

324. *The Nuclear Magnetic Resonance of Heterocyclic Systems.
Part I. Pyrylium Salts.*

By A. T. BALABAN, G. R. BEDFORD, and A. R. KATRITZKY.

Chemical shifts and spin-spin coupling constants are presented and discussed for a series of alkyl- and aryl-substituted pyrylium salts.

ALTHOUGH a large proportion of organic chemistry papers now contain some proton resonance data, relatively little systematic work has been devoted to heterocyclic systems.¹ This series of Papers will deal with the characteristic chemical shifts and coupling constants of protons of heteroaromatic rings and their substituent groups, and the effects of interaction between ring and substituent. The present Paper records work for pyrylium salts, the synthesis² and infrared spectra³ of which were previously discussed by one of us. The only previous reference to the proton spectra of pyrylium salts appears to be ref. 4.

The spectra (Table 1) were obtained as solutions in liquid sulphur dioxide of perchlorate salts. Measurements of some tetrafluoroborates and hexachloroantimonates indicated that the anion had little effect, cf. Table 1 compounds 1 and 2, 17 and 18, 24 and 25. The

¹ For a review see White in "Physical Methods in Heterocyclic Chemistry, Vol. II" (ed. Katritzky), Academic Press, London, 1963.

² Balaban and Nenitsescu, *Studii si Ceretări Chim Acad. R.P.R.*, 1961, **9**, 251; *Rev. de Chim. (Acad. R.P.R.)*, 1961, **6**, 269.

³ Balaban, Mateescu, and Elian, *Tetrahedron*, 1962, 1083.

⁴ LeGoff and LaCount, *J. Amer. Chem. Soc.*, 1963, **85**, 1354.

ranges given in the text are quoted for the perchlorates. A paramagnetic anion (FeCl_4^-) caused line broadening as expected.



Aromatic Protons.— β -Protons of the alkyl-substituted pyrylium ring (I) cause absorption at τ 2.02–2.30. Compounds with only primary or secondary alkyl substituents resonate in the upper part of this range, those with *t*-butyl groups in the lower part. β -Protons in phenyl-substituted pyrylium salts probably also absorb at *ca.* 2.1, but interpretation is difficult because of overlap with the benzenoid proton signals. γ -Protons on the pyrylium ring resonate at τ 1.5 (No. 10) and τ 1.14 (No. 29). The $\beta\gamma$ -coupling constant in No. 29 is 7.1 c./sec. The only compound available with α -protons is the unsubstituted ring; the A_2B_2C system of this has not yet been elucidated, but the α , β , and γ protons obviously resonate at approximately τ 0.4, 1.5, and 0.7, respectively. Comparison of these figures with the value 2.8–3.3 typical⁵ for the ring protons of alkyl-substituted benzenes indicates that any reduction in the ring current caused by substitution of an oxygen atom for CH is more than outweighed by the deshielding effect of the positive charge. In a previous Paper,⁶ chemical shifts of protons β to the cyclic heteroatom were shown to lie at fields decreasing in the order benzene > pyridine > pyridine 1-oxide > pyridinium ion > 1-hydroxypyridinium ion. The present results indicate that in this respect the pyrylium ring resembles the previous cationic systems. 1,2,4,6-Tetramethylpyridinium perchlorate showed the β -proton peak at 2.38 in liquid sulphur dioxide.

Methyl Groups.— α -Methyl groups absorb at τ 7.04–7.13 for trialkyl derivatives and at τ 6.87–6.99 for compounds with phenyl groups, except that one of the methyl groups in compound (II) (No. 23) resonates at τ 7.19. This indicates that for this molecule an adjacent phenyl group takes up a position approaching perpendicular, relative to that of the pyrylium ring, and the ring current in the benzene ring shields the methyl group. For the single dialkylpyrylium salt available (No. 29), the peak occurred at τ 6.96; this low value may be partially due to the influence of the anion, cf. Table 1, compounds 1 and 2.

β -Methyl groups absorb at τ 7.50–7.57, except that the single compound (No. 27) containing phenyl groups in addition shows a β -methyl at τ 7.36. γ -Methyl groups are found at τ 7.17–7.29 for compounds without a phenyl group. One and two α -phenyl groups (*i.e.*, non-adjacent) cause low field shifts to τ 7.14 and 7.04–7.08, respectively, but the ring current of the β -phenyl group in compound No. 28 compensates for this and resonance is here found at τ 7.27.

Ethyl Groups [Table 2].—Compounds containing ethyl groups show the typical triplet-quadruplet pattern. For compounds without phenyl groups, the methylene shift is at τ 6.74–6.79 and 6.91–6.98 for α - and γ -ethyl groups, respectively. The corresponding methyl resonances are at τ 8.53–8.56 (except No. 12, which resonates at 8.76) and 8.60–8.61. The two available compounds containing phenyl groups (Nos. 21 and 26) show methylene and methyl resonance displaced appreciably to lower field: it is remarkable that this effect is transmitted so strongly to the methyl group. The $\text{CH}_2\text{-CH}_3$ coupling constant of 7.4–7.5 c./sec. is typical: the $\text{CD}_2\text{-CH}_3$ value of 1.1 c./sec. agrees well with the ratio of the magnetogyric ratios $\gamma_{\text{H}}/\gamma_{\text{D}} = 6.55$.

