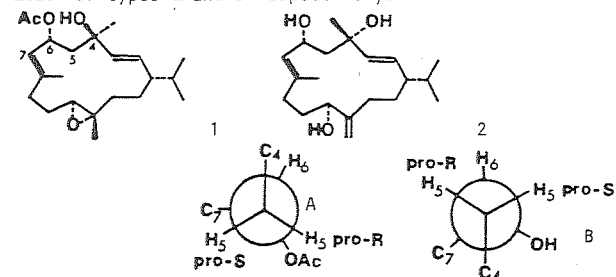


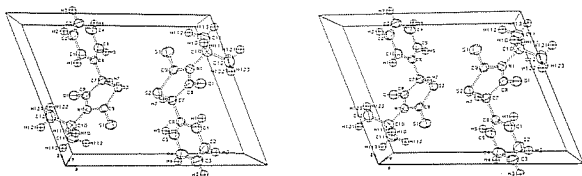
## 09.2-33 CONFORMATIONAL STUDIES ON SOME TOBACCO CEMBRANOIDS

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Results from X-ray diffraction determination have shown that (1S,2E,4R,6R,7E,11S,12S)-11,12-epoxy-6-acetoxy-2,7-cembradien-4-ol (1) and (1S,2E,4S,6R,7E,11S)-2,7,12(20)-cembratriene-4,6,11-triol (2) exist as conformers A and B about the 5,6-bond. An analysis of the <sup>1</sup>H and <sup>13</sup>C NMR spectra suggests that these conformations are retained in solution and that other cembranoid alcohols or acetates are conformationally reminiscent of either 1 or 2. We have now carried out molecular mechanics (MM2) calculations using X-ray data of 1 and 2 as inputs. These show that for each compound, the geometry at the local energy minimum is close to that existing in the crystalline state. Further calculations using the dihedral driver of MM2 varying the 4,5,6,7 dihedral angle indicate that both 1 and 2 have two local energy minima occupied by conformers of types A and B respectively.

09.2-34 STRUCTURE OF 3-ISOPROPYL-5-PHENYL-THIAZOLIDIN-4-ONE-2-THIONE. By Q.B. Yang<sup>a</sup> and L. Thell, Department of Inorganic Chemistry 2, and J. Sandström, Department of Organic Chemistry 3, Chemical Center, University of Lund, P.O. Box 740, S-220 07 Lund, Sweden.

3-Isopropyl-5-phenyl-thiazolidin-4-one-2-thione (C<sub>12</sub>H<sub>13</sub>NOS<sub>2</sub>) crystallizes in the monoclinic space group P2<sub>1</sub> with a = 12.273(30) Å, b = 5.425(8) Å, c = 9.888(17) Å, β = 111.40(2)°, V = 613.0 Å<sup>3</sup>, D<sub>0</sub> = 1.34 g/cm<sup>3</sup>, D<sub>c</sub> = 1.36 g/cm<sup>3</sup>, Z = 2 obtained by refining of 28 single indexed Guinier powder photography lines. The intensities of 1219 reflections were collected by a Nicolet P3m X-ray diffractometer and the structure was refined to final R = 0.022 and R<sub>w</sub> = 0.025. There are two rings located in two planes respectively. They are C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub>, C<sub>6</sub> and C<sub>7</sub>, C<sub>8</sub>, N<sub>1</sub>, C<sub>9</sub>, S<sub>2</sub>. The angle between these rings is 86 degrees. The structure is shown by a stereoscopic view as follows:

