

# PROTON MAGNETIC RESONANCE IN COUMARINS

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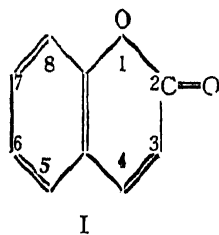
## ABSTRACT

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- $\alpha$ -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 ( $\sigma$ ) 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- $\alpha$ -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  $D_2O$ . 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  $H_2O$  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

*et al.*, 1960); the resolution achieved at 60 Mc./s. is certainly better and spectrum is therefore amenable for more detailed analysis (Govil *et al.*, 1961). From the intensity and the line separations, the first two and the last two lines can be readily identified as a quartet of the AB type arising from protons attached to carbon atoms in positions 3 and 4. The first two lines of the quartet probably arise from proton in 4 position as it is  $\beta$  to carbonyl

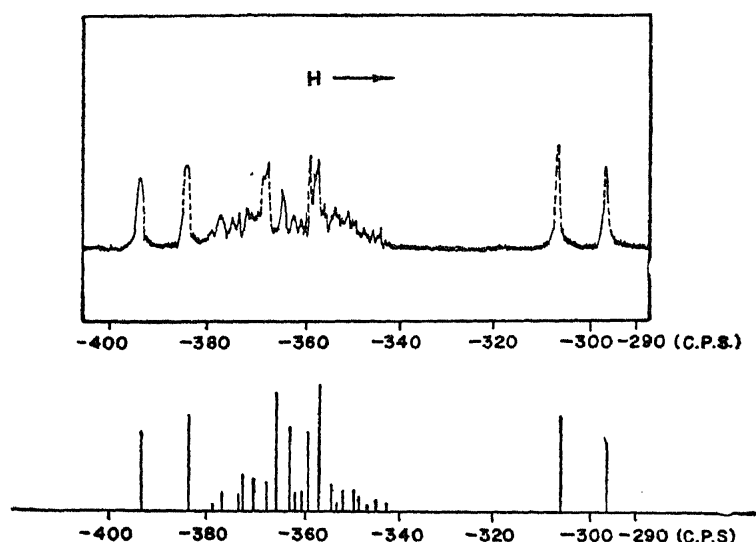


FIG. 1. Observed and calculated spectra of coumarin (frequencies are relative to cyclohexane as an internal standard).

group and  $\alpha$  to the phenyl group. The quartet was fully analysed on the AB theory and the values for the chemical shifts for the two protons (relative to cyclohexane) and spin coupling constant ( $J_{34}$ ) thus obtained are given in Table I. The remaining lines can then be ascribed to the four protons attached to the phenyl part of the benzo- $\alpha$ -pyrone ring. These form a system of the ABCD type.

The secular equation for this system set up on the basis of the usual Hamiltonian,

$$H = \sum_i \nu_i I_z(i) + \sum_{i < j} J_{ij} I_i \cdot I_j$$

gets factorised into two  $1 \times 1$ , two  $4 \times 4$  and one  $6 \times 6$  matrices. Table II gives the diagonal and non-diagonal matrix elements for the ABCD system. The eigen-values and the *ortho*-normalised eigen-vectors corresponding to  $4 \times 4$  and  $6 \times 6$  matrices could be obtained for any set of numerical values of  $\nu_s$  and  $J_s$  using our digital computer (TIFRAC). There are 56 allowed transitions for such a system out of which 24 are the combination transitions. The frequencies and the intensities of the allowed

