	
6bis-5			13.6	
6bis-6			25.6	
6bis-7			14.9	
6bis-8			9.6	

Gas chromatographic benzoin yields (see Experimental) under the following conditions: A) 4.9 mmol of benzaldehyde; 0.49 mmol of salt (0.98 for **7** and **8**); 1.4 mmol of DIEA; 5 ml of anh. dioxane; 101 °C; 24 h.; argon atm. B) 4.9 mmol of benzaldehyde; 0.05 mmol of salt (0.1 for **7**); 0.14 mmol of DIEA. Working conditions as in A). C) 4.9 mmol of benzaldehyde; "dimer" prepared from 0.49 mmol of salt (0.98 for **7** and **8**). Working conditions as in A). D) Conditions as in A) but changing refluxing dioxane by refluxing ethanol.

Comparative experiments conducted under a variety of conditions confirm the above results. Experiments in column **5/B**, in which the proportion of catalyst was smaller, and in column **6/D**, in which ethanol was the solvent instead of dioxane, show the same trends, respectively, than in **5/A** and **6/A**. The experiments with pre-formed "dimers" (columns **5bis/C** and **6bis/C**) also confirm these trends. An interesting point is the different behaviour of **5-8** and **5bis-8**. The yield obtained from **5-8** is abnormally low, probably because the difficult formation of the dimeric system in conventional conditions, due to the members of the resulting cyclic system. But when **5-8** is previously converted into **5bis-8** the observed yield fits perfectly in the statistical distribution. In relation to the abnormally high yield observed when **5-3** is used in conventional basic medium and the normal one observed from **5bis-3**, analogous explanation is applicable. The correction

of such abnormal behaviours when the salts are converted into its corresponding bis(thiazolin-2-ylidene)s could be considered as a proof of our statement.

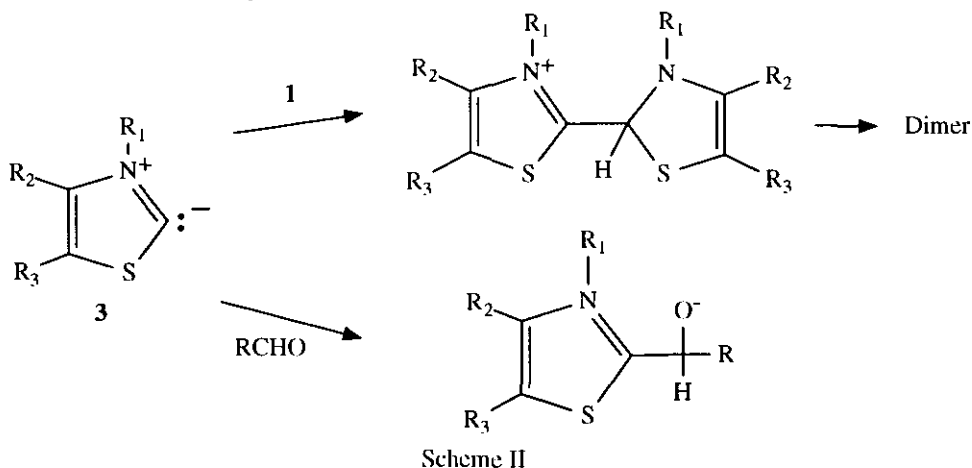
The clear influence of the methylene bridge length on reaction yield supports our previous postulation that bis(thiazolin-2-ylidene)s (2), and not thiazolin-2-ylidenes (3) are the real catalytic species in the benzoin condensation catalyzed by thiazolium salts in basic medium because in the reported cases the formation of the bis(thiazolin-2-ylidene) system gives rise to diaza-ring formation and the obvious thing is to base the explanation of that dependency on the relationship between size and properties (stability, ease of formation, etc.) of the new formed ring. As a logical consequence of the present results in this and in previous papers, and with the aid of theoretical calculations, we reinforce our proposal¹³ of a new mechanism for the benzoin condensation.

A NEW MECHANISM FOR THE BENZOIN CONDENSATION

We have applied AM1 calculations to determine thermodynamic parameters of significative species in the studied processes; such parameters and some important geometric characteristics of intermediates are collected in the following figures and schemes. To dispose of homogeneous data, we have also calculated the heats of formation of formaldehyde (-31.5 kcal/mol) and glycolaldehyde (-85.7 kcal/mol) by AM1 theoretical calculations.

A: ATTACK OF THE CONJUGATE BASE OF A THIAZOLIUM CATION TO AN ALDEHYDE UNIT vs. ATTACK TO OTHER UNIT OF THIAZOLIUM CATION WITH FORMATION OF A BIS(THIAZOLIN-2-YLIDENE).

As repeatedly indicated, the benzoin condensation is carried out by placing in a basic medium a thiazolium cation and an aldehyde. In such basic conditions the conjugate base of the thiazolium cation (3) is formed. This species (3) is a nucleophile and can react with the two electrophiles present in the reaction medium: a thiazolium cation (1), or an aldehyde unit (Scheme II).



The attack of (3) to a formaldehyde, first step of the Breslow's mechanism, has a $\Delta H_r = -2.7$ kcal/mol and a $\Delta E_{act} = 2.1$ kcal/mol; formation of the dimer has a $\Delta H_r = -233.5$ kcal/mol, if we consider the process $OH^- + Tz^+-H + Tz^+ \rightarrow Tz=Tz + H_2O$, while the process $Tz^+ + Tz^+-H \rightarrow Tz^+-Tz-H$ (formation of the intermediate species between the thiazolium cation, Tz^+-H , its conjugate base, Tz^+ , and the dimer) has a $\Delta H_r = -42.2$ kcal/mol and no appreciable activation energy. In other words, from the conjugate base of a thiazolium cation, the formation of the dimer from the conjugate base of a thiazolium cation is faster and thermodynamically much more favorable than formation of the first intermediate in the classical mechanism. However, as all these are equilibrium processes, if the rest of steps in the Breslow mechanism would be more favorable, this could operate.

B: THEORETICAL STUDY OF THE BRESLOW MECHANISM.

We have calculate all the parameters of the Breslow mechanism, and they are represented in summary in the Figure 1. From the calculated values of ΔH_r of the significative structures, it is deduced that the state named as C in Figure 1 (the carbanionic-enol intermediate of Breslow (11) plus formaldehyde) is the most stable state in the global theoretical reaction, and consequently should be the end point in this process. In fact, such intermediates are tautomeric structures of the known 2-acylthiazolines (13) stable and isolable molecules; Metzger¹⁰ has described the preparation of 3-methyl-2-benzoylbenzothiazoline by the reaction between benzaldehyde and 3-methylbenzothiazolium salt plus triethylamine, with 70 % yield, that is to say, in the benzoin condensation conventional conditions, in total agreement with our thermodynamic-based reasoning. Furthermore, in reference to such structures (13) Wanzlick²¹ showed to be inactive in neutral conditions in one case, to have some activity in other, and to have an enhanced activity if the compound is placed in pyridine as solvent. If these such compounds were the real intermediates, they would be able to tautomerize easily to the enol-enamine form, and, in this way, they would have nucleophilic character enough over the exocyclic carbon atom to attack to a new formaldehyde molecule in the way proposed in the classical mechanism, and such characteristics would be present in all cases. We described¹³ that the nucleophilic position, if any, in the enol-enamine structures would be C-5, the olefinic carbon atom directly linked to the sulfur atom. Moreover, to have some activity in one case is not an evidence of the character of intermediate of structures (13): we think that it only proves its instability. In our view, if a 2-acylthiazoline catalyzes the reaction it is because decomposes into their precursors in the conditions of reaction, generating indirectly the corresponding dimer. This decomposition is strongly supported by the reported enhanced activity in basic medium, because, as it is represented in the Scheme III, such 2-acylthiazolines must lose the acidic proton in C-2 by the action of the pyridine, tautomerize to the enol-enamine form, decompose into thiazolin-2-ylidenes (3) and, *via* formation of thiazolium cations and reactions between the two species, the corresponding dimers must to be formed.

