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# Glass-forming Photoconductive Organic Compounds II[1]: Glass-forming Properties of 1,3,5-Triaryl-2-pyrazolines

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# Glass-forming Photoconductive Organic Compounds II[1]

## Glass-forming Properties of 1,3,5-Triaryl-2-pyrazolines

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Glass-forming properties of 2-pyrazoline derivatives were examined and discussed in terms of the molecular structure. The results show that the molecular shape of 1,3,5-triaryl-2-pyrazolines is responsible for the glass-forming properties of these compounds. Glass transition points of several 1,3,5-triaryl-2-pyrazoline derivatives were measured.

### INTRODUCTION

Numerous investigations have been reported on the optical and electrical properties of organic compounds in the crystalline state. Recently, increasing attention has been paid to the above properties of organic compounds in the amorphous glassy state.[2] For example, amorphous tetracene films evaporated onto a substrate at low temperatures (90–180°K)[3] have been used for these studies.[4–8] It is of great interest to obtain information on the optical and electrical properties of organic compounds in the amorphous glassy state over a wide range of temperatures, including room temperature, and to compare these properties in the crystalline and glassy states of different structures over the same temperature range.

1,3,5-Triaryl-2-pyrazolines represent one class of ideal compounds for these studies since, as described in this paper, they are easily supercooled and then change into a stable glassy state at or above room temperature. In addition, they have intense fluorescent characteristics[9] and photoconductive properties.[10] In this study we have examined the glass-forming properties of 2-pyrazoline derivatives in terms of the molecular structure and made measurement of glass transition points of several 1,3,5-triaryl-2-pyrazoline derivatives in order to distinguish the glassy state from the supercooled liquid state.



## EXPERIMENTAL

### Materials

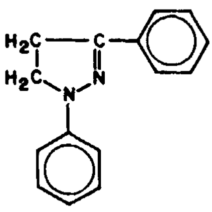
1,3,5-Triaryl-2-pyrazoline derivatives were prepared from the corresponding chalcones by condensation with phenylhydrazine, according to the method described in the literature,[11] purified by repeated recrystallizations from ethanol and dried *in vacuo*. 1,3-Diphenyl-2-pyrazoline was synthesized by the reaction of $\beta$-dimethylaminopropiophenone with phenylhydrazine,[12] purified by repeated recrystallizations from ethanol and dried *in vacuo*.

### Measurement of Glass Transition Points

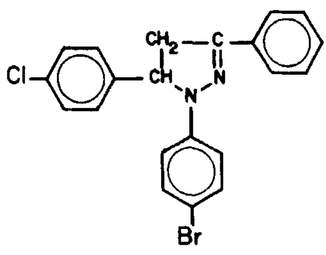
Glass transition points were measured with Rigaku TG-DSC using the amorphous glassy sample prepared by quenching the melted sample at below room temperature *in vacuo*.

## RESULTS AND DISCUSSION

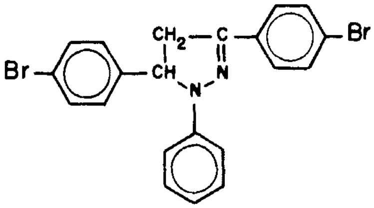
2-Pyrazoline derivatives studied here are 1,3-diphenyl-2-pyrazoline (I), 1-(*p*-bromophenyl)-3-phenyl-5-(*p*-chlorophenyl)-2-pyrazoline (II), 1-phenyl-3,5-di-(*p*-bromophenyl)-2-pyrazoline (III), 1,3,5-tri-(*p*-bromophenyl)-2-pyrazoline (IV), 1-($\alpha$-naphthyl)-3,5-diphenyl-2-pyrazoline (V), 1,5-diphenyl-3-($\alpha$-naphthyl)-2-pyrazoline (VI), and 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline (VII). The compounds (II), (III), (IV), and (V) are new compounds, and were identified by the elemental analysis, IR, NMR and mass spectra.



