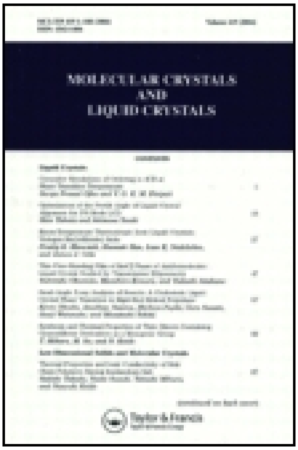

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Infrared Absorption and Calorimetric Evidence for the Existence of Two Forms of 1.8 Dihydroxyanthraquinone

Giulietta Smulevich [a], Giulio G. T. Guarini [a] & Mario P. Marzochi [a]

[a] Dipartimento di Chimica, Università di Firenze, Via G. Capponi, 9, 50121, Firenze, Italy

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Infrared Absorption and Calorimetric Evidence for the Existence of Two Forms of 1.8 Dihydroxyanthraquinone

GIULIETTA SMULEVICH, GIULIO G. T. GUARINI and MARIO P. MARZOCCHI

Dipartimento di Chimica, Università di Firenze, Via G. Capponi, 9, 50121 Firenze, Italy

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The combined analysis of infrared absorption and calorimetric measurements allowed us to show the existence of two crystal forms for 1.8 dihydroxyanthraquinone. The phase transition is assisted by a change of the molecular configuration involving the intramolecular hydrogen bond. The results are correlated with the occurrence of dual fluorescence associated to the excited state intramolecular proton transfer already reported for this molecule.

Keywords: infrared spectra, calorimetry, phase transitions

INTRODUCTION

Dihydroxyanthraquinones are model chromophores for antitumor anthracyclines which bind the base pairs of DNA via stacking interactions.[1] 1.5 and 1.8 dihydroxyanthraquinones, as other aromatic molecules with intramolecular hydrogen bonds, give rise to dual fluorescence associated to excited state proton transfer.[2–4] The implication of the proton transfer on the intercalative interaction between the anthracycline chromophores and the base pairs of DNA can be very important in the context of the structure-biological activity relationship.

1.8 dihydroxyanthraquinone (hereafter 1.8$(OH)_2$AQ) has been studied by several spectroscopic methods including polarized infrared spectra,[5] low temperature Raman excitation profiles,[6] second derivative absorption and fluorescence spectra at low temperature and in different solvents.[7,8] Since the spectral properties, especially fluorescence, depend very much on solvent polarity as well as on temperature, in the present paper we focus our attention on the molecular and crystal structure of the ground state. By calorimetric and infrared absorption methods we found that $1.8(OH)_2AQ$ exists into two crystal forms. The phase transition involves also an intramolecular rearrangement of the hydrogen bonds.

EXPERIMENTAL

$1.8(OH)_2AQ$ from Fluka was purified by repeated crystallizations from CH_3CN and subsequent preparative high performance thin layer chromatography.

The infrared spectra on KBr pellets and in solution were measured with the aid of a Perkin–Elmer 225 spectrometer. A variable temperature cell with the thermocouple for the temperature control directly inserted into the KBr pellet was used. The intensity measurements were performed via graphyc integration.

The calorimetric measurements were obtained with a Mettler TA 2000 thermal analyzer.

The changes with temperature of the optical properties of single crystal were followed with a polarizing microscope.

RESULTS AND DISCUSSION

$1.8(OH)_2AQ$ crystallizes in the tetragonal system (space group $P4_1$) with four molecules in general positions, the molecular parameters being determined.[9] Even if the hydrogen atoms have not been located, the C—O and 0..0 distances indicate that the two intramolecular hydrogen bonds are unequivalent according to the structure of Figure 1 (Form I). In the attempt to obtain a high purity compound by sublimation we discovered the existence of another crystal form. Figure 1 shows in fact that the infrared spectrum of the compound obtained by crystallization from ethanol (Form I) is remarkably different from the infrared spectrum of the sublimed compound (Form II). Large differences between the two forms in number, frequency and relative intensity of bands are found all over the spectra, but striking changes are observed in the 850-700 cm^{-1} region where the

