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THERMAL STUDIES ON N-SUBSTITUTED MALEIC ACID AMIDES

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Eight N–substituted maleic acid monoamide derivatives were studied by DSC, TG (DTG) and IR techniques. The thermal studies revealed that the compounds containing a free carboxyl group start to decompose before melting, and the decomposition continues in the melt phase as the temperature is elevated. This was explained by the presence of dimers involving strong intermolecular hydrogen-bonds. This assumption concerning the structure was supported by the results of the IR spectroscopic studies.

N–Substituted maleic acid amides prepared from maleic anhydride are important intermediates in the production of biologically active compounds obtained mostly in cyclization reactions. Hence, it is important to know the physical, chemical and thermal behaviour of these compounds. It may be presumed that both in the solid state and in solution (depending on the solvent) hydrogen-bonding may lead to the formation of associates. Eight different N–substituted maleic acid amides were investigated in order to test the above assumption, and to find out what kind of associates are present. Inverse gas chromatography [1], thermal analysis and IR spectrometry were used to study the compounds. The present paper briefly reports the results obtained with the latter two methods.

Experimental

DSC was used to follow phase transitions, and TG and DTG served to study the decomposition processes. DSC measurements were carried out with a DuPont M–900 instrument, in argon atmosphere, using 5 mg samples and a heating rate of 10 deg/min.

Thermogravimetric measurements were made with a DuPont M–951 instrument, using an argon stream at 15 dm^3/h. The sample weight was about 5 mg, and the heating rate was 10 deg/min. Thermal studies were supplemented by visual observation of the behaviour of samples on heating under a microscope.

IR spectra were taken with a Zeiss (Jena) UR–10 instrument in the range 1800-4000 cm^{-1}.

Solid samples were prepared as KBr pellets with a sample to KBr ratio of 1 : 300. Solution studies were made at concentrations of 0.004 mol/dm^3 and 0.002 mol/dm^3 in DMSO.

Results and conclusion

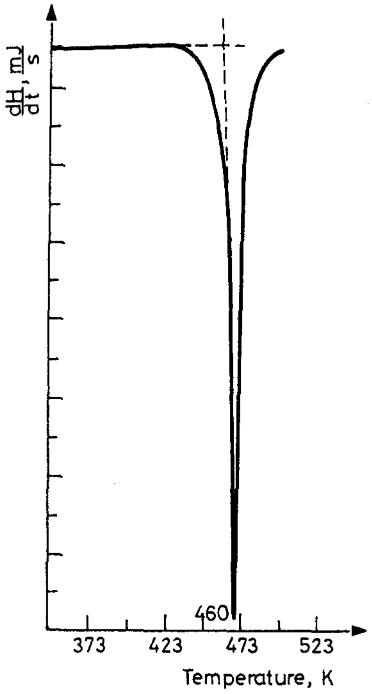

Fig. 1 DSC diagram of N–(4–chlorophenyl)maleic acid monoamide

Melting point data and heats of melting calculated from the DSC results for the eight maleic acid amide derivatives are listed in Table 1, and data (temperatures of onset and maximum rate of decomposition) determined from TG and DTG curves in Table 2. The observations under the microscope showed that, with the exception of the N–carbamoylmaleic acid monoamide methyl ester, the decomposition starts before the crystalline particles melt. The decomposition continues in the melt phase, at an increased rate. As an example, the DSC curve and the TG and DTG curves of N–(4–chlorophenyl)maleic acid monoamide are shown in Figs 1 and 2, respectively. The other derivatives decompose quantitatively in a single step. A marked difference is observed in the behaviour of N–carbamoylmaleic acid monoamide methyl ester: as expected, this first melts at 360 K, and decomposition starts above this temperature. From this, it can be concluded that the intermolecular hydrogen-bonding assumed to exist in the solid phase is weaker in this compound than in the other samples also containing a free carboxyl group; hence, it melts before decomposing. The observation

