PROTON MAGNETIC RESONANCE IN COUMARINS

BY S. S. DHARMATTI, F. A. Sc., G. GOVIL, C. R. KANEKAR,
C. L. KHETRAPAL AND Y. P. VIRMANI

(Tata Institute of Fundamental Research and Atomic Energy Establishment,
Trombay, Bombay-5)

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ABSTRACT

The high resolution proton magnetic resonance spectra of AB, ABC and ABCD systems in fourteen coumarins have been studied. Chemical shifts and spin coupling constants for the protons in various positions in the benzo-α-pyrone ring have been obtained. The spectrum of coumarin confirms the ethylenic nature of double bond between carbon atoms in positions 3 and 4. The chemical shifts for the phenyl protons are in conformity with the reactivities of the coumarins at various positions in the ring. A linear relation has been observed between the chemical shift for proton in 8 position in various 6 substituted coumarins and the Hammett's constants (σ) for substituents in the meta position. The NMR spectra offer a very convenient method for distinguishing between 3 and 4 substituted coumarins on account of the large chemical shift for the protons in positions 3 and 4.

The results do not substantiate resonance of the naphthalene type in coumarin as suggested to explain its dipole moment.

INTRODUCTION

Not much work seems to have been reported in literature on the nuclear magnetic resonance spectra of heterocyclic compounds. The work described in this paper was undertaken with a view to get an insight into the structure of benzo-α-pyrone ring (I) specially with regard to the nature of the double bond between carbon atoms in positions 3 and 4 and to understand the chemical reactivity of these compounds at different positions in the ring.
in presence of various substituents from the study of the chemical shifts of the various protons. In this investigation, it may be noticed that the spectra belong to any of the systems AB, ABC and ABCD (Pople, Schneider and Bernstein, 1959).

**EXPERIMENTAL**

**Chemicals.**—Coumarin used in this work was Rhodia's 100% pure product. *Ortho-*coumaric acid was obtained from Hopkins and Williams Ltd. and was used after crystallisation from hot water. Samples of 3 and 4 phenyl coumarins were kindly supplied by Professor T. R. Seshadri, F.R.S., of Delhi University. Samples of various hydroxy coumarins were provided to us by Professor S. M. Sethna of Baroda University. 6-Nitro coumarin, coumarin 6-sulphonic acid (sodium salt), coumarin-6 aldehyde and 6-amino coumarin were prepared in the laboratory and purified by standard methods given in literature (Clayton, 1910; Sen and Chakravarty, 1928; Sen and Chakravarty, 1928; Morgan, 1904). The purity of all the samples was determined from their melting points.

**NMR Measurements.**—The spectra were recorded in solution on Varian Associates' High Resolution Spectrometer. All the compounds (except sodium salt of coumarin-6 sulphonic acid) were dissolved in tetra-hydrofuran so as to make a saturated solution in each case. Coumarin-6 sodium sulphonate was dissolved in D₂O. In each case nitrogen gas was bubbled through the solution to drive off any dissolved oxygen.

The spectra were obtained both at 30 Mc./s. and 60 Mc./s. in order to confirm the assignments of the chemical shifts. The frequencies were measured by the usual side-band technique relative to cyclo-hexane used as an internal standard except in coumarin-6 sodium sulphonate in which H₂O was used as internal standard and later the frequencies were converted to the cyclo-hexane standard for the sake of uniformity. Some of the spectra had to be taken at a relatively high R.F. power and with fast scanning, the two factors varying from sample to sample depending upon the solubilities of the compounds. The resolution, therefore, ranges from 0.3 c./s. for compounds having high solubility to 1.5 c./s. for samples with relatively poor solubility.

**RESULTS AND DISCUSSION**

1. *Spectrum of coumarin.*—The high resolution proton magnetic resonance spectrum of coumarin at 60 Mc./s. is shown in Fig. 1. A spectrum of this molecule observed at 30 Mc./s has been reported earlier (Dharmatti...