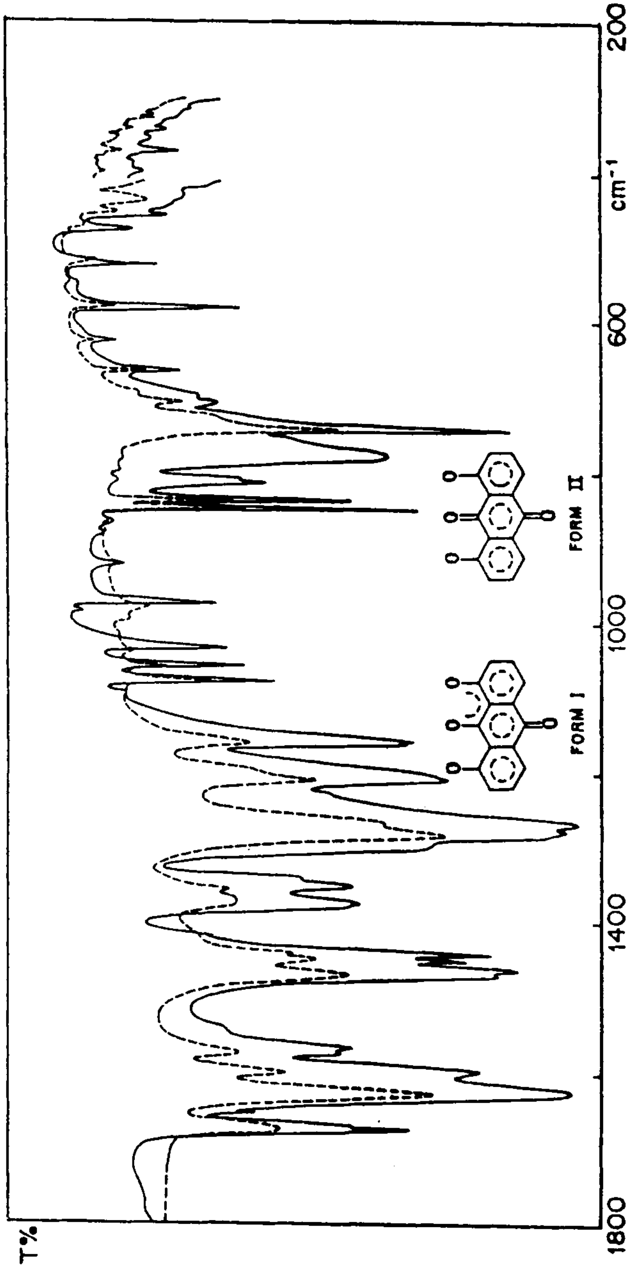

FIGURE 1 Infrared spectra at room temperature of 1.8 dihydroxyanthraquinone in KBr pellet. Form I, full line; Form II, dotted line.

γ(OH) mode is expected to occur. On the basis of the infrared spectra of 1.8$(OH)_2$AQ in polarized light and of 1.8$(OD)_2$AQ, the γ(OH) mode has been assigned to the strong band at 775 cm^{-1} for Form I and to the broad shoulder at 735 cm^{-1} for Form II.[5]

In order to characterize Form II and its relationship to Form I we studied the variations of the infrared band intensities with temperature and performed a calorimetric analysis.

Figure 2 shows the changes with temperature in the 900-600 cm^{-1} spectral region of a KBr pellet of Form I. It is seen that the 775 cm^{-1} band gradually decreases in intensity with increasing temperature vanishing at 178°C while the band at 735 cm^{-1} arises as a shoulder at 158°C becoming most pronounced at 178°C. Other variations are observed in the spectra, for example in the relative intensities of the 849-839 cm^{-1} doublet.

Figure 3 shows the plot of the integrated intensity of the 775 cm^{-1} band vs temperature. It is seen that the intensity reduction is moderate from 50 to 130°C, the slope tending towards a zero value with temperature increasing. Above 130°C an abrupt change occurs and the band being strongly reduced with a linear dependence on temperature disappears at 178°C. Since we ensured that no time dependent effects occur by successively measuring the spectra at the same temperature, it is clear that a gradual phase transformation takes place in the 130–180°C range. The transformation is poorly reversible since by lowering temperature from 180°C the 775 cm^{-1} band appears again but its intensity is weak even at room temperature.

Figure 3 shows also the thermal analysis of Form I from 100 to 220°C. It is seen that a broad maximum occurs at 155°C in the ΔT vs T curve. The solid phase transition (ΔH = 1090 cal/M) begins at 140°C, i.e. at higher temperature with respect to the infrared measurements. These are therefore strongly sensitive to the transformation. The thermal analysis shows clearly the peak at 195°C corresponding to the melting point (ΔH_m = 5200 cal/M). The thermal analysis of Form II shows the same solid-liquid transition as Form I but no solid-solid transition.

The solid phase transition of Form I is not reversible since it is neither observed on returning to room temperature from 200 or 180°C nor on successively rising up temperature. On the other hand a very weak maximum at 155°C could be detected by grinding the powder at room temperature after the first thermal cycle.