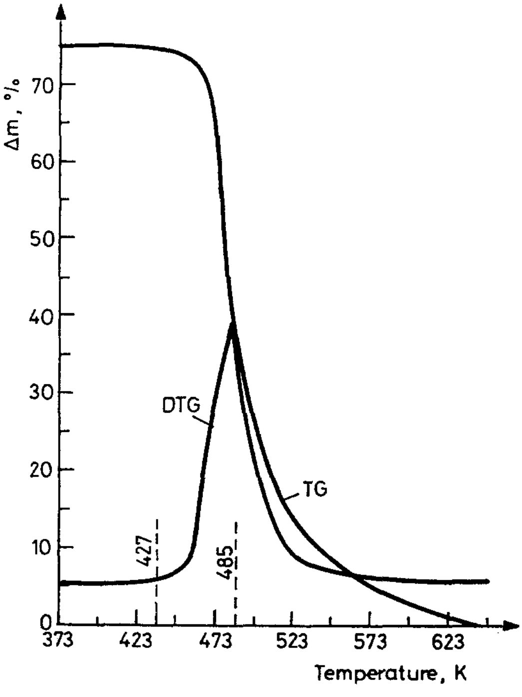

Fig. 2 Simultaneous TG, DTG curves of N–(4–chlorophenyl)maleic acid monoamide

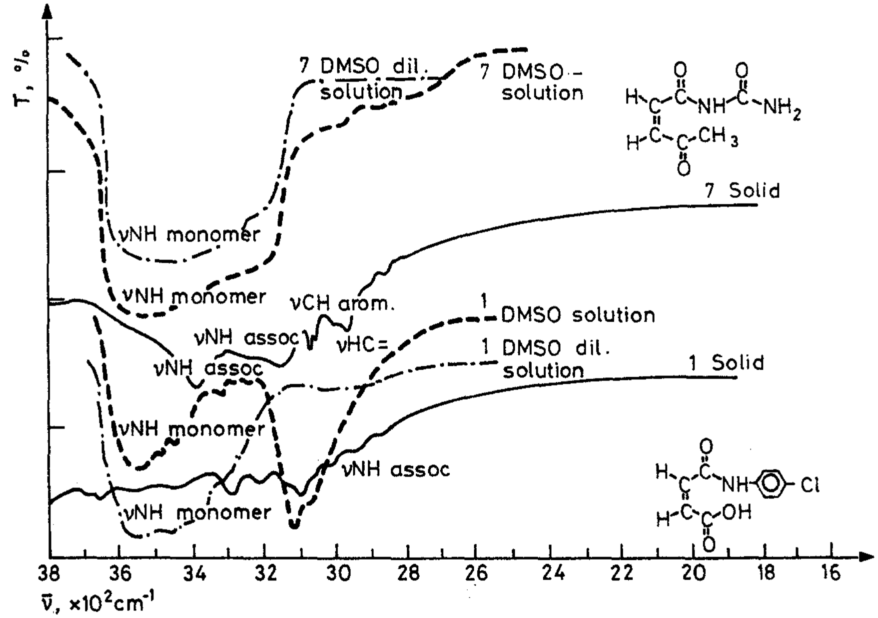

Fig. 3 IR spectra of N-(4-chlorophenyl)maleic acid monoamide (1), and N-carbamoylmaleic acid monoamide methyl ester (7)

