

Rotational Energy Barrier of the Polarized Carbon-Carbon Double Bond in 3-(4-Dimethylaminobenzylidene)pentane-2,4-dione

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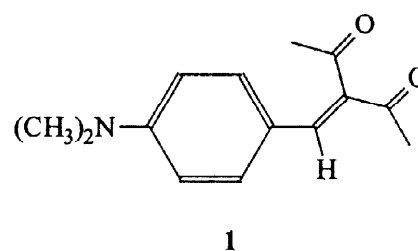
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Abstract: A dynamic NMR effect is observed in the ^1H NMR spectra of the title compound in the vicinity of 186 °C, and is attributed to restricted rotation around the polarized carbon-carbon double bond. The free energy of activation (ΔG^\ddagger) for this process is $105 \pm 2 \text{ kJ mol}^{-1}$ in nitrobenzene as a solvent.

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The concept of polarized (or push-pull) olefinic systems has played an important role in organic chemistry for three decades.¹ The barrier to rotation around the carbon-carbon double bond in ethylenes with strong donor groups on one carbon atom and strong acceptors on the other may be quite low owing to a superior stabilization of the zwitterionic transition state. Thus, substitution of one carbon atom of the double bond with electron-donating groups and of the other with electron-withdrawing groups diminishes the double bond order by charge separation.

While the configurational properties of polarized ethylenes with strong electron-donating substituents, such as dialkylamino groups, on one carbon atom and electron-accepting substituents, such as acetyl groups, on the other carbon atom have been studied both experimentally^{1,2} and theoretically,³ there are no published experimental or theoretical data on the configurational features of push-pull ethylenes with a dimethylamino group separated by a benzene ring, such as **1**. The combination of the very strong electron-donating ability of the dimethylaminobenzene system and the strong electron-attracting acyl groups give rise to a polarized olefine which exhibits a dynamic ^1H NMR effect in the vicinity of 186 °C for double bond rotation. We now report the results of our ^1H dynamic NMR spectroscopic study for 3-(4-dimethylaminobenzylidene)pentane-2,4-dione (**1**).⁴



The ^1H NMR spectrum⁵ of **1** in nitrobenzene solution at ambient temperature displays three sharp singlets for the methyl groups: one due to the NMe_2 protons at δ 3.01, and two for the acetyl protons at δ 2.57 and 2.62. At about 100 °C, the resonances arising from the acetyl protons are appreciably broadened when compared to the same bands in the spectrum measured at room temperature, while the NMe_2 resonance remains unchanged. The acetyl protons have coalesced near 186 °C and appear as a fairly broad symmetrical band at 198 °C, the highest temperature reached.

Although an extensive line-shape analysis in relation to the dynamic ^1H NMR effect observed for **1** was not undertaken in the present work, the variable temperature spectra are sufficient to calculate the free energy barrier (if not the enthalpy and entropy of activation) for the restricted carbon-carbon double bond rotation in **1**. From the coalescence

of the acetyl proton resonances and using the expression

$$k = \pi \Delta \nu / \sqrt{2}$$

we calculate that the first-order constant (k) for carbon-carbon double bond rotation in **1** is 10 s^{-1} at 186°C . Application of the absolute rate theory with a transmission coefficient of 1 gives a free-energy of activation (ΔG^\ddagger) of $105 \pm 2 \text{ kJmol}^{-1}$, where all known sources of errors are estimated and included.⁶ The experimental data available are not suitable for obtaining meaningful values of ΔH^\ddagger and ΔS^\ddagger , even though the errors in ΔG^\ddagger are not large.⁷

The ^1H NMR spectrum of **1** was also investigated in 1,2-dichlorobenzene as a solvent in the temperature range of 30 to 198°C , and the results are shown in Table 1.

Table 1 Selected proton chemical shifts (in ppm, Me_4Si) and activation parameters (kJmol^{-1}) for **1**.

Solvent	NMe ₂	COCH ₃		Δν(Hz)	T _c (°C)	ΔG [‡]	k(s ⁻¹)
Nitrobenzene	3.01	2.62	2.57	4.5	186(459 K)	105.3	10
1,2-Dichlorobenzene	2.99	2.64	2.56	7.2	197(470 K)	106.0	16

The changes observed in the acetyl proton resonances⁸ of **1** clearly are the result of a dynamic NMR effect, and not, for example, merely the result of temperature-dependent chemical shifts. Restricted rotation of the acetyl groups in **1** almost certainly has a barrier lower than 50 kJmol^{-1} and should be a very fast process above 100°C . Rotation around the polarized carbon-carbon double bond in **1**, on the other hand, is expected to have a quite high barrier. Thus we attribute the observed ^1H dynamic NMR effect to the latter process.

References and Notes

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2. Kolle, U., Kolb, B. and Mannschreck, A. *Chem. Ber.*, **1980**, *113*, 2545; Sandström, J. *Acc. Chem. Res.*, **1985**, *18*, 148; Sjöstrand, U. and Sandström, J. *Tetrahedron*, **1978**, *34*, 3305.
3. Fischer, G., Rudolf, W. -D. and Kleinpeter, E. *Magn. Reson. Chem.*, **1991**, *29*, 212.
4. Compound **1** was prepared by known methods (McIntee, M. E. and Pinder, A. R. *J. Chem. Soc.*, **1957**, 4419) and identified as deep yellow crystals m.p. 85°C (cyclohexane), ^1H NMR (CDCl_3) δ : 2.38 and 2.41 (6H, 2s, 2 CH_3), 3.10 (6H, s, NMe_2), 6.67 (2H, d $J=9.0 \text{ Hz}$, arom CH), 7.80 (2H, d $J=9.0 \text{ Hz}$, arom CH), 7.42 (1H, s, CH). ^{13}C NMR (CDCl_3) δ : 25.86 and 31.35 (2 CH_3), 39.62 (NMe_2), 111.41 (arom CH), 119.47(C), 131.97(arom CH), 137.31(C), 140.77 (CH), 151.64 (C-N), 196.11 and 206.78 (2 C=O).
5. Proton and carbon-13 NMR spectra were recorded on a Jeol JNM-EX90 FT NMR spectrometer operating at a field of 21.15 kG. The temperature of the probe was adjusted with a temperature control unit using a heating element. To reach the equilibrium temperature, each sample tube was left in the probe for at least 5 min before measurement.
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8. We have studied the temperature dependence of the methyl region of the ^{13}C NMR spectrum of **1** in nitrobenzene as a solvent. Although the $\Delta \nu$ value of the acetyl CH_3 resonances slightly decreased with increasing temperature, two fairly sharp signals was still visible at 190°C , the highest temperature investigated.