Summarizing, the consequences of the previous reasoning are: a/ the stability of the Breslow's intermediates (13) is very high, and the reaction cannot progress towards the condensation because it is thermodynamically impossible; and b/ the observed, *only in one case*, activity of a molecule of type (13) is perfectly justifiable from our mechanistic proposal.

One interesting, but irrelevant, formal aspect is the predicted concerted character of the step from the Breslow

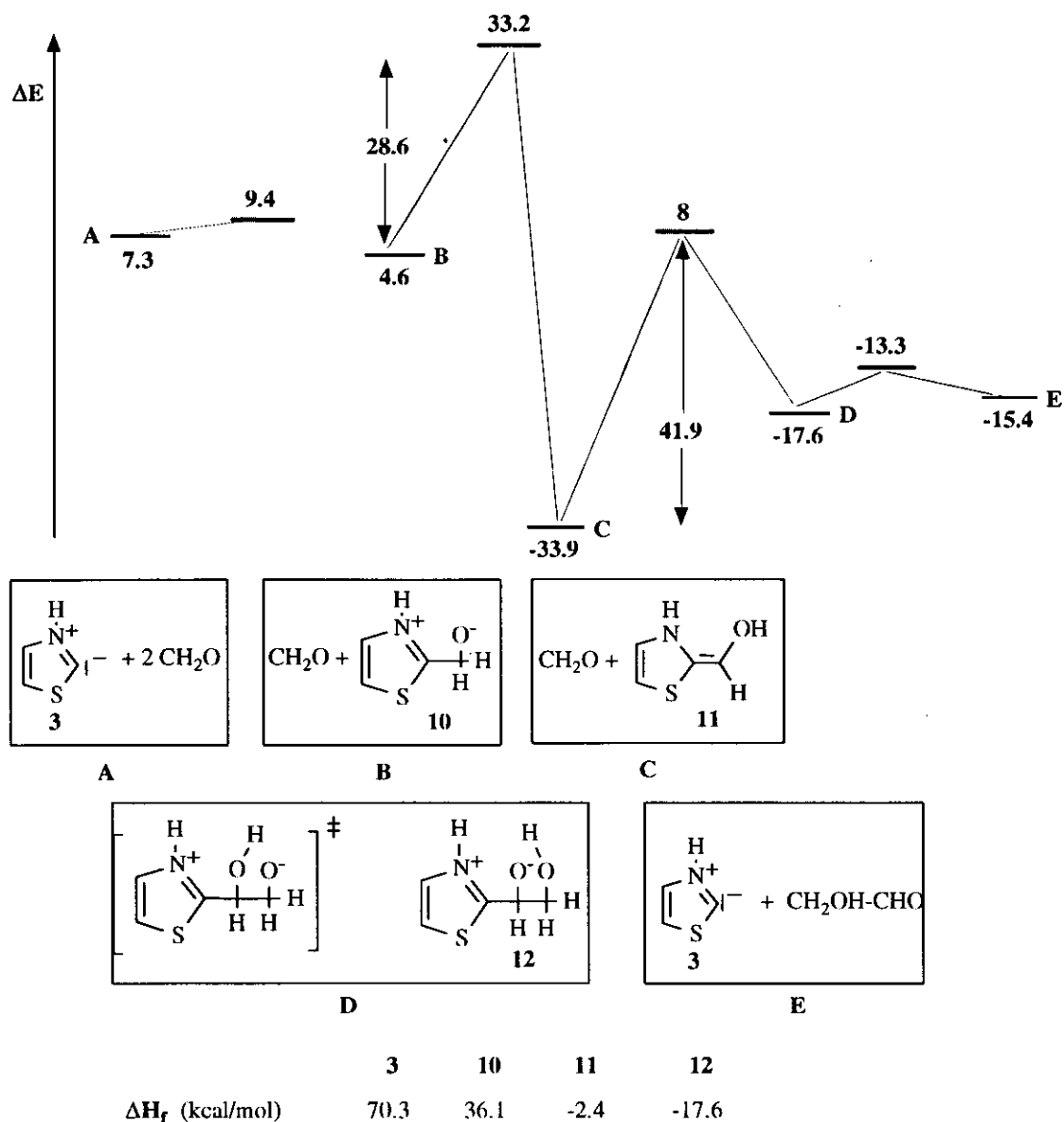
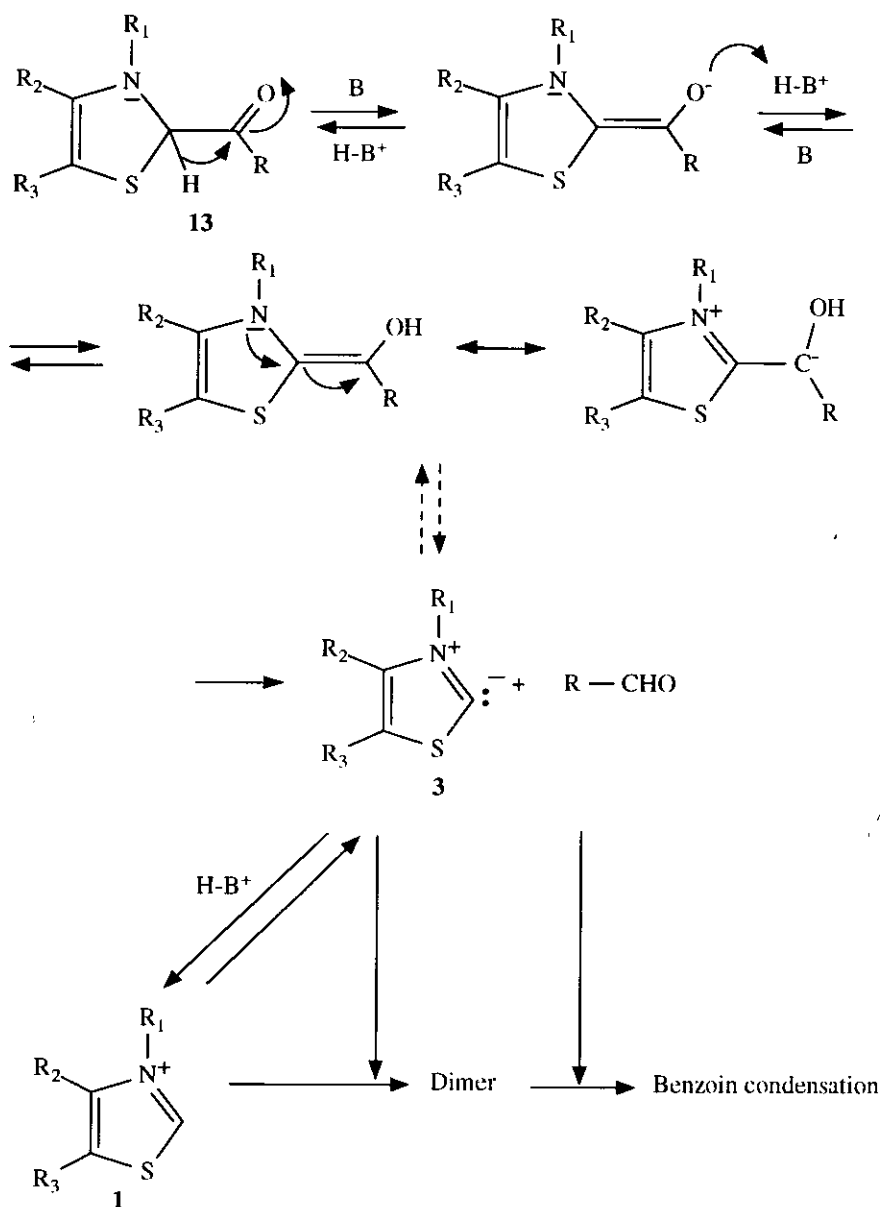


Figure 1. Thermodynamic parameters (kcal/mol) of the Breslow mechanism calculated by the AM1 method. intermediate to the immediate precursor of the final product (see step D in Figure 1) if the reaction could take place, behaviour different of the described for the classical benzoin condensation with cyanide ion as catalyst, and in the calculated by us from bis(thiazolin-2-ylidene)s.

