Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Nadezhda Martemyanova , Yuriy Chunaev , Nina Przhiyalgovskaya , Lidiya Kurkovskaya , Raisa Ambartsumova , Olga Filipenko & Sergey Aldoshin (1994): Interaction of 2-Imino-3-Methylbenzothiazoline With Salicylic Aldehydes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 45-48

To link to this article: http://dx.doi.org/10.1080/10587259408037786

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 45–48
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Printed in the United States of America

INTERACTION OF 2-IMINO-3-METHYLBENZOTHIAZOLINE WITH SALICYLIC ALDEHYDES

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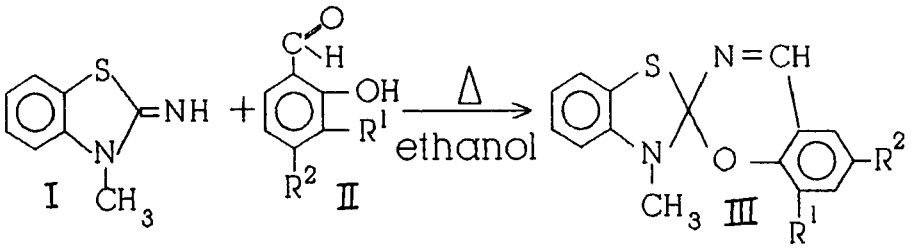
Abstract *Non* spiro-1,3-oxazines, but bisbenzothiazoline derivatives formation during condensing process of 2-imino-3-methylbenzothiazoline with salicylic aldehydes was found by ^{1}H NMR and X-ray structure investigation analyses.

Heterocyclic spiro-1,3-oxazines are scantily known class of substances, although they would display photochromic properties similar to their 1,4-isomers[1]. We have found only one report confirming that spiro-1,3-oxazines of benzothiazoline species III prepared by 2-imino-3-methylbenzothiazoline (I) with various salicylic aldehydes (IIa-e) condensation exhibit thermochromic properties[2] (Figure 1).

In our previous investigation[3] the attempt to synthesize spiro-1,3-oxazines in a similar manner on the basis of 2-imino-3,5-dimethylthiazolidine was made, but instead of expected products we have isolated bisthiazolidine derivatives of structure IV in pure form which are not susceptible to spirocyclization and therefore posess no photochromic properties (Figure 2).
This failure stimulated us to reproduce the experiments[2] for to investigate whether spiro-1,3-oxazines III show photochromic properties. The interaction between imine I and aldehydes IIb and IIc gave the products which have melting points (m.p.) coinciding with m.p.'s published in the patent[2], but our following studies did not confirm their spiro-1,3-oxazine structure III. ^{1}H NMR spectra of these products seemed to be very like to the spectra of



a $R^1=R^2=H$; b $R^1=H, R^2=NO_2$; c $R^1=R^2=Br$;
d $R^1=CHO, R^2=NO_2$; e $R^1=OCH_3, R^2=NO_2$.

FIGURE 1.

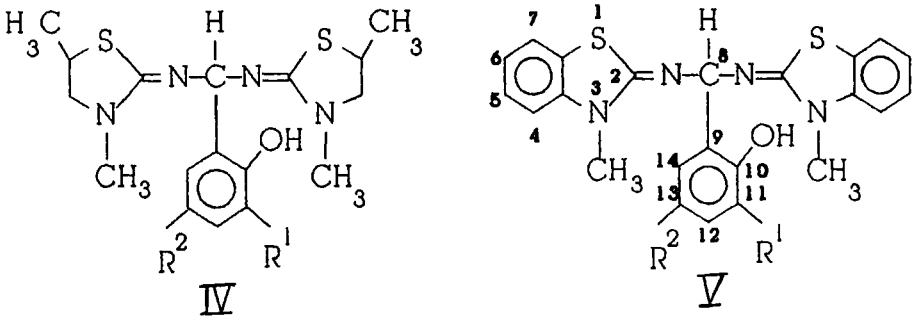


FIGURE 2.

