

AMIC ACID COMPLEXES WITH APROTIC POLAR SOLVENTS

V. Complexes with amide solvents and isomerism of trimellite-dianilic acid

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Complexes of trimellite-dianilic acid (TMA) with aprotic amide solvents have been synthesized, separated and investigated by TG and MTA methods. It was shown that the composition of these complexes is $[TMA]_1 \cdot [Sol]_1$. The PMR spectra were used to show the ability of TMA to undergo isomeric transitions under mild conditions in an aprotic solvent.

It has been shown previously [1–3] that pyromellitic-dianilic acid (PMA) forms crystalline complexes with aprotic polar solvents such as dimethylformamide (DMF), dimethylacetamide (DMAA), N-methyl-2-pyrrolidone (N-MP) and dimethylsulphoxide (DMSO); these complexes are stable on prolonged storage. Crystalline complexes containing only the para isomer of PMA have been separated by selective precipitation. It has been shown that isomeric PMA transitions in solution are possible under relatively mild conditions [4] and a mechanism on which this process is based has been suggested [5].

In order to check the validity of the established relationships for other representative aromatic amic acids, we have synthesized trimellite-dianilic acid (TMA) and studied its complexation with aprotic solvents and its isomerism.

Experimental

TMA was obtained by the interaction between the anhydride-chloroanhydride of trimellitic acid and aniline in the medium of a matching amide solvent at 50° in dry argon. Depending on the precipitation method (Table 1), a precipitate was formed at various rates, filtered and dried to constant weight under vacuum.

Mass-spectrometric thermal analysis (MTA) was carried out with an MKh-1320 mass-spectrometer (USSR) by a published method [2].

The PMR spectra were recorded with a JEOL C-60 HL spectrometer at an operating frequency of 60 MHz for 10% solutions in DMA, DMF-D and N-MP amide solvents at 20°.

Table 1 Characterization of synthesized products

N	Solvent	Precipitant	Precipitate characteristic	Precipitation rate
I	DMAA	Acetone	Large white particles	24 hours
II		Benzene	Small white aggregated particles	24 hours
III		None	Large spherical crystalline lemon-coloured products	2 months
IV	DMF	Acetone	Small yellowish particles	2 weeks
V		Benzene	Small yellowish particles	24 hours
VI		None	Large crystalline products	2 months
VII	N-MP	Acetone	Small yellowish particles	2 weeks
VIII		Benzene	Small yellowish particles	24 hours
IX		None	No precipitate was formed	2 months

The PMR spectrum of TMA in the range of signals of aromatic protons (7.5–8.4 ppm) exhibits a complex form characteristic of the tri-spin ABC-type system. Hence, a precise assignment of the signals belonging to different isomers is difficult. However, in the range of signals of amide protons (10.2–10.8 ppm) single signals are observed for each NH-CO group (in N-MP, 10.24 and 10.55 ppm for the para isomer and 10.65 and 10.83 ppm for the meta isomer). For TMA, an amide signal appears at 10.55 ppm, and in the range of signals of anilide protons, apart from the multiplet anilide spectrum at 7.0–7.5 ppm, a strong singlet appears at 4.4 ppm, corresponding to anilide protons.

Discussion

The investigation of the separated crystalline products of TMA synthesis showed that they differ greatly from the analogous products of PMA synthesis with respect to crystallosolvate formation. Thus, a stable crystallosolvate was obtained only for case 1 (Table 1). The thermal analysis curves for product 1 shown in Fig. 1, together with the elemental analysis data (Table 2), made it possible to determine the composition of crystallosolvate 1. It was found to be close to $[TMA]_1 \cdot [DMAA]_1$ which corresponds to the concepts on the nature of complexation of o-amic acids with aprotic solvents [5].

However, when a more active precipitant, benzene, was used, TMA crystals devoid of solvent were precipitated from DMAA solution (Table 2). DMF (Table 1, samples IV and V) and N-MP (Table 1, samples VII and VIII) also form complexes with TMA (Figs 2 and 3, respectively). However, in these cases the separation of crystallosolvates of a definite composition is difficult.

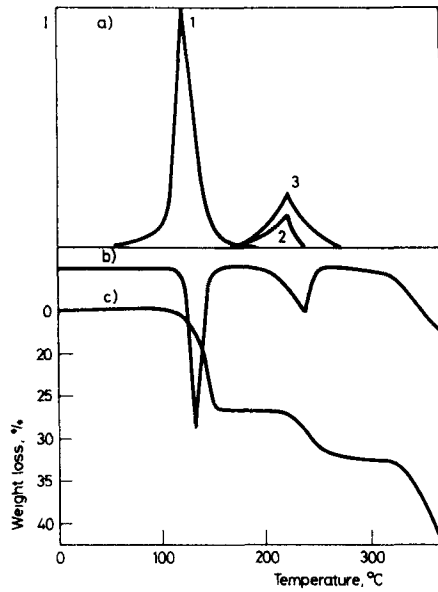


Fig. 1 Compound I. Curves of a) MTA, b) DTG and c) TG. 1 – DMA (mass. eq. = 87), 2 – aniline (mass. eq. = 93), 3 – H₂O (mass. eq. = 17)