TABLE I  
Chemical shifts and coupling constants

No.	Compound	Chemical shifts in p.p.m. relative to cyclo-hexane								Coupling constants in c./s.							
		$\delta_3$	$\delta_4$	$\delta_5$	$\delta_6$	$\delta_7$	$\delta_8$	$J_{34}$	$J_{56}$	$J_{57}$	$J_{58}$	$J_{67}$	$J_{68}$	$J_{78}$			
1.	Coumarin	..	-5.03	-6.48	-6.31	-5.90	-6.13	-5.88	9.8	8.5	2.0	0.0	8.6	1.8	8.5		
2.	3-Phenyl 7, 8-dihydroxy coumarin	..	-6.57		Not analysed			..	..	..	..	..	..	..	..		
3.	3-Phenyl 7, 8-dimethoxy coumarin	..	-6.55		Not analysed			..	..	..	..	..	..	..	..		
4.	4-Phenyl-6, 7-dimethoxy coumarin	-4.65	..		Not analysed			..	..	..	..	..	..	..	..		
5.	4-Phenyl-6, 7-dihydroxy coumarin	-4.60	..		Not analysed			..	..	..	..	..	..	..	..		
6.	5-Hydroxy-4-methyl coumarin	-4.50	..	..	-5.18	-5.80	-5.20	..	..	..	..	8.3	2.5	8.3			
7.	6-Hydroxy-4-methyl coumarin	-4.66	..	-5.59	..	-5.59	-5.59							Not analysed			
8.	7-Hydroxy-4-methyl coumarin	-4.57	..	-6.05	-5.34	..	-5.18	..	8.6	..	0.0	..	2.0	..			
9.	7-Hydroxy coumarin	-4.61	-6.22	-5.89	-5.23	..	-5.18	9.8	8.8	..	0.0	..	2.5	..			

10. 8-Hydroxy coumarin	-4.80	-6.36	-5.54	-5.54	..	10.0	..	..	..	..
11. 6-Nitro coumarin	..	-5.10	-6.60	-7.16	..	-7.00	-6.10	9.9	2.4	0.0
12. Na salt of coumarin-6-sulphonic acid	-5.04	-6.48	-6.55	-6.51	-5.86	9.4	2.1	0.0	..	9.4
13. Coumarin-6-aldehyde	-4.97	-6.63	-6.48	-6.48	-5.97	10.4	..	0.0	..	10.2
14. 6-Amino coumarin	-4.81	-6.23	-5.44	-5.49	-5.58	8.7	2.6	0.0	..	8.5
15. 0-Coumaric acid	..	-5.11	-6.60	Not analysed for this part						

