Rotational Energy Barrier of the Polarized Carbon–Carbon Double Bond in Quinophthalone

Issa Yavari1,*, Mehdi Adib1, Hamid R. Bijanzadeh1, Majid M. M. Sadegi2, Hossein Loghani-Khouzani2, and Javad Safari2

1 Department of Chemistry, University of Tarbiat Modares, Tehran, Iran
2 Department of Chemistry, University of Isfahan, Isfahan, Iran

Summary. A dynamic NMR effect is observed in the $^{13}$C NMR spectra of anhydrous quinophthalone (quinoline yellow) and its monohydrate in the vicinity of 47°C and 0°C, respectively, and is attributed to a restricted rotation around the polarized carbon–carbon double bond. The free energy of activation for this process in anhydrous quinophthalone and the monohydrate is 65±2 and 55±2 kJ·mol$^{-1}$, respectively, in CDCl$_3$.

Keywords. Restricted rotation; Quinoline yellow; Dynamic NMR; Push-pull olefines.

Introduction

Quinophthalone dyes are fascinating for their color brilliance and light fastness [1] and are among the most important yellow dyes. Quinoline yellow (quinophthalone), which was first discovered by Jacobsen in 1882, is probably the most widely used yellow compound for trichromatic dyeing of bulk textile goods made from polyester fibers. Its structure was a matter of debate for several decades. Infrared and NMR data given by Kehler et al. [2] verified structure 1 (2-(2(1H)-quinolinyliden)-1H-indene-1,3(2H)-dione) and excluded 2. Thus, compound 1 possesses a highly polarized carbon–carbon double bond in its enaminone moiety and is therefore expected to exhibit restricted rotation around this bond.

1

2

* Corresponding author. E-mail: isayavar@yahoo.com
Barriers to rotation in olefins that possess electron-donating groups at one end and electron-withdrawing groups at another end, named push-pull olefins, have been examined [3, 4]. This type of olefins exhibit fairly low barriers to rotation around the carbon–carbon double bond owing to dipolar canonical structures in the ground state and a superior stabilization of the zwitterionic transition state.

Whereas the configurational properties of polarized olefins with strong electron-donating substituents, such as amino groups, on one carbon atom and electron-withdrawing substituents, such as carbonyl groups, on the other carbon atom have been studied [3–7], there are no published experimental data on the configurational features of the push-pull system of 1. The combination of the very strong electron-donating ability of its enamine system and the strong electron-attracting carbonyl groups give rise to a polarized olefin which might exhibit a dynamic NMR effect for rotation around the double bond. We here report the results of our $^{13}$C NMR spectroscopic study of 1.

Enaminoketones 3 are vinylogues of amides. The carbon–carbon double bond in these compounds possesses some single bond character. Therefore, the rotational barrier about this bond should be lower relative to that in normal olefins. This consideration has aroused the interest of many investigators, and a wealth of information concerning restricted rotation in enaminoketones has been acquired [8, 9]. The barrier to rotation about the C=C bond in these compounds is a measure of the electron-donating ability of a group at one end and the electron-attracting ability of another group at the other end.

Results and Discussion

The $^{13}$C NMR spectrum of the monohydrate of 1 in CDCl$_3$ at $-40^\circ$C displays 18 signals (see Fig. 1). At about 0°C, six signals of the indane-1,3-dione moiety at 120.11, 120.66, 132.29, 132.57, 138.56, and 139.12 ppm become very broad and mutate to three lines at about 50°C. This dynamic effect is interpreted in terms of a restricted rotation around the carbon–carbon double bond of the enaminone moiety.

Although an extensive lineshape analysis in relation to the dynamic effect observed for 1 was not undertaken in the present work, the variable temperature spectra are sufficient to calculate the free energy barrier as well as enthalpy and entropy of activation for the restricted carbon–carbon double bond rotation. From the coalescence of the CH-4,7 and CH-5,6 carbon resonances and using the