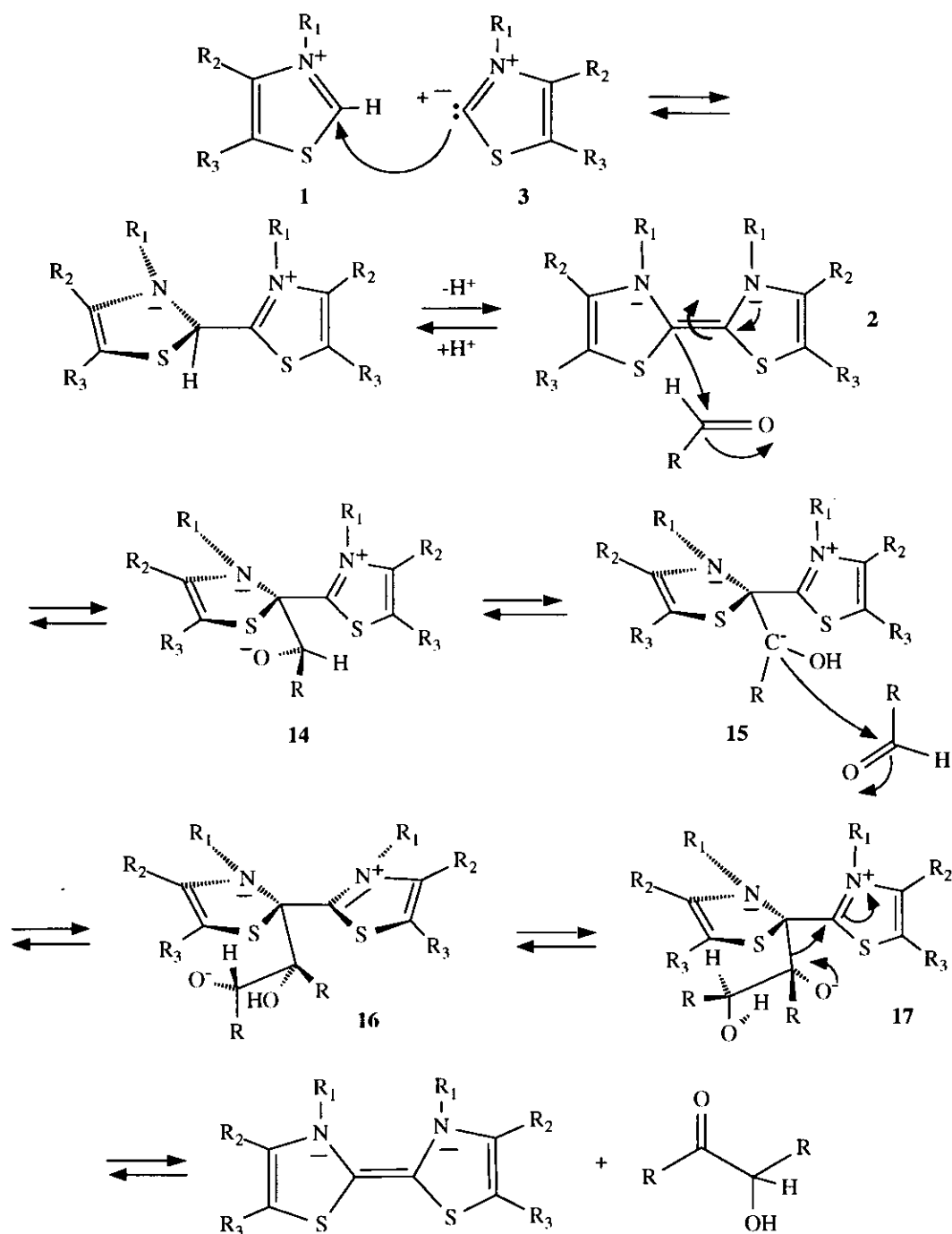
C: THEORETICAL STUDY OF A NEW MECHANISM OF THE BENZOIN CONDENSATION, BASED IN THE BIS(THIAZOLIN-2-YLIDENE)S AS REAL CATALYTIC SPECIES IN APROTIC MEDIUM.

Our mechanistic proposal, already published¹³ in its general guidelines, is the one represented in Scheme IV; thermodynamic and geometric parameters of intermediates are given in Figures 2 and 3.



Scheme III

It is important to observe some interesting characteristics of the calculated structures of the intermediates. The first is the non-planar geometry of the bisthiazole unit in the intermediate in the process of formation of the dimer ("asymmetric dimer" in the terminology of Jordan¹⁹), and in all the intermediates of the catalytic process except **16**: this supposes a clear geometrical distortion in the formation of the dimer from their precursors, and analogously, in the formation and evolution of the intermediates. These geometrical changes must be one of the most important reasons to explain the relation yield-length of the bridge between two



Scheme IV

thiazole moieties (see general structure 18).

The most important feature of the proposed mechanism is the very high stability of the carbanion (15), more

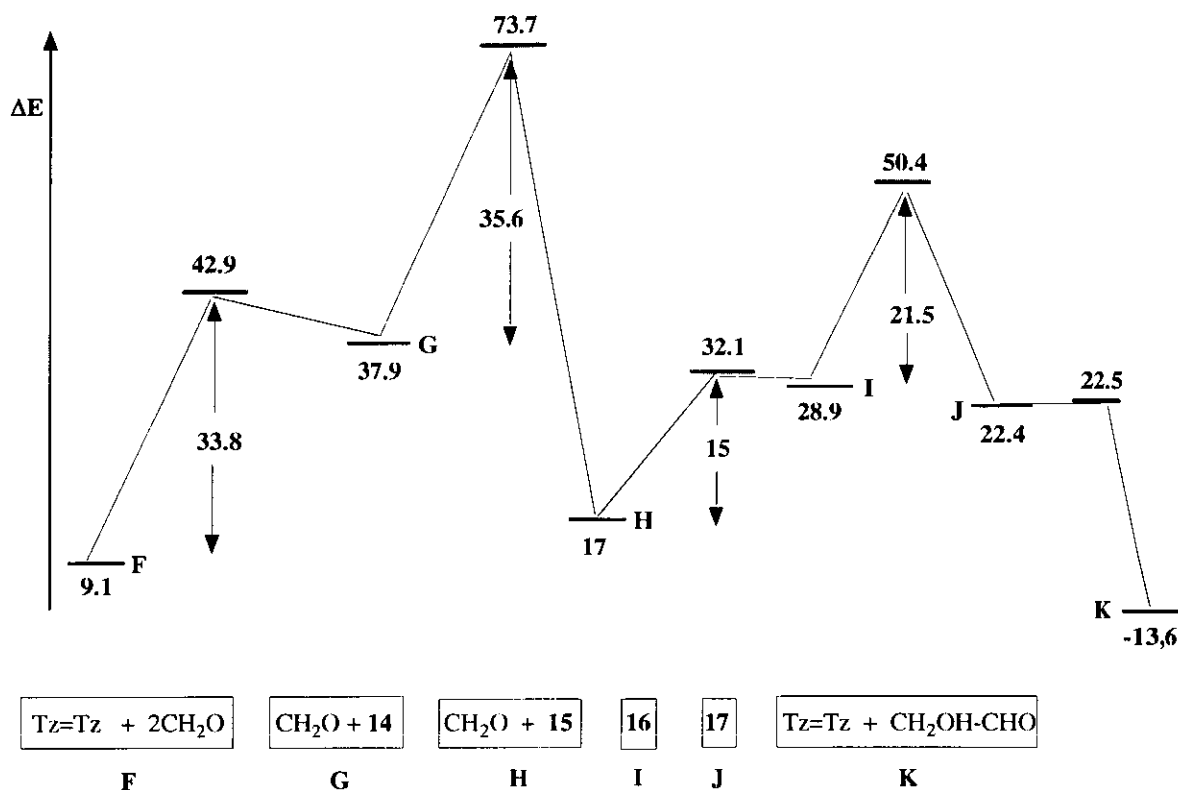


Figure 2. Thermodynamic parameters (kcal/mol) of the benzoin condensation catalyzed by bis(thiazolin-2-ylidene)s calculated by the AM1 method. Structures (14, 15, 16 and 17) as represented in Scheme V for $R = R_1 = R_2 = R_3 = H$.