All the above results give evidence for the existence of two forms of 1.8 dihydroxyanthraquinone. Form I is stable below 130°C, while Form II exists as a neat crystal phase between 170°C and the melting

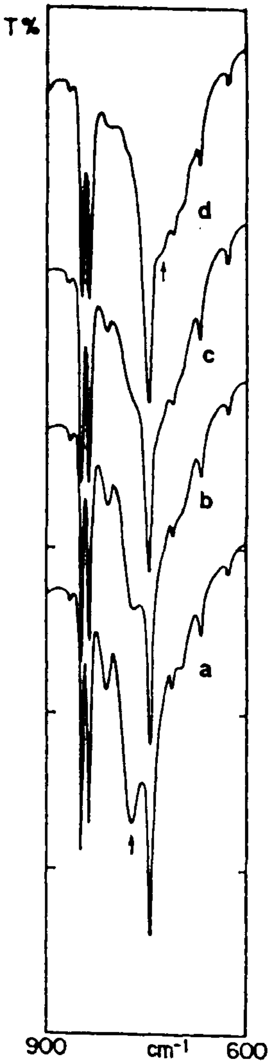

FIGURE 2 Infrared spectra between 900 and 600 cm^{-1} of 1.8 dihydroxyanthraquinone (Form I) at increasing temperature (a, 143; b, 158; c, 164; d, 178°C). The arrows indicate the γ(OH) mode at 775 cm^{-1} for Form I and at 735 cm^{-1} for Form II.

point. Because of the poor reversibility of the solid phase transition Form II can exist as a metastable form also at room temperature. The two forms exhibit different crystal structures, Form I being tetragonal while Form II is orthorombic or monoclinic-pseudo-orthorombic. This has been inferred by the examination of single crystals

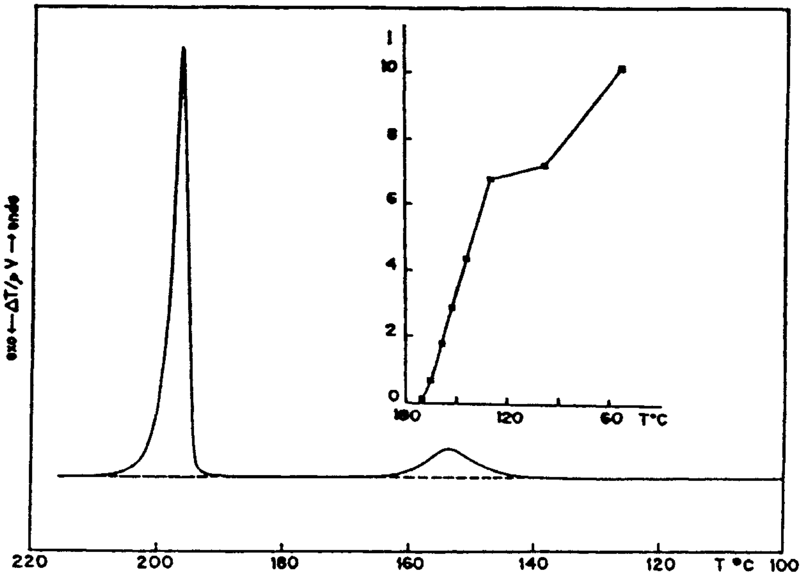

FIGURE 3 Calorimetric analysis of 1.8 dihydroxyanthraquinone in Form I. The inserted graph shows the intensity of the 775 cm^{-1} infrared band as function of temperature.

at various temperatures with the aid of a polarizing microscope. In addition the two forms exhibit different molecular configurations involving essentially the intramolecular hydrogen bonds. The frequency shift and the intensity change of the γ(OH) mode upon the transition are in fact too large to be ascribed exclusively to the effect of the crystal field. The occurrence of such an intramolecular transformation assisted by a crystal modification justifies the large temperature range necessary to complete the transition. In order to prove the existence of two molecular configurations we measured the infrared spectra of 1.8$(OH)_2$AQ in solvents of different polarity and quite transparent in the 800-700 cm^{-1} region. We found that the γ(OH) mode occurs at 760 cm^{-1} in CD_3CN and at 730 cm^{-1} in CS_2. Clearly Form I is present in the first case and Form II in the latter confirming the observation that Form I and Form II are obtained by crystallization from polar and non-polar solvents, respectively.

We assign to Form II the symmetric structure (C_{2v} symmetry) with two equivalent hydrogen bonds (Fig. 1) as expected for a configuration stable at high temperature. This symmetry has been inferred also by the analysis of the fluorescence spectrum in n.hexane at 8K.[2]

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