TABLE II

Diagonal and non-diagonal elements for the matrix of ABCD system

TABLE II DIAGONAL AND NON-DIAGONAL ELEMENTS FOR THE MATRIX OF ABCD SYSTEM.				
NO.	F <sub>z</sub>	BASIC WAVE FUNCTION	DIAGONAL ELEMENTS OF THE MATRIX.	OFF-DIAGONAL MATRIX ELEMENTS.
1	+2	α α α α α	$\frac{1}{2}(\nu_A + \nu_B + \nu_C + \nu_D) + \frac{1}{4}(J_{AB} + J_{AC} + J_{AD} + J_{BC} + J_{BD} + J_{CD})$	
2	+1	α α α α β	$\frac{1}{2}(\nu_A + \nu_B + \nu_C - \nu_D) + \frac{1}{4}(J_{AB} + J_{AC} - J_{AD} + J_{BC} - J_{BD} - J_{CD})$	H <sub>23</sub> = H <sub>32</sub> = $\frac{1}{2}J_{CD}$
3		α α β α α	$\frac{1}{2}(\nu_A + \nu_B - \nu_C + \nu_D) + \frac{1}{4}(J_{AB} - J_{AC} + J_{AD} - J_{BC} + J_{BD} - J_{CD})$	H <sub>24</sub> = H <sub>42</sub> = $\frac{1}{2}J_{BD}$ H <sub>45</sub> = H <sub>54</sub> = $\frac{1}{2}J_{AB}$
4		α β α α α	$\frac{1}{2}(\nu_A - \nu_B + \nu_C + \nu_D) + \frac{1}{4}(-J_{AB} + J_{AC} + J_{AD} - J_{BC} - J_{BD} + J_{CD})$	H <sub>25</sub> = H <sub>52</sub> = $\frac{1}{2}J_{AD}$
5		β α α α α	$\frac{1}{2}(-\nu_A + \nu_B + \nu_C + \nu_D) + \frac{1}{4}(-J_{AB} - J_{AC} - J_{AD} + J_{BC} + J_{BD} + J_{CD})$	H <sub>34</sub> = H <sub>43</sub> = $\frac{1}{2}J_{BC}$ H <sub>35</sub> = H <sub>53</sub> = $\frac{1}{2}J_{AC}$
6		0	α α β β β	$\frac{1}{2}(\nu_A + \nu_B - \nu_C - \nu_D) + \frac{1}{4}(J_{AB} - J_{AC} - J_{AD} - J_{BC} - J_{BD} + J_{CD})$
7	α β α β β		$\frac{1}{2}(\nu_A - \nu_B + \nu_C - \nu_D) + \frac{1}{4}(-J_{AB} + J_{AC} - J_{AD} - J_{BC} + J_{BD} - J_{CD})$	H <sub>610</sub> = H <sub>106</sub> = $\frac{1}{2}J_{AD} = H_{711} = H_{117}$
8	α β β α β		$\frac{1}{2}(\nu_A - \nu_B - \nu_C + \nu_D) + \frac{1}{4}(-J_{AB} - J_{AC} + J_{AD} + J_{BC} - J_{BD} - J_{CD})$	H <sub>611</sub> = H <sub>116</sub> = H <sub>710</sub> = H <sub>107</sub> = H <sub>89</sub> = H <sub>98</sub> = 0
9	β α α β β		$\frac{1}{2}(-\nu_A + \nu_B + \nu_C - \nu_D) + \frac{1}{4}(-J_{AB} - J_{AC} + J_{AD} + J_{BC} - J_{BD} - J_{CD})$	H <sub>78</sub> = H <sub>87</sub> = H <sub>910</sub> = H <sub>109</sub> = $\frac{1}{2}J_{CD}$
10	β α β α β		$\frac{1}{2}(-\nu_A + \nu_B - \nu_C + \nu_D) + \frac{1}{4}(-J_{AB} + J_{AC} - J_{AD} - J_{BC} + J_{BD} - J_{CD})$	H <sub>79</sub> = H <sub>97</sub> = H <sub>810</sub> = H <sub>108</sub> = $\frac{1}{2}J_{AB}$
11	β β α α β		$\frac{1}{2}(-\nu_A - \nu_B + \nu_C + \nu_D) + \frac{1}{4}(J_{AB} - J_{AC} - J_{AD} - J_{BC} - J_{BD} + J_{CD})$	
12	-1	α β β β β	$\frac{1}{2}(\nu_A - \nu_B - \nu_C - \nu_D) + \frac{1}{4}(-J_{AB} - J_{AC} - J_{AD} + J_{BC} + J_{BD} + J_{CD})$	H <sub>1213</sub> = H <sub>1312</sub> = $\frac{1}{2}J_{AB}$
13		β α β β β	$\frac{1}{2}(-\nu_A + \nu_B - \nu_C - \nu_D) + \frac{1}{4}(-J_{AB} + J_{AC} + J_{AD} - J_{BC} - J_{BD} + J_{CD})$	H <sub>1214</sub> = H <sub>1412</sub> = $\frac{1}{2}J_{AC}$
14		β β α β β	$\frac{1}{2}(-\nu_A - \nu_B + \nu_C - \nu_D) + \frac{1}{4}(J_{AB} - J_{AC} + J_{AD} - J_{BC} + J_{BD} - J_{CD})$	H <sub>1215</sub> = H <sub>1512</sub> = $\frac{1}{2}J_{AD}$
15		β β β α β	$\frac{1}{2}(-\nu_A - \nu_B - \nu_C + \nu_D) + \frac{1}{4}(J_{AB} + J_{AC} - J_{AD} + J_{BC} - J_{BD} - J_{CD})$	H <sub>1314</sub> = H <sub>1413</sub> = $\frac{1}{2}J_{BC}$ H <sub>1315</sub> = H <sub>1513</sub> = $\frac{1}{2}J_{BD}$ , H <sub>1415</sub> = H <sub>1514</sub> = $\frac{1}{2}J_{CD}$
16	-2	β β β β β	$\frac{1}{2}(-\nu_A - \nu_B - \nu_C - \nu_D) + \frac{1}{4}(J_{AB} + J_{AC} + J_{AD} + J_{BC} + J_{BD} + J_{CD})$	

transitions (e.g., for ΔF<sub>z</sub> = ± 1) are given in Table II a. The frequencies