stable than the oxanion (16) in 21 kcal/mol; the reason could be the almost parallel disposition of its full p_z orbital and the positively charged π system of the thiazolium moiety in the intermediate with the consequent stabilizing orbital interaction. In fact, the presence of this charged aromatic thiazolium ring in this and others intermediates would be the explanation of their stability and the thermodynamic justification of the mechanism.

From the kinetic standpoint, the reaction between the two uncharged initial species, the dimer (2) and the aldehyde, commonly accepted as possible from Lemal work, and the proton transference in the oxanion (14) to yield the carbanion (15), present essentially the same activation energy. In the case of aromatic aldehydes, the relative stability of the last kind of intermediates would be still higher because of the extra stabilization of the negative charge by resonance with the aromatic ring, and we can expect a lower, more favorable, activation energy. In any case, the present numerical values refer, as obvious, to a reaction in gas phase; probably in a protic medium all these energy barriers would be much lower.

Another important aspect to consider is the conformational change from carbanion (15), with the two thiazole ring almost perpendicular, to intermediate (16), in which such rings are approximately in the same plane. The reason of such conformational change is, very probably, the steric interaction between the growing chain and a thiazole ring, and, specially, the electrostatic repulsion between the new negatively charged oxygen atom

Intermediate 14

$\Delta H_f = 69.4 \text{ kcal/mol}$

$\langle S^2 \rangle = 1.259$

Dihedral angles

$S_4-C_2-C_1-S_3 \quad 73.9^\circ$

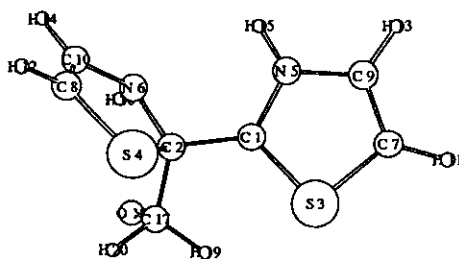
$O_{18}-C_{17}-C_2-C_1 \quad -108.5^\circ$

$C_{17}-C_2-C_1-S_3 \quad -39.5^\circ$

Bond distances (Å)

$C_1-C_2 \quad 1.47$

$C_{17}-C_2 \quad 1.56$

**Intermediate 15**

$\Delta H_f = 48.5 \text{ kcal/mol}$

$\langle S^2 \rangle = 1.234$

Dihedral angles

$S_4-C_2-C_1-S_3 \quad 64.8^\circ$

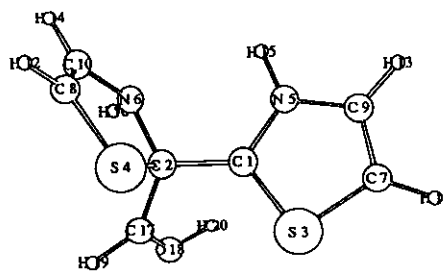
$O_{18}-C_{17}-C_2-C_1 \quad -50.0^\circ$

$C_{17}-C_2-C_1-S_3 \quad -50.5^\circ$

Bond distances (Å)

$C_1-C_2 \quad 1.48$

$C_{17}-C_2 \quad 1.49$

**Intermediate 16**

$\Delta H_f = 28.9 \text{ kcal/mol}$

Dihedral angles

$S_4-C_2-C_1-S_3 \quad -7.3^\circ$

$O_{18}-C_{17}-C_2-C_1 \quad -54.7^\circ$

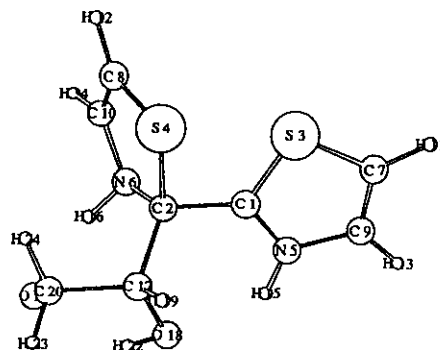
$C_{17}-C_2-C_1-S_3 \quad -126.8^\circ$

Bond distances (Å)

$C_1-C_2 \quad 1.51$

$C_{17}-C_2 \quad 1.55$

$C_{17}-C_{20} \quad 1.59$

**Intermediate 17**

$\Delta H_f = 22.4 \text{ kcal/mol}$

$\langle S^2 \rangle = 1.265$

Dihedral angles

$S_4-C_2-C_1-S_3 \quad 68.7^\circ$

$O_{18}-C_{17}-C_2-C_1 \quad -81.7^\circ$

$C_{17}-C_2-C_1-S_3 \quad -48.6^\circ$

Bond distances (Å)

$C_1-C_2 \quad 1.48$

$C_{12}-C_2 \quad 1.56$

$C_{17}-C_{20} \quad 1.54$

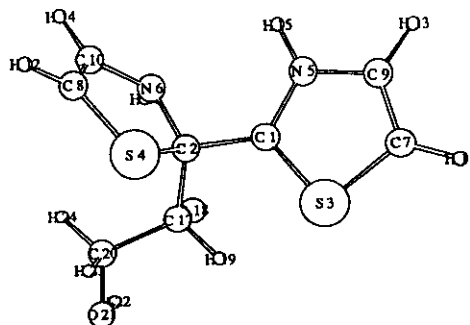
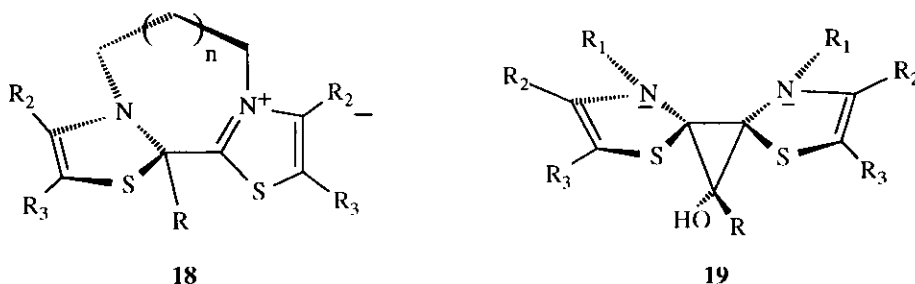


Figure 3. Ball and SticksTM representation, significant geometric characteristics and heats of formation of the intermediates of the benzoin condensation catalyzed by bis(thiazolin-2-ylidene)s.

and the two electronegative atoms, N and S, in the non aromatic ring, interaction that would be present if the dihedral angle between the two thiazole ring would be about 90° , as in the rest of the intermediates. We have looked for different geometries for **16**, but it has been impossible to localize a different minimum in the reaction hypersurface. The last step, in which the intermediate (**17**) gives rise to dimer and benzoin, has a negligible activation energy.



