J. Guzman

Instituto de Plásticos y Caucho, Juan de la Cierva, 3, Madrid-6, Spain

and

J. Largo-Cabrerizo

Departamento de Investigaciones Químicas, C.S.I.C. Facultad de Ciencias, Valladolid, Spain

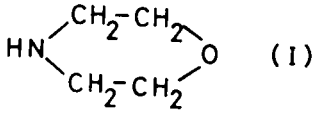
Received June 26, 1978

The existence of two conformational isomers (A and B) with different crystal structures in 2-(4-morpholinothio)benzothiazole is shown. The melting temperatures of the two conformers are 345° and 357° K, respectively. The difference between the values of the melting enthalpies and entropies gives an indication of the two isomers flexibility whose proportion depends on the thermal history of the sample.

J. Heterocyclic Chem., 15, 1531 (1978)

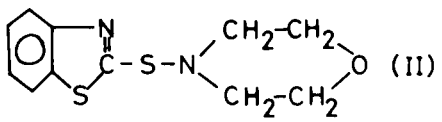
The behaviour of six-membered saturated heterocycles containing C-N-C and/or C-O-C- groups is similar to that of cyclohexane with respect to the adoption of different molecular conformations (1). As it is well known, cyclohexane molecule is non-planar, although its bond angles are not strained. There are two possible conformations for which that condition is fulfilled, *chair* and *boat*, this one being more flexible while the former is the preferred molecular conformation.

When we have substituted cycles or heterocycles, the substituents can be linked to the ring along axial or equatorial bonds, so giving rise to different conformations. Having this in mind, it is hardly strange that the derivatives of the morpholine (I) could be present in different conformations, that, of course, will show different physical and chemical properties.



(I)

The aim of this note is to report some findings which account for the existence of two different conformers (conformational isomers), with crystal structures obviously different, of the 2-(4-morpholinothio)benzothiazole (MT BT) (II).



(II)

The curves in Figure 1 were obtained by differential scanning calorimetry of two specimens of MT BT, one of them crystallized directly from a liquid sample, and the other obtained through lyophilization of a diluted solution in benzene. In both cases two distinct melting picks appear at 339° and 350° K. These are the actual temperatures given by the calorimeter, but the use of the corresponding calibration curves shows that they correspond to 345° and 357° K, respectively, in real temperatures. Their corresponding melting surfaces (areas enclosed) are very different as a consequence of the quite

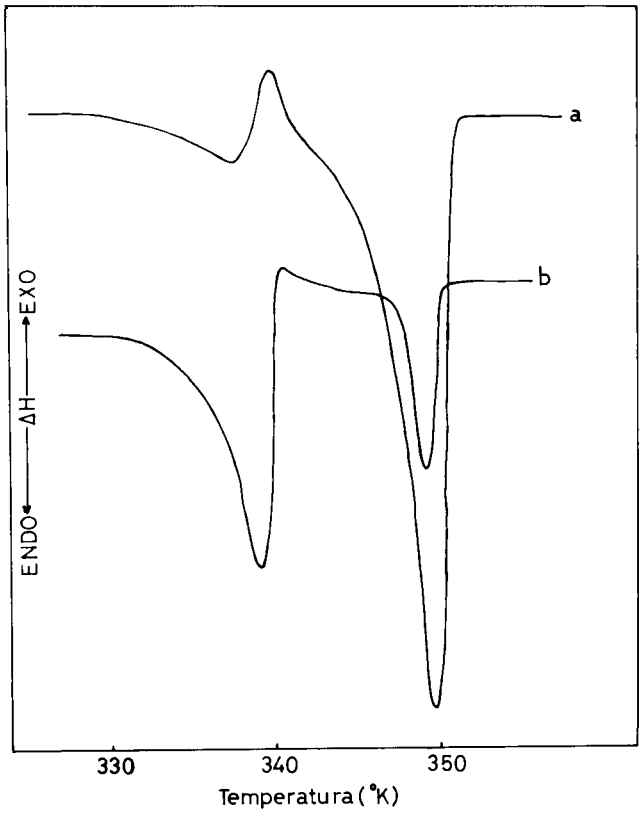


Figure 1. DSC curves for two samples of MT BT obtained: (a) By solidification of the melt; (b) By lyophilization of a diluted solution.

different treatment each sample underwent. As the lyophilization implies a sudden cooling, it favors the formation of the crystal structure with lower melting point, that being shown in Figure 1 by the relative increase of the area enclosed in the first peak.