TABLE II a

Frequencies and intensities of the allowed transitions in an ABCD system

TABLE II a FREQUENCIES AND INTENSITIES OF THE ALLOWED TRANSITIONS IN AN ABCD SYSTEM.								
TRANSITION	No. OF LINES	FREQUENCY	INTENSITY	GROUP				
				A	B	C	D	Comb.
E <sub>i</sub> <sup>(2)</sup> → E <sub>i</sub> <sup>(1)</sup> i = 2, 3, 4, 5	4	E <sub>i</sub> - E <sub>i</sub>	(C <sub>11</sub> + C <sub>12</sub> + C <sub>13</sub> + C <sub>14</sub> ) <sup>2</sup>	1 → 5	1 → 4	1 → 3	1 → 2	—
E <sub>i</sub> <sup>(1)</sup> → E <sub>j</sub> <sup>(0)</sup> j = 6, 7, 8, 9, 10, 11	24	(E <sub>i</sub> - E <sub>j</sub> )	[C <sub>11</sub> (C <sub>j1</sub> + C <sub>j2</sub> + C <sub>j4</sub> ) + C <sub>12</sub> (C <sub>j1</sub> + C <sub>j3</sub> + C <sub>j5</sub> ) + C <sub>13</sub> (C <sub>j2</sub> + C <sub>j3</sub> + C <sub>j6</sub> ) + C <sub>14</sub> (C <sub>j4</sub> + C <sub>j5</sub> + C <sub>j6</sub> )] <sup>2</sup>	2 → 9 3 → 10 4 → 11	2 → 7 3 → 8 5 → 11	2 → 6 4 → 8 5 → 10	3 → 6 4 → 7 5 → 9	12 LINES
E <sub>j</sub> <sup>(0)</sup> → E <sub>k</sub> <sup>(-1)</sup> k = 12, 13, 14, 15	24	E <sub>j</sub> - E <sub>k</sub>	[C <sub>j1</sub> (C <sub>k1</sub> + C <sub>k2</sub> ) + C <sub>j2</sub> (C <sub>k1</sub> + C <sub>k3</sub> ) + C <sub>j3</sub> (C <sub>k1</sub> + C <sub>k4</sub> ) + C <sub>j4</sub> (C <sub>k2</sub> + C <sub>k3</sub> ) + C <sub>j5</sub> (C <sub>k2</sub> + C <sub>k4</sub> ) + C <sub>j6</sub> (C <sub>k3</sub> + C <sub>k4</sub> )] <sup>2</sup>	6 → 13 7 → 14 8 → 15	6 → 12 9 → 14 10 → 15	7 → 12 9 → 13 11 → 15	8 → 12 10 → 13 11 → 14	12 LINES
E <sub>k</sub> <sup>(-1)</sup> → E <sub>16</sub> <sup>(-2)</sup>	4	E <sub>k</sub> - E <sub>16</sub>	(C <sub>k1</sub> + C <sub>k2</sub> + C <sub>k3</sub> + C <sub>k4</sub> ) <sup>2</sup>	12 → 16	13 → 16	14 → 16	15 → 16	—

HERE C<sub>1q</sub> REPRESENTS THE COEFFICIENTS OF THE BASIC PRODUCT FUNCTION Φ<sub>q</sub>, THE LINEAR COMBINATIONS OF WHICH FORM THE STATIONARY STATE WAVE FUNCTION Φ<sub>l</sub>, CORRESPONDING TO EIGEN VALUE E<sub>l</sub> (l = i, j or k) IN E<sub>l</sub><sup>(s)</sup> REPRESENTS THE TOTAL SPIN OF THE STATE.

and the intensities of the various lines shown in Table III for coumarin have been obtained by trial and error calculations using different chemical

TABLE III

*Calculated and observed spectra of the four phenyl protons in coumarin (ABCD system)*

No.	Group	Frequency		Intensity	
		Calculated cps.	Observed cps.	Calculated	Observed
3	C	-379.2	-379.1	0.30	.35
4	Comb	-377.5	-377.0	0.16	.80
	A	-376.6		0.35	
	C	-376.5		0.32	
5	A	-375.7	-375.0	0.11	.30
6	A	-372.8	-373.8	0.68	.50
7	C	-372.2	-371.6	0.61	1.00
	A	-372.2		0	
	C	-372.3		0.43	
	A	-372.8		0.68	
8	Comb	-370.5	-370.2	0.59	1.00
	C	-370.1		0.88	
9	A	-368.2	-368.3	0.38	.80
	C	-368.6		0.40	
	Comb	-366.9		0.58	
10	A	-365.7	-366.0	2.55	3.60
	A	-365.6		1.85	
	Comb	-365.2		0.93	
11	A	-363.5	-363.8	0.15	3.30
	C	-363.0		3.74	

TABLE III—(Contd.)