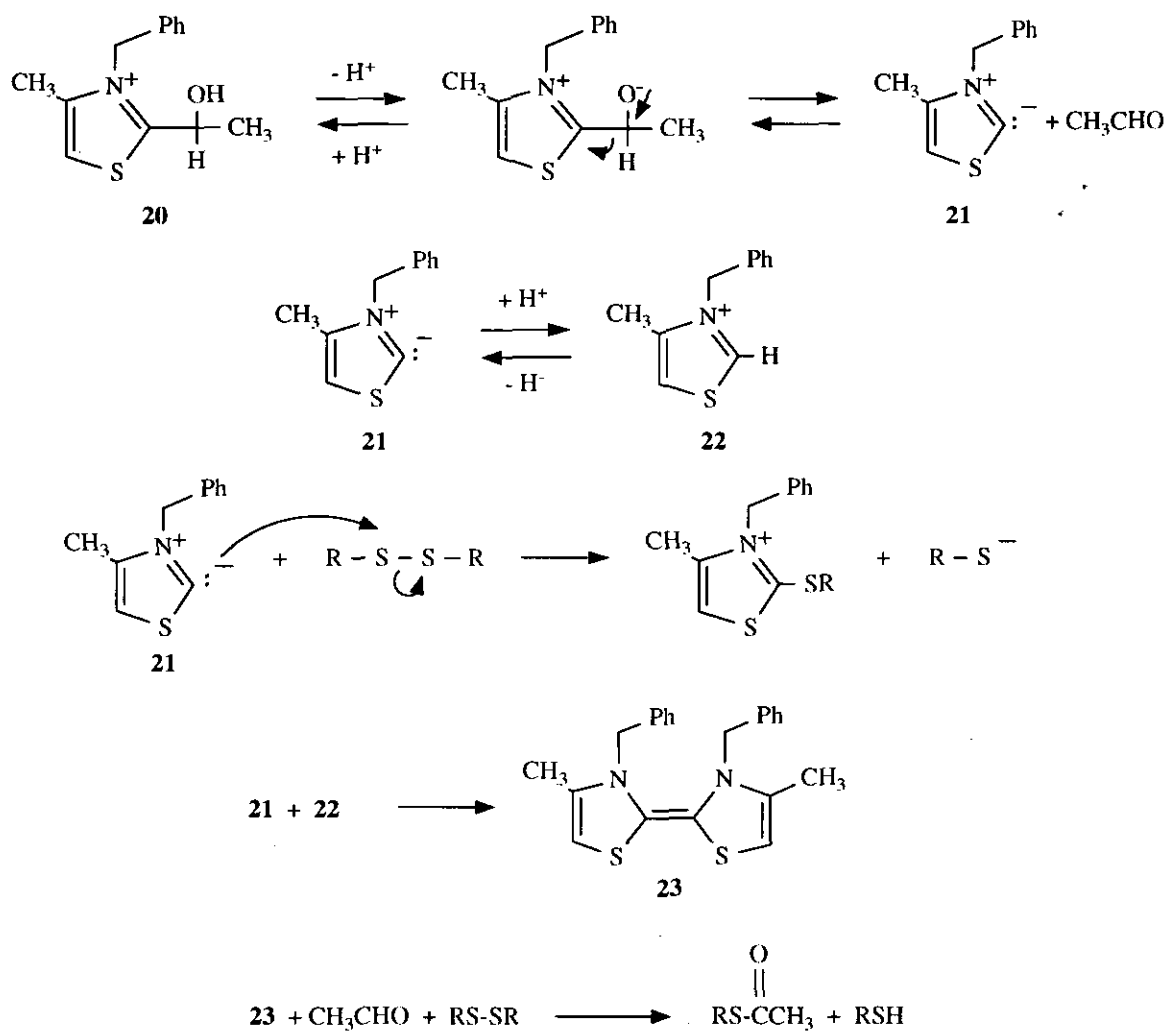
In a certain moment of our studies we believed that the tricyclic compound (**19**) could be as good a candidate to be a key intermediate of the process as carbanion (**15**). We have rejected such idea because, although its thermodynamic stability is the same ($\Delta H_f = 48.5$ kcal/mol), we have not been able to link such supposed intermediate with the anterior and the posterior intermediates through reasonable transition states, probably because the inadequate topology of the tricyclic compound. However, the relative stability of **19** converts it in a good candidate of future mechanistic and synthetic studies, as possible indirect precursor of the carbanionic intermediate (**15**).

DISCUSSION OF SEVERAL DESCRIBED PROCESSES RELATED WITH THE BENZOIN CONDENSATION AND THEIR JUSTIFICATION FROM THE PROPOSED MECHANISM.

At this point in the discussion it might be interesting to point out several facts, that, although do not demonstrate properly our proposal, they can be easily explained from the hypothesis of bis(thiazolin-2-ylidene)s as real catalytic species in this group of reactions.

Rastetter *et al.*, described²² the reaction between 3-benzyl-2-(α -hydroxyethyl)-4-methylthiazolium tetrafluoroborate (**20**) and different disulfides in the presence of a base. As the authors indicate **20** is, in fact, a protonated Breslow intermediate (**4**), and this product decomposes when treated with a base in acetaldehyde and the conjugate base of the thiazolium cation; the conjugate base attacks disulfides affording thiols and the thiazolium salt substituted in 2 by a sulfide as the main products of the reaction; however, also thioesters are isolated to some extent, but always in low yields. It is possible to explain these facts using our proposal (Scheme V): the salt (**20**) decomposes, as the authors described, affording species (**21**), of the same kind of (**3**); this acts as a base, taking a proton from **20**, forming the corresponding thiazolium salt (**22**); the new species (**21**) formed reacts with the former thiazolium cation (**22**), and a bis(thiazolin-2-ylidene) unit (**23**) is formed, that reacts with the acetaldehyde now present in the medium and the acyl anion equivalent intermediate, formed in the way proposed by us, reacts with the disulfide leading the thioester.

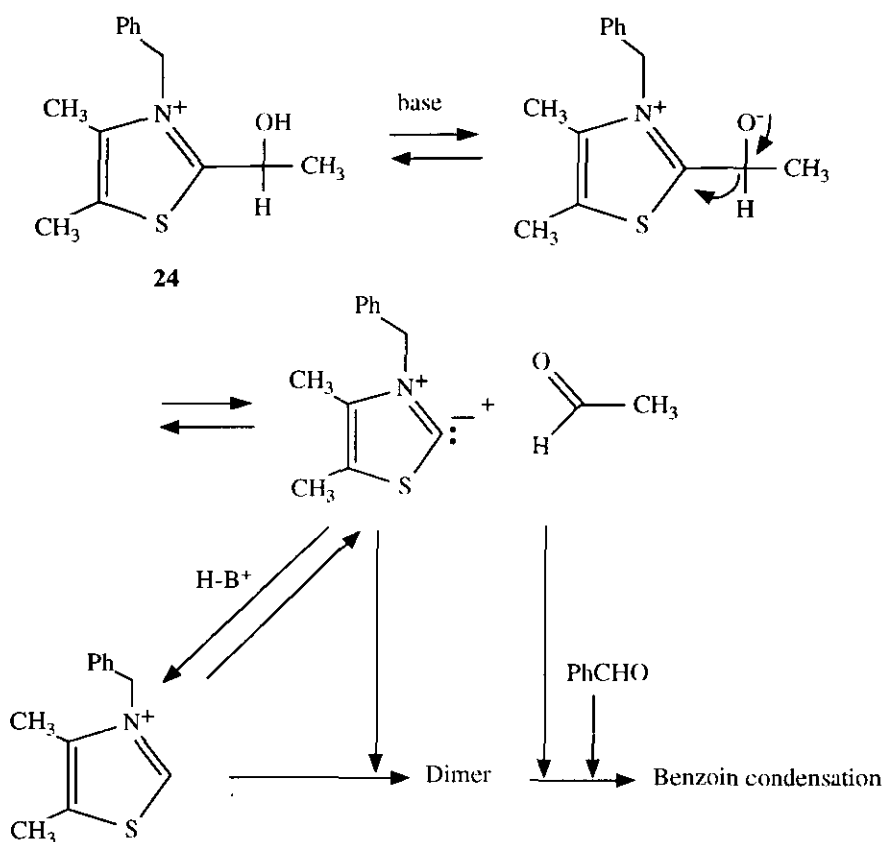
Analogously, we described in our previous paper¹³ that when 3-benzyl-2-(α -hydroxyethyl)-3,4-dimethylthiazolium ion (**24**), a salt very similar to **20**, is treated under the reaction conditions with an



