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Charge-transfer Interaction in Supercooled Melts of Some Derivatives of *N*-Picrylaniline

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Synopsis. Supercooled melts of *N*-picrylaniline and its derivatives, the molecules of which consist of electron-donating and -accepting moieties, are colored more deeply than the crystals. Many of them exhibit glass transitions.

Some derivatives of *N*-picrylaniline have been known to be obtained in differently colored forms. For example, Grison has prepared *N*-picryl-*p*-iodoaniline in yellow, orange, and red forms, and determined the crystal and molecular structures.[1] The arrangement of the molecules is quite different in these polymorphic forms, but the structure of the molecule itself remains almost the same. In addition, he has noted that the melt is readily supercooled. Such a sample is red-colored and can be kept at room temperature without crystallization over a period of months. As we have reported for the dimorphic forms of *o*- and *p*-anisyl-*p*-benzoquinones,[2] the difference in color may be explained by the difference in the intermolecular charge-transfer (CT) interaction between the electron-donating moiety of a molecule and the accepting moiety of the neighboring molecule. Both the intensity and the location of the CT absorption are expected to be modified, to some extent, by the mode of molecular packing. As the readiness of supercooling might be correlated with an enhanced CT interaction, the spectral measurement and thermal analysis of supercooled melts have been attempted for a number of the derivatives.

The *N*-picrylanilines were prepared by the condensation reaction between picryl chloride and anilines in boiling ethanol.[3] The latter carried one of the following substituents: methyl, methoxy, ethoxy, chloro, bromo, and iodo. The compounds were melted in small aluminum pans, and then they were quickly cooled by being placed on a cold metal block. For the spectral measurements, the supercooled melts were ground with sodium chloride in concentrations of the order of one weight percent. The spectra were measured by means of a Beckman DK 2A spectroreflectometer as the difference in reflectance between the mixture and pure sodium chloride, and were plotted using the Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where R is the reflectance.[4] The calorimetric curves were recorded on a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C, at a heating rate of 5 °C/min. The glass transitions were measured with samples stored for several days at room temperature.

The color of all the compounds examined here becomes deeper upon melting. The melts are easily supercooled without color change. The most remarkable changes were observed with the derivatives carrying methyl. methoxy, and ethoxy groups. For example, *N*-picryl-*m*-anisidine is yellow in the crystalline state and is reddish orange in the molten and supercooled states. As is shown in Fig. 1, this change is ascribed to the appearance of an additional absorption on the longer wavelength side of the main absorption, having a maximum at about 400 nm. The former may be assigned to the intermolecular CT absorption, and the latter to the intramolecular CT absorption involving the transfer of an electron from the electron-donating moiety to the accepting moiety. The molecular packing in the crystalline state seems to be unfavorable to the intermolecular CT interaction, but a contact between the two moieties may be allowed by the disorder introduced by melting. If the interaction operating in the melt is strong, the disorder is to be conserved below the melting point. The color change observed with *N*-picryl-*o*-anisidine is similar to the afore-mentioned: namely, reddish orange in the crystalline state and deep red in the supercooled state. In this case, the spectral change suggests that the main absorption in the former state arises from the intermolecular CT interaction (see Fig. 1). The maximum of the intramolecular CT absorption may be located at 400 nm.

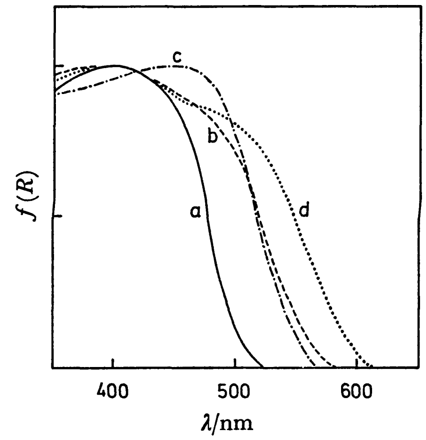

Fig. 1. Spectra of *N*-picryl-*m*-anisidine in the crystalline state (a) and in the glassy state (b) and those of *N*-picryl-*o*-anisidine in the crystalline state (c) and in the glassy state (d). The maximum is arbitrarily taken as 1.00 in each spectrum.

Another feature of interest is the appearance of a glass transition. For instance, the supercooled melt of *N*-picryl-*p*-iodoaniline described by Grison was found to show a small endothermic peak around 60 °C, a large exothermic one around 110 °C, and a large endothermic one near 190 °C. As the location of the last is close to the melting point of the red form, the large exothermic peak must be due to the crystallization of the supercooled melt. The above-mentioned temperature is consistent with Grison's observation that the crystallization into the orange form is rapid in the range from 100 to 120 °C. This form has been reported

Table 1. Glass transition temperatures and crystallization temperatures of supercooled melts of *N*-picrylanilines
(heating rate: 5 °C/min)

Substituent	Glass transition (°C)	Crystallization (°C)
None	—	70
o-Methyl	—	80
m-Methyl	40	—
p-Methyl	—	80
o-Methoxy	40	[a]
m-Methoxy	45	—
p-Methoxy	—	75
o-Ethoxy	—	—
m-Ethoxy	30	90
p-Ethoxy	—	75
o-Chloro	—	85
m-Chloro	45	—
p-Chloro	50	90
m-Bromo	50	[a]
p-Bromo	55	85
m-Iodo	55	—
p-Iodo	60	110

a) Partial crystallization occurred, but the peak was too broad to be located.

to be transformed into the red form around 145 °C, but this transition was not detected on our calorimetric curves. One may consider the small endothermic peak around 60 °C as an indication of a glass transition. Such peaks, with areas of 0.3—0.8 kcal/mol at the present heating rate, could be observed with many derivatives, as summarized in Table 1. All the *m*- and *p*-halo derivatives exhibit the transitions. The temperatures in the *p*-derivatives are consistently higher than those in the corresponding *m*-derivatives. In each group, the transition temperature becomes progressively higher with increasing the atomic weight of the halogen. On the other hand, the *m*-ethoxy derivative shows a peak located 15°C lower than the *m*-methoxy derivative; therefore, the transition in the *o*-ethoxy derivative might be below room temperature. It is particularly interesting to note that no crystallization can be observed in derivatives carrying the substituent on the *o*- or *m*-position upon heating to their melting points, suggesting the presence of strong molecular entanglement assisted by an intermolecular CT interaction.

References

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