No.	Group	Frequency		Intensity	
		Calculated cps.	Observed cps.	Calculated	Observed
12	B	-361.6	-361.5	0.90	.90
13	C	-360.4	-359.9	0.80	0.70
14	B	-358.8	-358.0	3.67	3.60
15	B	-357.3	-356.0	0.60	4.20
	D	-356.1		1.79	
	D	-356.2		2.46	
	D	-356.4		1.02	
16	B	-354.5	-354.0	0.73	1.20
	D	-353.5		0.45	
17	Comb.	-352.8	-352.5	0.28	0.60
	Comb.	-352.8		0.11	
18	B	-351.6	-351.6	0.84	0.60
19	B	-349.5	-349.5	0.43	.90
	D	-349.3		0.59	
20	D	-348.6	-348.0	0.72	.60
21	D	-346.4	-346.2	0.34	.30
22	B	-345.2	-344.5	0.28	.30
	D	-344.2		0.21	
23	B	-342.7	-343.0	0.31	0.30

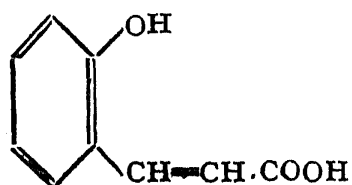


Other combination lines of very weak intensities (calculated) are as follows:

Frequency	Intensity	Frequency	Intensity
-354.8	0.00	-367.0	0.00
-385.6	0.01	-368.7	0.09
-346.0	0.06	-326.0	0.00
-347.9	0.01	-370.9	.08
-390.5	0.01	-339.5	0.00
-358.2	0.06	-382.2	0.00
-331.2	0.00	-349.5	0.00
-373.5	0.00	-395.8	0.00
-335.8	0.01		

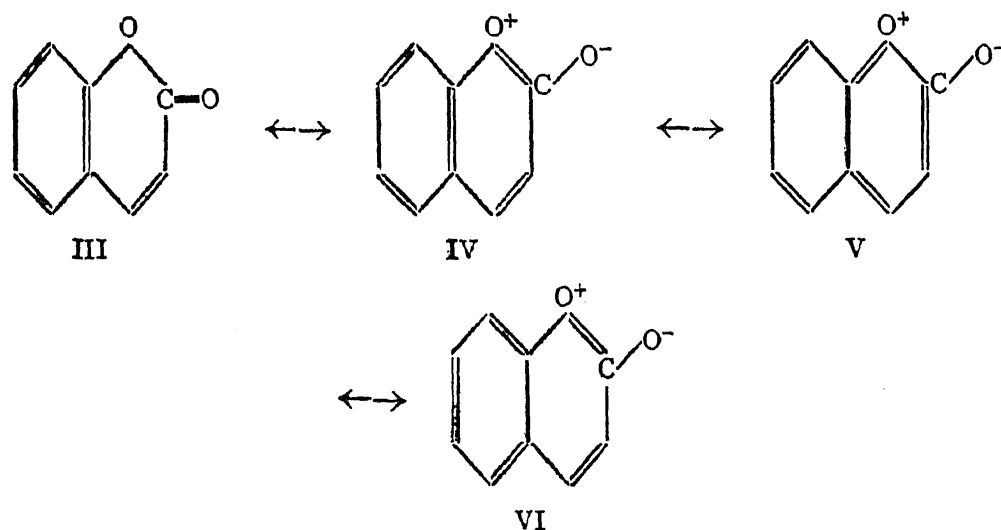
shifts and coupling constants until a good fit between the observed and the calculated spectra was observed. The values of the various chemical shifts and the coupling constants given in Table I were found to give a satisfactory agreement between the observed and the calculated spectra for the ABCD protons in coumarin. Table III shows the theoretical and experimental values of the intensities and resonance frequencies for the various lines in the ABCD spectrum of coumarin. The error in the observed values is of the order of  $\pm 0.3$  c./s.

The values of the chemical shifts for protons in 3 and 4 positions in coumarin are nearly the same as those observed for ethylenic protons in *ortho*-coumaric acid structure II ( $-5.11$  and  $-6.60$  p.p.m. respectively).