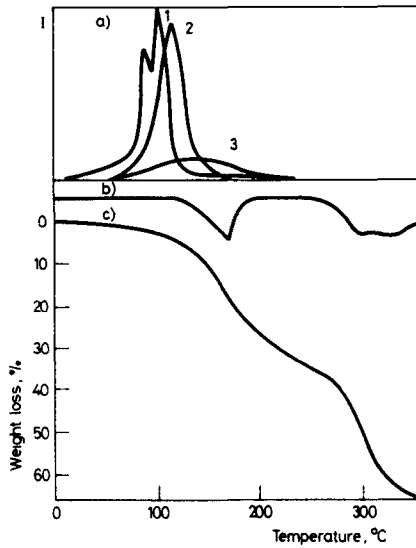


Fig. 2 Compound V. Curves of a) MTA, b) DTG and c) TG. 1 – DMFA (mass. eq. = 73), 2 – aniline (mass. eq. = 93), 3 – H₂O (mass. eq. = 17)

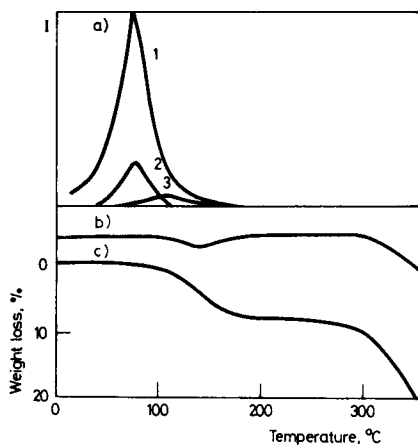
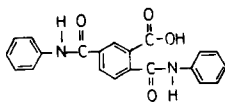


Fig. 3 Compound VIII. Curves a) MTA, b) DTG and c) TG. 1 – N-MP (mass. eq. = 99), 2 – aniline (mass. eq. = 93), 3 – H₂O (mass. eq. = 17)

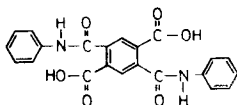
Table 2 Elemental analysis of separated crystalline products

Compound number	Tentative composition	Elemental analysis calculated/obtained		
		C	N	H
I	[TMA] ₁ · [DMAA] ₁	9.40	67.11	5.59
		9.50	67.04	5.62
II	TMA	7.78	70.00	4.44
		7.86	69.40	4.55
IV	TMA	7.78	70.00	4.44
		8.11	62.83	3.31
V	TMA	7.78	70.00	4.44
		8.58	67.95	3.19
VIII	TMA	7.78	70.00	4.44
		8.31	71.69	4.50

The reason for this behaviour of TMA is probably the asymmetry of its molecule:



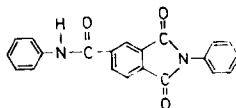
This asymmetry involves difficulties in the crystallization of both TMA itself and, may be to an even greater extent, of its complexes as compared to the crystallization of the symmetrical PMA molecule:



However, the experimental data suggest that the formation of *stable* complexes with polar solvents is a general property of ortho-amic acids.

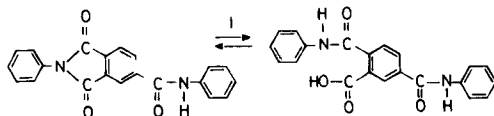
Complete similarity in the behaviour of TMA and its symmetrical analogue was found in the investigation of the isomeric composition. As in the case of PMA, in all cases in the process of synthesis an equimolar mixture of para and meta TMA isomers is formed. When TMA is precipitated by any precipitant, only the para isomer is precipitated and the ratio of para to meta isomers of 1:1 is restored in the solution.

When a solution of the para isomer of TMA in DMAA is maintained at 70°, the equimolar isomer ratio is attained in 45 h, i.e. faster by a factor of 1.5 than for PMA. However, it should be noted that by this time a large amount (up to 80 mol % of the total amount of dissolved products) of the corresponding imide:



is accumulated in the TMA solution, which is not characteristic of PMA.

Of particular interest is the case when a solid product is formed during a long (~ 2 months) precipitation from the reaction solution in the absence of the precipitant (samples III and VI). According to the PMR data, the resulting large crystals were the product of TMA imidization. Analysis of the supernatant liquid showed the usual equimolar ratio of TMA isomers and an almost complete absence of the imide form. It may be suggested that, due to the structural features of TMA, the corresponding imide is crystallized more readily than the amic acid itself. Hence two mechanisms are possible for the rapid imidization of TMA. First, fast crystallization of the imide leads to a decrease in the imide concentration in solution, thereby increasing the imidization rate.



Secondly, since the structures of TMA and its imide are similar, TMA can be sorbed on the surface of the crystal, acquiring the shape closest to the imide configuration. This shape should evidently also be best suited for the closure of the imide ring.

Conclusions

1. With aprotic polar solvents, TMA forms complexes with the composition $[TMA]_1 \cdot [Sol]_1$. However, since the TMA molecule is asymmetrical, the formation of crystalloolvates is difficult.

2. Under mild conditions in solutions of aprotic solvents, mutual transformations of para and meta isomeric forms of TMA are observed.

3. An anomalously fast spontaneous imidization of TMA is observed in solution. This is evidently due to the easiers crystallization of the imide than of the initial amic acid.

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Zusammenfassung — Komplexe von Trimellitdianilinsäure (TMA) mit aprotischen Amid-Lösungsmitteln wurden synthetisiert, getrennt und mittels TG und MTA untersucht. Es wurde gezeigt, daß die Zusammensetzung der Komplexe der Formel $[TMA]_1 \cdot [Sol]_1$ entspricht. An Hand der PMR-Spektren wird gezeigt, daß TMA in einem aprotischen Lösungsmittel unter milden Bedingungen isomerisiert.

Резюме — Синтезированы, разделены и исследованы методом ТГ и МТА комплексы дианилидтримеллитовой кислоты с апротонными амидными растворителями. Показано, что состав комплексов соответствует стехиометрии 1:1. Спектры ПМР показали способность дианилида тримеллитовой кислоты подвергаться в мягких условиях изомерным переходам в апротонных растворителях.