The polimorphic form obtained is a result of the crystallization conditions and depends heavily on kinetic factors. Changes in pressure, temperature, cooling rate, *etc.*, can affect the conversion of one crystal structure into another (2). The interconversion can take place by

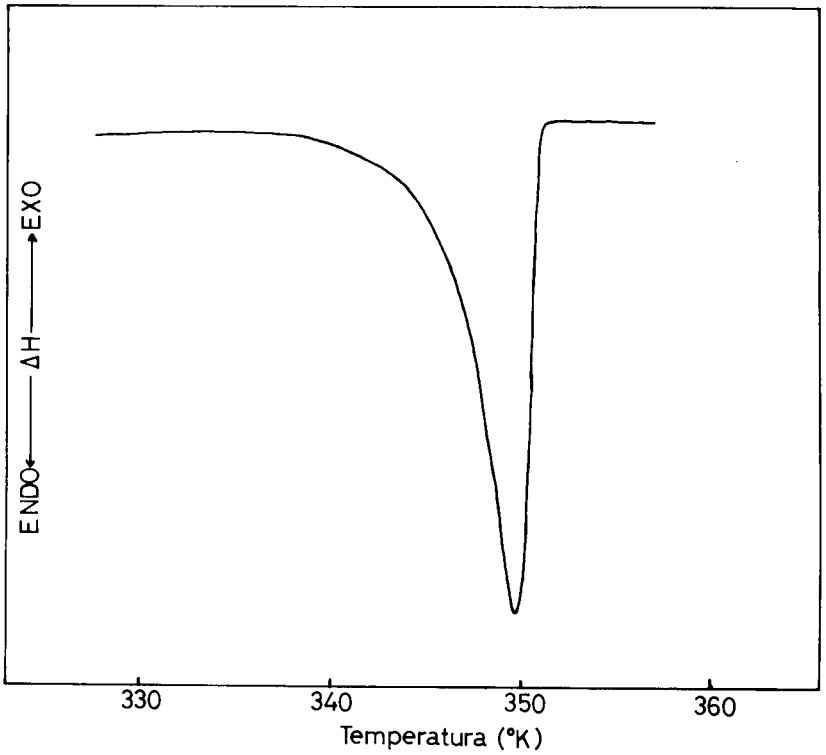


Figure 2. DSC curve for a sample of MT BT obtained by crystallization at 345° K for 12-15 hours.