II

This indicates that the double bond between carbon atoms in positions 3 and 4 is predominantly ethylenic in nature. M. A. Govinda Rao (1936) and Lewis (1951) have proposed a resonance of the type



to explain the dipole moment of coumarin and its failure to copolymerise. The resonance structures of the type IV to VI should give rise to ring currents in the  $\alpha$ -pyrone ring and this would cause less shielding of protons in 3 and 4 positions by an amount  $\Delta\sigma$  (10 b)

$$\Delta\sigma = -\frac{e^2a^2}{2mc^2R^3}$$

where  $a$  = radius of the ring and  $R$  is the distance of the proton from the centre of the ring. With reasonable values of  $a = 1.4 \text{ \AA}$  and  $R = 2.5 \text{ \AA}$  one gets a value for  $\Delta\sigma = -1.75 \text{ p.p.m.}$  Using refined method of Waugh and Fessenden (1957) in which a mean value of  $R$  is chosen for both circular and elliptical currents one gets  $\Delta\sigma = -2.2 \text{ p.p.m.}$  almost equal to the above value.

The chemical shifts for the protons in 3 and 4 positions for structure (III) should be very nearly the same as those for the corresponding protons in *ortho*-coumaric acid (II) ( $-5.11$  and  $-6.60 \text{ p.p.m.}$ ). The chemical shifts for the corresponding protons in structures IV, V and VI should be different from those in structure (III) by an amount  $\Delta\sigma$  and hence should have the values  $-7.31$  and  $-8.80 \text{ p.p.m.}$  If resonance occurs among all these structures one expects a weighted average of the chemical shifts for all these structures and hence much lower than  $-5.11$  and  $-6.60 \text{ p.p.m.}$  for the two protons. But the observed higher values  $-5.03$  and  $-6.48 \text{ p.p.m.}$  for these protons in coumarin molecule indicate negligible resonance of the type shown above.

From the values of the coupling constants, it is easily seen that the *ortho*-coupling constants for the protons in the phenyl part of the benzo- $\alpha$ -pyrone ring have nearly the same values as those observed for protons in substituted benzenes.  $J_{34}$  in coumarins has, however, a larger value

but closer to the coupling constant observed for ethylenic protons attached to phenyl ring (Bishop and Richards, 1960). The differing values of  $J_{cis}$  (8–12 cps.) and  $J_{trans}$  (15–18 cps.) observed for ethylenic and vinyl compounds (1) confirm that the protons in position 3 and 4 ( $J_{34} = 9.8$ ) in coumarin are *cis* to each other.

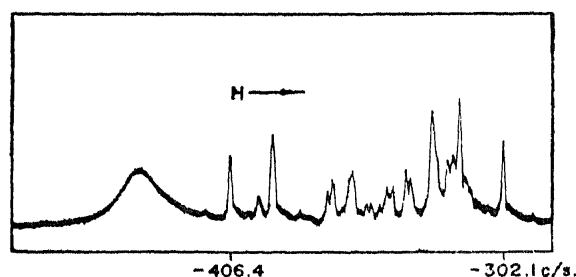


FIG. 2. NMR spectrum of O-coumaric acid. (Frequencies are relative to cyclo-hexane at 60 Mc./s.).

2. *Identification of 3 and 4 substituted coumarins by NMR.*—The widely different chemical shifts of protons in 3 and 4 positions in coumarin enables one to distinguish between 3 and 4 substituted coumarins from their proton resonance spectra. When 3 position is substituted for example by phenyl group, the lines at  $-4.96$  and  $-5.10$  p.p.m. found in coumarin disappear and one gets in addition to the lines due to phenyl protons a single line at about  $-6.50$  p.p.m. having intensity corresponding to 1 proton per molecule. On the other hand, in 4 phenyl coumarin, a singlet is observed at about  $-5.03$  p.p.m. in addition to the usual lines for the phenyl protons. Table I (rows 2 and 5) gives the results of the analysis of NMR spectra of four such phenyl coumarins. Typical spectrum of the later type has also been given in Fig. 3. The ease with which NMR can distinguish between 3 and 4 substituted coumarins is noteworthy. The conventional chemical methods used generally for distinguishing these isomers depend upon the opening of the ring and are, therefore, quite cumbersome and sometimes not reliable.