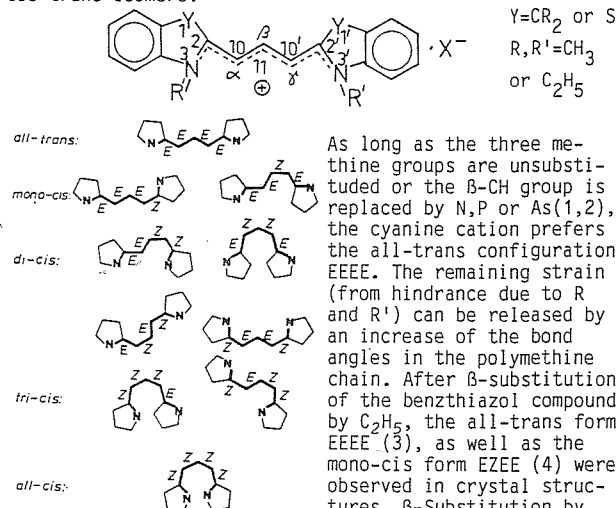


Bond lengths and angles in the thiazolidinone-thione part agree well with recent data for 5-methyl-thiazolidin-2-one-4-thione (Gattow et al., Z. anorg. Allg. Chem. 506 (1983) 145). The orientation of the 3-isopropyl group is as expected from steric considerations.

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## 09.2-35 CIS-TRANS-ISOMERISM OF TRIMETHINE (OR CARBO-) CYANINE DYES INDUCED BY STERIC HINDRANCE. By R. Allmann, Institut für Mineralogie der Philipps-Universität, Lahnberge, D-3550 Marburg, FRG

Symmetrical trimethinecyanine dyes allow 10 different cis-trans isomers:



As long as the three methine groups are unsubstituted or the β-CH group is replaced by N, P or As(1,2), the cyanine cation prefers the all-trans configuration EEEE. The remaining strain (from hindrance due to R and R') can be released by an increase of the bond angles in the polymethine chain. After β-substitution of the benzthiazol compound by C<sub>2</sub>H<sub>5</sub>, the all-trans form EEEE (3), as well as the mono-cis form EZEE (4) were observed in crystal structures. β-Substitution by

CH<sub>3</sub> yields the same two conformations, as deduced by <sup>1</sup>H-NMR spectra (5, Y=S) but for the indoline-compound a tri-cis form ZEEZ was found in crystals and was confirmed by <sup>1</sup>H-NMR too (6).

An γ-substitution by CH<sub>3</sub> (Y=CR<sub>2</sub>) has little influence and keeps EEEE (7). But α,γ-disubstitution by CH<sub>3</sub> yields an ZEEE isomer (7), which still is nearly planar. β-Substitution of bulky t-butyl groups leads to screw-like compounds far from planarity: all-cis for Y=CR<sub>2</sub> and EZEE for Y=S (6). Phenyl in β-position has less effect: ZEEZ for indoline end groups as deduced by <sup>1</sup>H-NMR and all-trans for Y=S in a crystal structure (8) and EZEE besides EEEE in solution (5). So by now, 6 of the 10 possible isomers are proved to exist.

The following table gives for several above mentioned compounds the four central torsion angles and the dihedral angle φ (in°) between both indoline or benzthiazol end groups.

Y substit.	X <sup>-</sup>	torsion angles				φ	R(%)	Lit	
		2-10	10-11	11-10	10'-2'				
CR <sub>2</sub>	none	C10 <sub>d</sub>	179.0	174.8	-179.2	176.6	13.8	9.8	1
CR <sub>2</sub>	γ-CH <sub>3</sub>	BF <sub>4</sub>	-178.0	-175.7	179.9	-160.5	32.0	5.6	7
CR <sub>2</sub>	γ-CH <sub>3</sub>	I	178.7	-175.6	-178.2	-159.5	30.7	4.4	7
S	β-C <sub>6</sub> H <sub>5</sub>	I	179.0	172.2	-178.3	176.7	15.7	5.1	8
S	β-C <sub>2</sub> H <sub>5</sub>	C10 <sub>d</sub>	-179.8	11.9	-174.1	-174.3	25.7	6.5	4
CR <sub>2</sub>	α, γ-CH <sub>3</sub>	BF <sub>4</sub>	39.6	16.9	-168.4	163.9	37.4	5.7	7
S	β-t but.	BF <sub>4</sub>	175.5	-12.3	-62.9	178.0	83.4	7.3	6
CR <sub>2</sub>	β-CH <sub>3</sub>	BF <sub>4</sub>	33.5	175.8	25.0	24.7	78.0	8.1	6
CR <sub>2</sub>	β-t-but	BF <sub>4</sub>	21	20	10	19	41	7.6	6

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