Scheme V

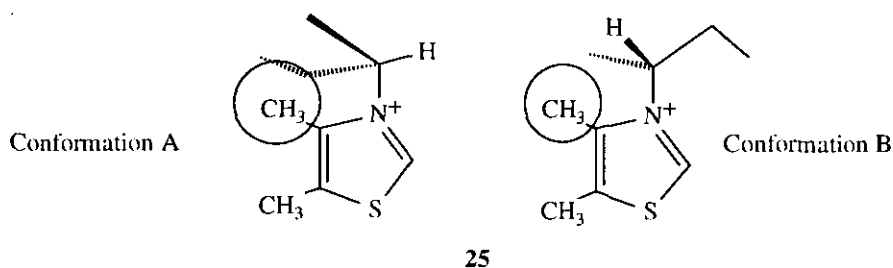
aldehyde different to acetaldehyde, the isolated compound is not the result of the attack of the Breslow's intermediate of the acetaldehyde to the new aldehyde, as it must be if the old mechanism was correct; the reaction product is a mixture of four acylins in approximately the same proportions, in other words, the process is (Scheme VI): a/ decomposition of the Breslow intermediate with liberation of acetaldehyde and a unit of thiazolin-2-ylidene; b/ conversion of this to a thiazolium cation; c/ formation of the bis(thiazolin-2-ylidene) from a thiazolium cation and a newly formed thiazolin-2-ylidene; and d/ the crossed reaction between the two aldehydes, yielding the four possible acylins, in a result which is in agreement with the facts described by Rastetter and with our mechanistic proposal.

An important fact described by us¹⁶ is that the 3-[(*R*)-2-butyl]-4,5-dimethylthiazolium iodide (**25**) does not catalyze the benzoin condensation at 30°C in methanol; however, the 3-[(*R*)-2-butyl]-thiazolium iodide (**26**), it is to say, a salt with the same bulky group over the nitrogen atom but without the methyl groups in 4 and 5,



Scheme VI

yields 100 % of benzoin. Our explanation is that in the case of **25** the methyl in position 4 forces the system to exist in conformation B (see Figure 4) and in such conformation the ethyl groups do not permit the approximation of the two rings to form the bis(thiazolin-2-ylidene). In salt (**26**), however, the absence of a methyl group in position 4 enables the existence of conformation A (or any other), the catalytic species is formed, and the reaction takes now place.

Figure 4. Conformations of the compound (**25**).

CONCLUSION

In the present paper, new experimental data are presented that give support to our previous claim¹³ that bis(thiazolin-2-ylidene)s (**2**) play a key role in the benzoin condensation and related processes in aprotic conditions; furthermore, theoretical AM1 calculations show that our mechanistic proposals are kinetically and thermodynamically reasonable. On the other hand, complementary calculations show that Breslow's intermediates should be in such conditions end points of a chemical reaction, and not intermediates in the reaction between thiazolin-2-ylidenes and aldehydes. This theoretical result is in full agreement with the experimentally established lack of catalytic activity when thiazolin-2-ylidenes are generated under conditions that preclude the formation of bis(thiazolin-2-ylidene)s.

THEORETICAL PROCEDURE

The calculations were carried out by using the standard AM1²³ procedure, as implemented in the MOPAC program.²⁴ It was necessary to use procedures applicable to open-shell systems. The calculations were, therefore, carried out with the UHF formalism (UAM1).²⁵ Transition states were located by minimizing the norm of the gradient²⁶ and characterized by calculating force constants.²⁶ All geometries were found by minimizing the energy without making any assumptions. Options for all these procedures are included in MOPAC.

EXPERIMENTAL SECTION

3,4,5-Trimethylthiazolium iodide and 3-Methylbenzothiazolium iodide. These two salts were prepared by quaternization with methyl iodide of 4,5-dimethylthiazol and benzothiazol, respectively.

1,2-Bis(4,5-dimethyl-3-thiazolio)ethane dichloride. 1,2-Diaminoethane (2.2 g; 37 mmol) was added dropwise to a mixture of ethyl thioformate (80%; nmr quantification) and ethyl formate prepared from ethyl orthoformate (16 g; 110 mmol) and hydrogen sulphide²⁷ in excess; a white solid appeared at once. After an hour, solvent was removed and the residual solid material was chromatographed in silica gel using dichloromethane with methanol (5%) as eluent to give **1,2-bis(thioformylamino)ethane** (1.5 g; 10 mmol), mp 121-123°C. Ir (KBr): 3170, 2970, 1540, 1460, 1430, 1330, 1300 cm⁻¹. ¹H Nmr (CD₃OD): δ 9.44 (s, 2H), 4.03 (s, 4H). ¹³C Nmr (CD₃OD): δ 190.8 (CH), 41.7 (CH₂). Ms (EI) (m/z): 148 (M), 114 (M-H₂S), 87 (base peak) (M-CH₂NS). Anal. Calcd for C₄H₈N₂S₂: C, 32.1; H, 5.4; N, 18.0; S, 43.6. Found: C, 32.4; H, 5.5; N, 18.8; S, 43.0. Yield, 27%.

A mixture of 1,2-bis(thioformylamino)ethane (1.0 g; 6.76 mmol) and 3-chloro-2-butanone (7.4 g; 69.7 mmol) was refluxed during 5 min; almost instantaneously the initial white precipitate disappeared and a new white solid was formed. After cooling, the solution was decanted and the residual solid was recrystallised from methanol-ether and methanol-acetone to give pure **1,2-bis(4,5-dimethyl-3-thiazolio)ethane dichloride (5, n=2)**. Yield and physical properties are found in the sequel together with those for the other members of the series.

α,ω-Bis(4,5-dimethyl-3-thiazolio)- and α,ω-bis(3-benzothiazolio)-alkane dibromides (n = 3-8)²⁸. Preparation of 1,3-bis(4,5-dimethyl-3-thiazolio)propane dibromide (**5, n=3**) is given as a representative example.

An acetonitrile (5 ml) solution of 4,5-dimethylthiazol (1.67 g; 14.8 mmol) and 1,3-dibromopropane (0.696 g; 3.5 mmol) was refluxed for 48 h. After cooling, the solution was decanted and the residual solid material was washed several times with ether and recrystallised from methanol/ether to give 1,3-bis(4,5-dimethyl-3-thiazolio)propane dibromide (**6, n=3**). Yield and physical properties are found in the sequel together with those for the other members.

1,2-Bis(4,5-dimethyl-3-thiazolio)ethane dichloride (5, n=2): mp 191-193 °C. Ir (KBr): 3400, 3060, 2970, 1585, 1450, 1400, 1190 cm⁻¹. ¹H Nmr (CD₃OD): δ 5.2 (s, 4H), 2.7 (s, 6H), 2.7 (s, 6H). ¹³C Nmr (CD₃OD): δ 157.6 (C₂), 143.8 and 136.4 (C₄ and C₅), 52.3 (C₈), 12.6 and 11.8 (C₆ and C₇). Ms (EI) (m/z): 252 (M-2), 224

(base peak) (252-C₇H₄), 209 (224-CH₃), 191, 156, 139, 126 (C₅H₇NS+CH), 71, 59. Anal. Calcd for C₁₉H₁₈N₂S₂Cl₂·2H₂O: C, 39.9; H, 6.1; N, 7.7; S, 17.7; Cl, 19.6. Found: C, 39.9; H, 6.2; N, 7.9; S, 17.7; Cl, 19.7. Yield: 50%.