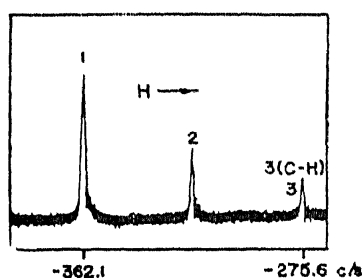


FIG. 3. NMR Spectrum of 4-phenyl, 6:7-Dihydroxy coumarin (at 60 Mc./s., (Frequencies are relative to cyclo-hexane) (Peak No. 3 is due to proton in position 3),

3. *Substituted coumarins*.—The spectra of a number of substituted coumarins have been studied and some typical spectra have been shown in Figs. 4 and 5. When the substitution of various groups is made in the phenyl part of the coumarin nucleus, the spectra become more simple and are of the type ABC (e.g., *mono-substituted coumarins*).

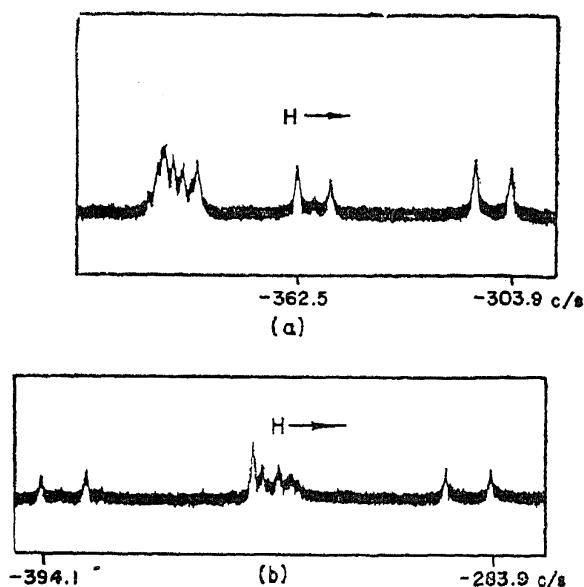


FIG. 4. NMR spectra of 6-substituted coumarins. (a) Coumarin 6-sodium sulphonate. b) 6-Amino coumarin. (At 60 Mc./s. relative to cyclo-hexane).

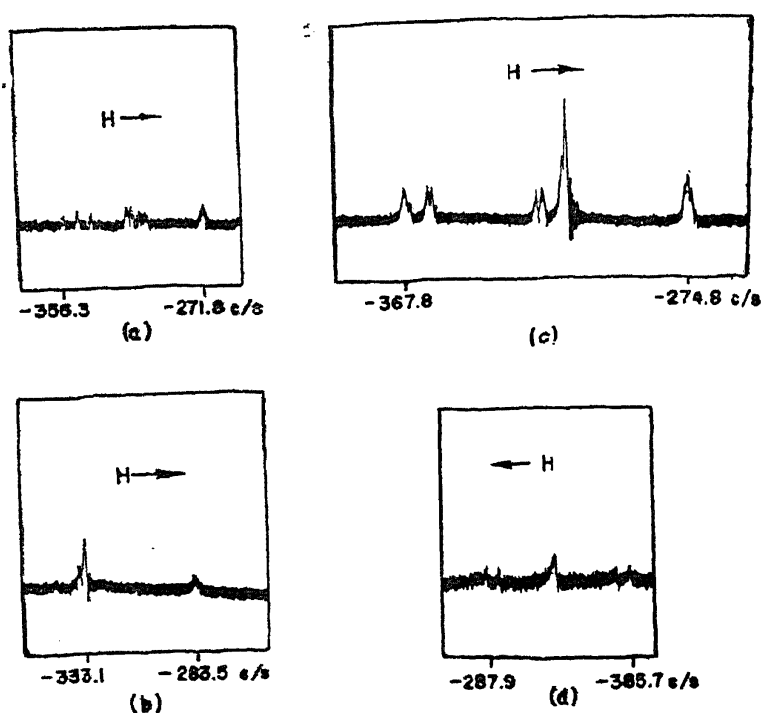


FIG. 5. NMR spectra of hydroxy coumarins. (a) 5-Hydroxy, 4-methyl. (b) 6-Hydroxy, 4-Methyl. (c) 7-Hydroxy, 4-methyl. (d) 8-Hydroxy. (Frequencies are relative to cyclo-hexane at 60 Mc./s.).

The explicit expressions obtained by Jha (1961) for an ABC system were used to analyse the phenyl part of the spectra of hydroxy and 6-substituted coumarins. The part of the spectrum arising from protons in 3 and 4 positions was analysed on the usual AB theory. The results obtained for the various chemical shifts and the coupling constants are given in Table I. These results also confirm the ethylenic character of the double bond between carbon atoms in positions 3 and 4.