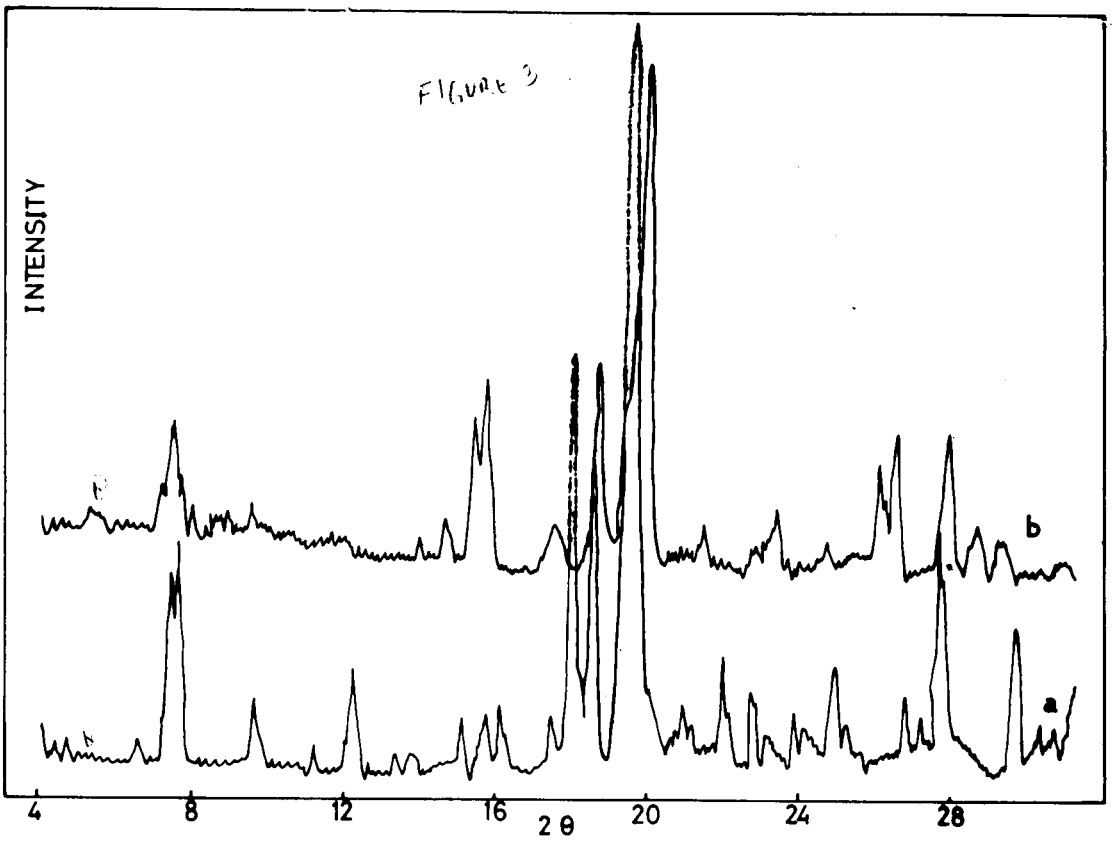


Figure 3. X-Ray diffraction patterns for the two samples of MT BT referred to in Figure 1.

direct conversion or can be produced by melting of one polymorphic species followed by recrystallization of the other from the melt.

In order to prove the existence of two conformers of MT BT and that, at the same time, they are interconvertible, the lyophilized sample was heated up to 345° K (melting temperature of first isomer) and then was maintained at this temperature for 12-15 hours. The DSC curve for the specimen so obtained is given in Figure 2, clearly indicating that practically all of the substance that initially was in the crystal form of lower melting temperature has been converted into the crystal form of higher melting temperature. The crystallization is favored by the presence of the solid part at that temperature. Conversely, if the initial sample is heated up to a temperature slightly higher than 357° K (the melting point of the second isomer) and then quickly cooled to around 300° K, only the first crystal structure is obtained.

Five determinations were made to evaluate, from the DSC curves, the melting enthalpies and entropies corresponding to both conformers; the results are given in Table I.

Table I

Thermal Properties of MT BT

Conformer	Melting Temp. °K	Melt Enthalpy Kcal/mole	Melt Entropy Cal/mole K
A	345	3.1 ± 0.1	9.0 ± 0.3
B	357	4.3 ± 0.1	12.0 ± 0.3

The order of magnitude for both the enthalpies and entropies lies in the typical range for organic compounds, but it is interesting to note the relatively high difference between the values of such quantities for the two conformers, which gives a clear indication of the different rigidity and flexibility they have.

X-Ray diffraction provides additional proof of the fact that both crystal structures appear in different proportions whether the sample is obtained by cooling the melt or by lyophilization of a solution, as it is clearly seen when looking at the corresponding patterns shown in Figure 3.

In conclusion, it can be said that the MT BT shows conformational isomerism, and its melting temperature depends on the thermal history of the sample. The melting temperature usually given in the literature is 357° K, but as indicated before, this is the melting temperature for the particular conformer we have called B. The MT BT is an important industrial product and is used as an accelerating reagent in vulcanization process. For that reason, it is very convenient to obtain the product with a quite well defined melting temperature, that corresponding to conformer B seeming more appropriate. We think the results reported here could be very useful to that goal.

EXPERIMENTAL

Melting temperatures, enthalpies and entropies were measured with a differential calorimeter Perkin Elmer DSC-1 1B. The instrument was calibrated with several standard substances whose melting temperatures are well known, and use was made of the melting enthalpy for Indium.

The X-ray diffraction patterns were recorded with a Geiger-counter X-ray diffractometer from Philips Co. using monochromatic radiation Cu/Kα and with the angle 2 θ ranging from 4 to 32 degrees.

REFERENCES AND NOTES

(1) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N. Y., 1962.

(2) L. Mandelkern, "Crystallization of Polymer", McGraw-Hill, New York, N. Y., 1964.