1,3-Bis(4,5-dimethyl-3-thiazolio)propane dibromide (5, n=3): mp 244-245 °C. Ir (KBr): 3000, 2920, 1650, 1590, 1575, 1440, 910 cm⁻¹. ¹H Nmr (D₂O): δ 9.5 (s, 2H), 4.5 (t, J=6 Hz, 4H), 2.4 (bs, 14H). Ms (EI)(m/z): 268 (M), 266 (M-2), 238, 224 (266-C₃H₆), 205, 179, 154 (C₅H₇NS+C₃H₅), 141, 126 (C₅H₇NS+CH), 113 (C₅H₇NS), 80 (base peak) (C₅H₆N). Anal. Calcd for C₁₃H₂₀N₂S₂Br₂: C, 36.4; H, 4.7; N, 6.5. Found: C, 36.4; H, 4.6; N, 6.5. Yield, 84%.

1,4-Bis(4,5-dimethyl-3-thiazolio)butane dibromide (5, n=4): mp 179-181 °C. Ir(KBr): 3000, 2960, 1590, 1440, 1190, 920 cm⁻¹. ¹H Nmr (CDCl₃/CD₃OD): δ 10.4 (s, 2H), 4.8-4.4 (m, 4H), 2.6 (bs, 12H), 2.4-1.9 (m, 4H). Ms (EI)(m/z): 280 (M-2), 224 (280-C₄H₈), 168 (C₅H₇NS+C₄H₇), 154 (C₅H₇NS+C₃H₅), 141 (M/2), 126 (C₅H₇NS+CH), 113 (base peak) (C₅H₇NS). Anal. Calcd for C₁₄H₂₂N₂S₂Br₂: C, 38.0; H, 5.0; N, 6.3. Found: C, 38.4; H, 4.9; N, 6.4. Yield, 97%.

1,5-Bis(4,5-dimethyl-3-thiazolio)pentane dibromide (5, n=5): mp 269-270 °C. Ir (KBr): 2960, 1590, 1460, 1440 cm⁻¹. ¹H Nmr (D₂O): δ 9.5 (s, 2H), 4.3 (t, J=7 Hz, 4H), 2.4 (bs, 12H), 2.2-1.6 (m, 4H), 1.6-1.1 (m, 2H). Ms (EI)(m/z): 296 (M), 294 (M-2), 224 (294-C₅H₁₀), 168 (C₅H₇NS+C₄H₇), 154 (C₅H₇NS+C₃H₅), 140 (C₅H₇NS+C₂H₃), 126 (C₅H₇NS+CH), 113 (base peak) (C₅H₇NS). Anal. Calcd for C₁₅H₂₄N₂S₂Br₂·1/2H₂O: C, 38.7; H, 5.4; N, 6.0. Found: C, 38.9; H, 5.4; N, 5.9. Yield, 98%.

1,6-Bis(4,5-dimethyl-3-thiazolio)hexane dibromide (5, n=6): mp 190-192 °C. Ir (KBr): 3000, 2940, 1590, 1490, 1400, 1250, 1220 cm⁻¹. ¹H Nmr (CD₃OD): δ 9.7 (s, 2H), 4.5 (t, J=7 Hz, 4H), 2.5 (s, 6H), 2.5 (s, 6H), 2.0 (m, 4H), 1.5 (m, 4H). ¹³C Nmr (D₂O): δ 154.2 (C₂), 143.1 and 134.7 (C₄ and C₅), 54.5 (C₈), 29.6 and 26.0 (C₉ and C₁₀), 12.8 and 11.9 (C₆ and C₇). Ms (EI)(m/z): 310 (M), 258, 224 (M-C₆H₁₄), 196 (C₅H₇NS+C₆H₁₃), 168 (C₅H₇NS+C₄H₇), 154 (C₅H₇NS+C₃H₅), 140 (C₅H₇NS+C₂H₃), 126 (C₅H₇NS+CH), 113 (base peak) (C₅H₇NS). Anal. Calcd for C₁₆H₂₆N₂S₂Br₂: C, 40.9; H, 5.5; N, 6.0. Found: C, 40.7; H, 5.4; N, 5.9. Yield, 84%.

1,7-Bis(4,5-dimethyl-3-thiazolio)heptane dibromide (5, n=7): Ir (KBr): 2940, 2860, 1595, 1485, 1455, 1445 cm⁻¹. ¹H Nmr (D₂O): δ 9.5 (s, 2H), 4.35 (t, J=7 Hz, 4H), 2.4 (bs, 12H), 2.1-1.6 (m, 4H), 1.6-1 (m, 6H). ¹³C Nmr (CD₃OD): δ 156.0 (C₂), 143.7 and 135.1 (C₄ and C₅), 54.8 (C₈), 30.0, 29.1 and 26.6 (C₉, C₁₀ and C₁₁), 12.7 and 11.9 (C₆ and C₇). Highly hygroscopic solid.

1,8-Bis(4,5-dimethyl-3-thiazolio)octane dibromide (5, n=8): mp 192-196 °C. Ir (KBr): 3040, 3000, 2960, 1600, 1460, 1450 cm⁻¹. ¹H Nmr (D₂O): δ 9.5 (s, 2H), 4.4 (t, J=7 Hz, 4H), 2.4 (bs, 12H), 2.2-1.5 (m, 4H), 1.5 (m, 8H). Ms (EI)(m/z): 340 (base peak) (M+2), 286, 224 (C₅H₇NS+C₈H₁₅), 182 (C₅H₇NS+C₆H₉), 168 (C₅H₇NS+C₄H₇), 154 (C₅H₇NS+C₃H₅), 140 (C₅H₇NS+C₂H₃), 126 (C₅H₇NS+CH), 113 (C₅H₇NS). Anal. Calcd for C₁₈H₃₀N₂S₂Br₂: C, 43.4; H, 6.0; N, 5.6. Found: C, 43.6; H, 6.1; N, 5.6. Hygroscopic solid. Yield, 96%.

1,3-Bis(3-benzothiazolio)propane dibromide (6, n=3): mp 236-238 °C. Ir (KBr): 3090, 3010, 1640, 1590, 1470, 1440, 790 cm⁻¹. ¹H Nmr (CDCl₃/CD₃OD): δ 11.2 (s, 2H), 9-7.7 (m, 8H), 5.6-5.3 (m, 4H), 3.2-2.9 (m, 2H). Ms (EI)(m/z): 312 (M), 310 (M-2), 281 (M-S+H), 269 (M-C₃H₄), 176 (C₇H₅NS+C₃H₅), 162 (C₇H₅NS+C₂H₃), 155 (M/2 -H), 149, 136 (C₇H₆NS), 121 (C₇H₅S), 108 (C₆H₄S). Anal. Calcd for C₁₇H₁₆N₂S₂Br₂·2/3H₂O: C, 42.1; H, 3.6; N, 5.8. Found: C, 41.8; H, 3.5; N, 5.6. Yield, 36%.