The chemical shifts for the various protons give information regarding their relative shielding and hence in a rough way relative electron densities at the proton sites. It is obvious that for a reaction with electrophilic reagent the most reactive position is the one at which the electron density is the highest and *vice versa*. Several organic chemists have studied the effect of substitution on the reactivity at various positions in the ring and their results have been interpreted by Thakore and Shah (1947) in terms of electron displacements when substitution is made at different positions. An attempt was therefore made to find a correlation if any between the reactivity of various coumarins and the chemical shifts. In unsubstituted coumarin the shifts decrease in the order  $\delta_8 \approx \delta_6 > \delta_7 > \delta_5$ . This means the shielding decreases in the same order. The chemical data show that the reactivity is more for 8 and 6 positions while it is less for 7 and 5 positions. In the 5-hydroxy 4-methyl coumarin the chemical shift data show that the shielding changes in the order  $\delta_6 > \delta_8 > \delta_7$ ; the reactivity is found to follow the same order (13). For other hydroxy coumarins such a comparison was not possible in the absence of the data on reactivities; but the chemical shift data should act as a rough guide in predicting the reactivity.

The effect of substitution of groups of different electron withdrawing and electron donating powers on the chemical shift was also studied. Since 6 position is the most reactive in coumarins, the 6 substituted derivatives were chosen. When the 6 position is substituted by an electron donating group, positions 5 and 7 are found to be more reactive while if the substituent is electron withdrawing 5 and 7 positions become less reactive than position 8. The electron density of the ring as a whole also decreases when the substituent is electron withdrawing and *vice versa*. These trends can be readily confirmed from Table I by the chemical shift data for the various protons under consideration in these derivatives.

The chemical shifts of the protons in 5 and 7 positions will be affected by (a) resonance, (b) inductive and (c) steric effects of the substituent. An effective measure of (a) and (b) is the Hammett's constant ( $\sigma$ ). But it is not always easy to estimate the steric effect. However, the situation is

slightly simplified for proton in position 8 in which the steric effects will be negligible. Hence, one expects a correlation between  $\delta_8$  and  $\sigma_m$  for the various 6 substituted coumarins. Such a correlation is shown in a

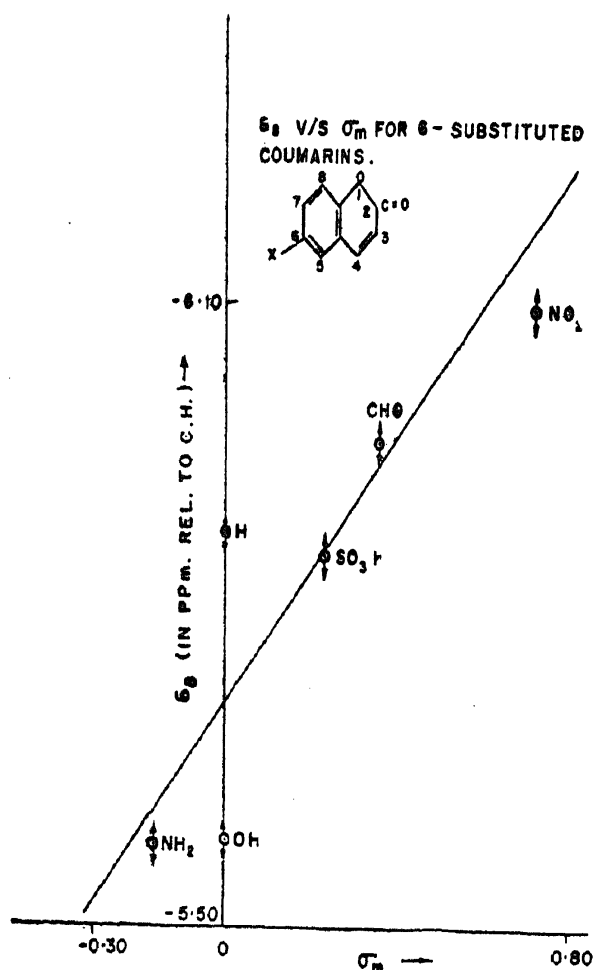


FIG. 6.

(Fig. 6) of  $\delta_8$  and  $\sigma_m$  which is nearly linear (except for H and OH). The values of  $\sigma_m$  are taken from the work of Jaeffe (1953).

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