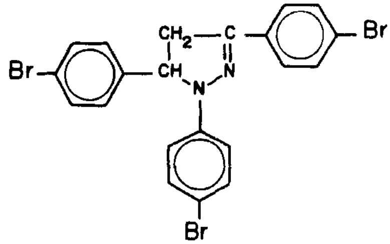

( I )



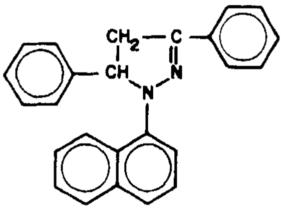

( II )



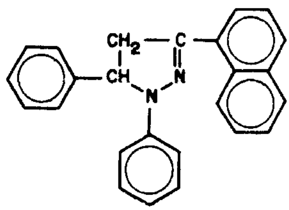
(III)



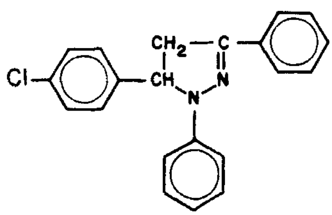
(IV)



(V)



(VI)



(VII)

It was found that 1,3-diphenyl-2-pyrazoline (I) crystallizes readily even when the melted sample is rapidly quenched with liquid nitrogen, whereas all 1,3,5-triaryl-2-pyrazoline derivatives examined in this study, when cooled from the melt, spontaneously form a supercooled liquid state, which then changes into a stable glassy state. Figure 1 shows a typical example of the measurement of the glass transition point by differential scanning calorimeter (DSC). When the amorphous glassy sample is heated slowly from a low temperature (*ca.* −20°C), the endothermic phenomenon can be observed at a temperature at which molecular motion begins, which corresponds to the glass transition point. Glass transition points determined in this way on these 1,3,5-triaryl-2-pyrazoline derivatives together with their melting points are listed in Table I. The results show that these compounds keep the amorphous glassy state instead of the supercooled liquid state around or above room temperature.

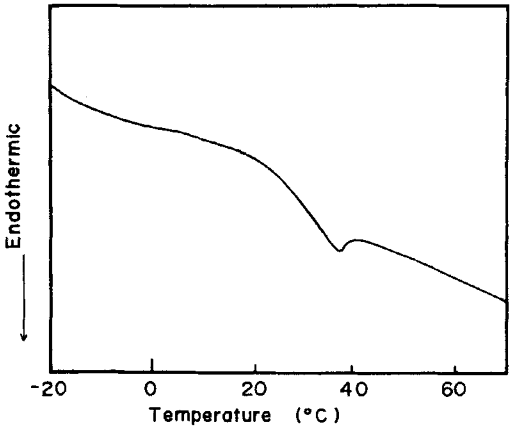



FIGURE 1 Measurement of the glass transition point of 1,5-diphenyl-3-(α-naphthyl-)-2-pyrazoline (VI)

The present results and the results of the X-ray structure analysis of 2-pyrazoline compounds described below indicate that the molecular shape of 1,3,5-triaryl-2-pyrazolines is responsible for giving readily a supercooled liquid state when cooled from the melt, which then changes into a stable glassy state. It has been shown by the X-ray structure analysis that the 1,3-diphenyl-2-pyrazoline molecule as a whole is not completely planar.[13] That is, the pyrazoline ring is slightly non-planar and the two phenyl rings at one and three positions are slightly bent downwards from the plane of the conjugated $\pi$-electron system extending from the one to the three position of the pyrazoline ring. This molecular shape, however, does not meet the requirement to give readily a supercooled liquid state which changes into a stable glassy state. The result of the X-ray structure analysis of 1,3-diphenyl-5-(*p*-chlorophenyl)-2-pyrazoline (VII) shows that the plane of the *p*-chloro-

TABLE I

Glass transition points (Tg) and melting point (Mp) of 2-pyrazoline derivatives

| Compound | Tg(°C) | Mp(°C) |
|---|---|---|
| I | non | 154 |
| II | 54 | 133 |
| III | 43 | 176 |
| IV | 53 | 164 |
| V | 38 | 156 |
| VI | 37 | 174 |
| VII | 16.5 | 130 |

phenyl ring at the five position is almost perpendicular to the plane of the pyrazoline ring.[14] That is, the introduction of the aryl group at the five position results in the increase of aplanarity of the molecule, forming a propeller-like molecular shape. Thus, rapid spacial arrangement of the molecule from the melt to the crystalline state may be impeded in 1,3,5-triaryl-2-pyrazoline molecules due to the increased intra and intermolecular interactions, and the supercooled liquid state is generated more easily than the crystalline state, which changes into the stable glassy solid state at the glass transition point.



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