1,4-Bis(3-benzothiazolio)butane dibromide (6, n=4): mp 237-238 °C. Ir(KBr): 3090, 3010, 2960, 1590, 1440, 780 cm⁻¹. ¹H RMN (CDCl₃/CD₃OD): δ 10.8 (s, 2H), 8.5-7.4 (m, 8H), 5.2-4.8 (m, 4H), 2.5-2.1 (m, 4H). Ms (EI)(m/z): 326 (M), 324 (M-2), 268 (324-C₄H₈), 190 (C₇H₅NS+C₄H₇), 176 (C₇H₅NS+C₃H₅), 162 (C₇H₅NS+C₂H₃), 149, 135 (C₇H₆NS), 109 (C₆H₅S). Anal. Calcd for: C₁₈H₁₈N₂S₂Br₂·2H₂O: C, 41.4; H, 4.1; N, 5.3. Found: C, 41.4; H, 4.2; N, 5.4. Yield, 95%.

1,5-Bis(3-benzothiazolio)pentane dibromide (6, n=5): mp 217 °C. Ir (KBr): 3085, 1630, 1580, 1500, 1460, 1430, 1120, 765 cm⁻¹. ¹H Nmr (CDCl₃/CD₃OD): δ 11.1 (s, 2H), 8.5-7.5 (m, 8H), 5.0 (bt, J=6 Hz, 4H), 2.5-1.4 (dm, 6H). Ms (EI)(m/z): 342 (M+2), 340 (M), 338 (M-2), 281, 268 (338-C₅H₁₀), 204 (C₇H₅NS+C₅H₉), 190 (C₇H₅NS+C₄H₇), 176 (C₇H₅NS+C₃H₅), 170 (M/2), 162 (C₇H₅NS+C₂H₃), 150 (C₈H₈NS), 136 (C₇H₆NS), 109 (C₆H₅S). Anal. Calcd for: C₁₉H₂₀N₂S₂Br₂·3/2H₂O: C, 43.3; H, 4.4; N, 5.3. Found: C, 43.4; H, 4.2; N, 5.2. Yield, 54%.

1,6-Bis(3-benzothiazolio)hexane dibromide (6, n=6): mp 229-230 °C. Ir (KBr): 3090, 3010, 2950, 1590, 1450, 1400, 1320, 760 cm⁻¹. ¹H Nmr (CD₃OD): δ 10.8 (s, 2H), 8.6-8.5 + 8.1-7.9 (m, 8H), 5.0 (t J=7 Hz, 4H), 2.2 (m, 4H), 1.7 (m, 4H). ¹³C Nmr (CD₃OD): δ 164.2 (C₂), 141.7, 132.9, 131.3, 130.1, 126.1 and 119.3 (C₄, C₅, C₆, C₇, C₈ and C₉), 54.2 (C₁₀), 29.7 and 26.7 (C₁₁ and C₁₂). Ms (EI)(m/z): 356 (M+2), 352 (M-2), 268 (base peak) (352-C₆H₁₂), 219 (M-C₇H₅NS), 204 (C₇H₅NS+C₅H₉), 190 (C₇H₅NS+C₄H₇), 177 (M/2), 176 (C₇H₅NS+C₃H₅), 162 (C₇H₅NS+C₂H₃), 150 (C₈H₈NS), 136 (C₇H₆NS), 109 (C₆H₅S). Anal. Calcd for C₂₀H₂₂N₂S₂Br₂: C, 46.7; H, 4.3; N, 5.4. Found: C, 46.5; H, 4.2; N, 5.6. Yield, 79%.

1,7-Bis(3-benzothiazolio)heptane dibromide (6, n=7): mp 141-143 °C. Ir (KBr): 3060, 3000, 2930, 1580, 1510, 1460, 1430, 770, 760 cm⁻¹. ¹H Nmr (D₂O): δ 10.1 (s, 2H), 8.4-7.5 (m, 8H), 5.7 (t, J=7 Hz, 4H), 2.2-1.6 (m, 4H), 1.5-1 (m, 6H). ¹³C Nmr (CDCl₃): δ 163.7 (C₂), 140.6, 131.7, 130.9, 129.7, 125.4 and 117.5 (C₄, C₅, C₆, C₇, C₈ and C₉), 53.5 (C₁₀), 28.9, 27.7 and 25.6 (C₁₁, C₁₂, and C₁₃). Ms (EI)(m/z): 370 (M+2), 366 (M-2), 268 (366-C₇H₁₄), 234 (M-C₇H₄NS), 218 (C₇H₅NS+C₆H₁₁), 204 (C₇H₅NS+C₅H₉), 190

(C₇H₅NS+C₄H₇), 176 (C₇H₅NS+C₃H₅), 162 (C₇H₅NS+C₂H₃), 150 (base peak) (C₈H₈NS), 136 (C₇H₆NS), 109 (C₆H₅S). Anal. Calcd for C₂₁H₂₄N₂S₂Br₂·3/2H₂O: C, 45.4; H, 4.9; N, 5.0. Found: C, 45.4; H, 4.2; N, 5.4. Yield, 98%.

1,8-Bis(3-benzothiazolio)octane dibromide (6, n=8): mp 256-257 °C. Ir (KBr): 3100, 3080, 2970, 2950, 1600, 1450, 1230, 790, 770 cm⁻¹. ¹H Nmr (D₂O): δ 10.1 (s, 2H), 8.3-7.5 (m, 8H), 4.6 (t, J=7Hz, 4H), 2-1.5 (m, 4H), 1.3-0.9 (m, 8H). Ms (EI)(m/z): 384 (M+2), 268 [(M-2)-C₈H₁₆], 246 (C₇H₅NS+C₈H₁₅), 233 (C₇H₅NS+C₇H₁₄), 219 (C₇H₅NS+C₆H₁₂), 204 (C₇H₅NS+C₅H₉), 190 (C₇H₅NS+C₄H₇), 176 (C₇H₅NS+C₃H₅), 163 (C₇H₅NS+C₂H₄), 150 (base peak) (C₈H₈NS), 136 (C₇H₆NS), 109 (C₆H₅S). Anal. Calcd for C₂₂H₂₆N₂S₂Br₂: C, 48.7; H, 4.8; N, 5.2. Found: C, 48.3; H, 4.4; N, 5.4. Yield, 97%.

Preparation and characterization of N,N'-polymethylenebis(thiazolin-2-ylidene)s (5bis) and (6bis).

General procedure.¹⁴ A solution of thiazolium or benzothiazolium salt (3.5 mmol) in methanol (10 ml) was passed through a 2.7x43 cm chromatographic column filled with Amberlite IRA-401 anionic exchange resin (OH⁻ form), thermostated at 0 °C, and previously washed with methanol up to neutral pH. The eluted was collected at 0 °C over 3 Å molecular sieves under an inert atmosphere until the eluate was colorless. The methanolic solution was evaporated under a nitrogen atmosphere at high vacuum and low temperature and the oily residue was used directly.

Ms (EI) (m/z): the mass spectrum of **5bis** and **6bis** were registered from the methanolic solution and the observed pattern was always the same. **5bis**: (M+1), 224, corresponding to the bis(thiazolin-2-ylidene) system unsubstituted at the nitrogen atoms, with a relative intensity of 1/3 of the analogous peak observed in the ms of the salts, and a series of unspecific peaks due to the fragmentation of the heterocyclic system. **6bis**: (M+1), 268, corresponding to the bis(benzothiazolin-2-ylidene) system, and a different series of non specific peaks from the heterocyclic system.

Benzoin condensations

Working conditions were those given in the Table caption: all experiments were conducted in anhydrous dioxane and an argon atmosphere at 100 °C during 24 h. The glc benzoin quantification of each experiment was realized from an aliquot taken after 24 h of reaction. A Hewlett-Packard 5890 chromatograph fitted with a Hewlett-Packard 19091/102 high-performance capillary cross-linked column, 5% phenylmethylsilicone, 25 m, 0.2 mm internal diameter and connected to a Hewlett-Packard 3390A integrator was used. A temperature program of 90 °C for 2 min and then 16 °C/min up to 300 °C and decanol as internal standard were employed.

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