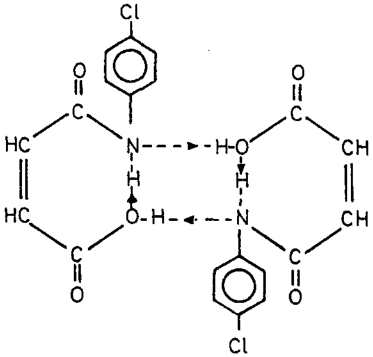

Fig. 4 Dimeric structure of N-(4-chlorophenyl)maleic acid monoamide

that the other derivatives studied start to decompose before melting begins can be explained only by assuming the predominance of intermolecular interactions. IR studies seem to justify this assumption. As examples, IR spectral details are shown in Fig. 3 for N-(4-chlorophenyl)maleic acid monoamide (1) and N-carbamoylmaleic acid monoamide methyl ester (7). Solid lines (—) denote the spectra of solid samples, dashed lines (– –)

those of 0.004 mol/dm^3 solutions, and dot-dash lines (.–.–.) those of 0.002 mol/dm^3 solutions in DMSO.

In the spectra of the solid samples, the bands at 3100 and 3400 cm^{-1}, assigned as NH stretching vibrations, indicate the presence of associates and suggest the existence of dimers [2, 3]. It is clear that in solutions of equal concentration the dimer is more stable for the compound containing a free carboxyl group. The assumed dimeric structure is shown in Fig. 4. A similar N–H–O hydrogen-bonded structure may be assumed for the other compounds.

Table 1 DSC analysis of N–substituted maleic acid amides

No.	Sample	Sample weight, mg	*ΔH* melt., kJ/mol	Melting point, K
1.	N–(4–chlorophenyl)maleic acid monoamide	5.30	1.08	460
2.	N–(4–thiophenyl)maleic acid monoamide	3.90	1.16	431
3.	N–(4–methoxyphenyl)maleic acid monoamide	5.08	1.27	459
4.	N–(2–nitrophenyl)maleic acid monoamide	5.24	0.45	384
5.	N–(2–methylphenyl)maleic acid monoamide	4.66	0.69	388
6.	N–(2–amino–1, 3, 5,–trioxyl)maleic acid monoamide	5.23	0.46	433
7.	N–carbamoylmaleic acid methyl ester	4.97	0.68	360
8.	N–(4–nitrophenyl)maleic acid diamide	4.15	0.59	403

Table 2 TG (DTG) data of N–substituted maleic acid amides

No.	Sample	Sample weight, mg	Onset of ther. decomp., K	Thermal decomp., K
1.	N–(4–chlorophenyl)maleic acid monoamide	5.88	427	485
2.	N–(4–thiophenyl)maleic acid monoamide	5.04	398	431
3.	N–(4–methoxyphenyl)maleic acid monoamide	5.65	433	481
4.	N–(2–nitrophenyl)maleic acid monoamide	5.86	358	452
5.	N–(2–methylphenyl)maleic acid monoamide	5.48	353	416
6.	N–(2–amino–1, 3, 5,–trioxyl)maleic acid monoamide	5.83	398	513
7.	N–carbamoylmaleic acid methyl ester	5.82	383	449
8.	N–(4–nitrophenyl)–maleic acid diamide	5.55	403	476

References

1 T. Halasi, Master thesis, Novy Sad, Yu., 1989.
2 K. E. Kissne, Az infravörös spektroszkópia analitikai alkalmazása, Müszaki Könyvkiadó, Budapest 1974, p. 210.
3 D. Dolphin and A. Wick, Tabulation of infrared spectral data, J. Wiley and Sons, Vancouver 1977., pp. 241, 267-269, 526.

Zusammenfassung — Mittels DSC, TG (DTG) und IR-Techniken wurden acht N-substituierte Maleinsäuremonoamidderivate untersucht. Die thermischen Untersuchungen zeigen, daß die Zersetzung von Verbindungen mit freier Carboxylgruppe schon vor dem Schmelzen beginnt und der Zersetzungsprozeß dann in der Schmelze bei Anheben der Temperatur fortgesetzt wird. Dies wurde mit der Existenz von Dimeren mit starken intermolekularen Wasserstoffbrückenbindungen erklärt. Diese Annahme zur Struktur wurde durch die Ergebnisse der IR-spektroskopischen Untersuchungen bekräftigt.