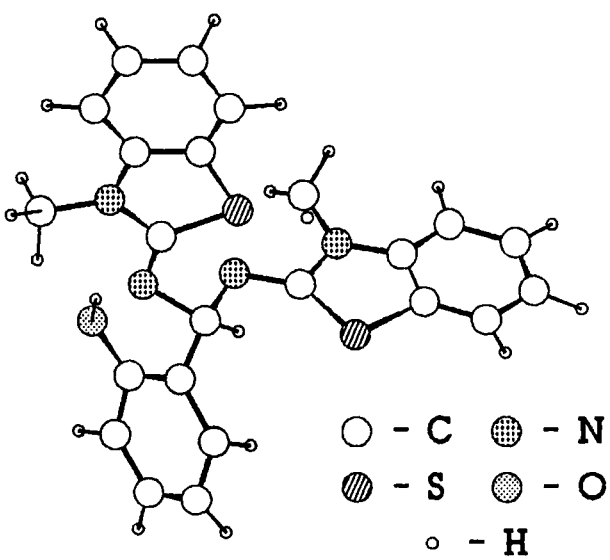


FIGURE 3. X-ray structure of Va

TABLE 1. Characteristics of bisbenzothiazoline compounds V.

Compound	Melting point, °C	^{1}H NMR spectra** N-CH_3	8-H	11-H	12-H	13-H	14-H	OH...N	Yield, %
Va*	141–143 155–159[2]	3.51	5.57	~6.9	~7.2	~6.8	~7.2	10.4	60
Va	178–180 155–159[2]	3.43	5.54	~6.9	~7.2	~6.8	~7.2	10.4	30
Vb	193–194 192–194[2]	3.53	5.61	–	7.55	–	7.38	11.7	57
Vc	194–196 195–198[2]	3.54	5.73	6.93	8.09	–	8.27	11.9	55

*ethanol signals present (0.5 mole per mole of Va);
**signals of protons 4-7 are about 7.0-7.4 ppm.

symmetric bisthiazolidine derivatives of species IV: besides of single intensity proton signal in sp^3-mezo-CH group and broadening downfield signal of OH group, these spectra contained proton signals of heterocyclic ring and N-CH_3 group of doubled intensity. It shows that spiro-1,3-oxazines IIIb and IIIc described in patent[2] are indeed bis(3-methylbenzothiazoline-2-ylidenamino)--2-hydroxyphenylmethanes corresponding to the structure Vb and Vc.

The product prepared in the reaction of imine I with unsubstituted salicylic aldehyde (IIa) has the same structure Va, but in this case the m.p.'s of the product and the similar ones described in patent[2] were not coinciding. Moreover, we have isolated two types of crystals from the reaction mixture: colourless product with lower m.p. 141-143°C and lilac coloured product with higher m.p. 178-180°.

^{1}H NMR spectra of these compounds are very similar (Table 1). The only spectral difference was that colourless crystals spectrum includes signals of ethanol solvent in which the reaction was carried out (0.5 mole per mole bisbenzothiazoline compound in accordance with integral curve).

The X-ray structure investigation analysis of the compound Va crystal gave us convincing arguments confirming the bisbenzothiazoline structure V for synthesized products Va,b,c (Figure 3).

The Va, Vb and Vc compounds have no photochromic properties, but change their colour while heating.

The results of this study as well as results obtained previously[3] show that spiro-1,3-oxazines are not formed in the condensation process of heterocyclic imines with salicylic aldehydes.

EXPERIMENTAL

^{1}H NMR spectra were recorded using a Bruker WP 200 SY spectrometer; chemical chifts are reported in ppm downfield from internal TMS in $CDCl_3$ solutions.

X-ray determination of Va structure

Crystallographic data were obtained with automatic fourcircle diffractometer KM-4 equipped with a graphite monochromator (Mo K_α = 0.7109 A). Scan type $\theta/2\theta$. θ limits: 12 deg.

Crystallographic system: monoclinic. Space group C 2/c, a=34.621(7); b=10.500(3); c=11.510(5)Å; β=90.30(5)°. V=4184.09 Å^3, Z=8 $C_{23}H_{20}N_4OS_2$, d=1.373 g/cm^3. Crystal dimensions (mm): 0.03*0.02*0.5.

The structure was determined by direct method according to program SHELXS-86[4].

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