Other Alkyl Groups.—Isopropyl groups show the expected doublet-septet spectrum: CH occurs at τ 6.72 and 6.50 and CH_3 at 8.63 and 8.50 for the γ (No. 13) and α examples (No. 15), respectively. The coupling constant is 6.8–7.0 c./sec.

⁵ Pople, Schneider, and Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, 1959, p. 263.

⁶ Katritzky and Lagowski, *J.*, 1961, 43.

1648 *The Nuclear Magnetic Resonance of Heterocyclic Systems. Part I.*
 TABLE 1.
 Chemical shifts for pyrylium salts.

No.	Subst. at posn.					Concn. (% w/w)	Arom. protons β -	Methyl			<i>t</i> -Bu
	2	3	4	5	6			α	β	γ	
1	Me		Me		Me	10.0	2.23	7.10	—	7.26	
2*	Me		Me		Me	7.1	2.13	7.03	—	7.19	
3	CD ₃		CD ₃		CD ₃	3.2	2.25	—	—	—	
4	Me		Et		Me	4.7	2.20	7.06	—	—	
5	CD ₃		CD ₂ Me		CD ₃	3.2	2.26	—	—	—	
6	Et		Me		Me	2.7	2.20	7.08	—	7.23	
7	CD ₂ Me		CD ₃		CD ₃	2.1	2.20	—	—	—	
7a	Et		Me		Et	5.5	2.21	—	—	7.21	
8	Me	Me	Me		Me	3.5	2.26	{7.10 7.13}	7.57	7.31	
9	CD ₃	Me	CD ₃		CD ₃	2.5	2.22	—	7.55	—	
10	Me	Me		Me	Me	2.5	1.50 †	7.10	7.50	—	
11	Et	Me	Me		Et	6.0	2.23	—	7.56	7.29	
12	Me	Me	Et	Me	Me	3.8	—	7.11	7.53	—	
13	Me		Pr ¹		Me	9.9	2.19	7.07	—	—	
14	Me		CH ₂ Bu [†]		Me	2.1	2.30 ‡	7.04	—	—	
15	Pr ¹		Me		Pr ¹	2.5	2.19	—	—	7.19	
16	Bu [†]		Me		Bu [†]	6.8	2.21	—	—	7.20	
17	Bu [†]		Me		Bu [†]	4.6	2.10	—	—	7.17	8.45
18*	Bu [†]		Me		Bu [†]	3.5	2.08	—	—	7.16	8.43
19	Me		Me		Ph	2.9	?	6.97	—	7.14	
20	Me		Ph		Me	4.9	?	6.99	—	—	
21	Et		Ph		Et	1.8	?	—	—	—	
22	Me	Ph	Ph		Me	2.7	?	{6.95 7.19}	—	—	
23	Ph		Ph		Me	0.6	?	6.87	—	—	
24	Ph		Me		Ph	1.3	?	—	—	7.04	
25*	Ph		Me		Ph	5.1	?	—	—	7.03	
26	Ph		Et		Ph	4.0	?	—	—	—	
27	Ph	Me	Me		Ph	8.9	?	—	7.36	7.08	
28	Ph	Ph	Me		Ph	2.9	?	—	—	7.27	
29*	Me				Me	5.7	2.02	6.96	—	—	
30	—	—	—		—	6.0	1.5	—	—	—	

* Anion: ClO₄⁻ except for Nos. 2 and 29, SbCl₆⁻, and Nos. 18 and 25, BF₄⁻. † Peak due to γ -proton, hardly distinguishable from noise. ‡ Broad.

The preparation of the salts is described in refs. 2 and 3 except for Nos. 14 and 28 (Balaban, *Tetrahedron Letters*, 1963, 91) and Nos. 3, 5, 7, and 9 (Balaban and Gird, unpublished work). We thank Dr. P. F. G. Prail for specimens of Nos. 10 and 12.

 TABLE 2.
 Peaks due to ethyl groups.

No.*	Posn. of Et	CH ₂ τ	CH ₃ τ	<i>J</i> (c./sec.)
4	4	6.91	8.61	7.5
5	4	(CD ₂)	8.60	1.1
6	2	6.79	8.55	7.4
7	2	(CD ₂)	8.54	1.1
7a	2, 6	6.78	8.53	7.5
11	2, 6	6.79, 6.74	8.56	7.4
12	4	6.98	8.76	7.5
21	2, 6	6.67	8.44	7.4
26	4	6.73	8.47	7.4

* See footnote in Table 1.

The one neopentyl compound (No. 14) shows peaks at 7.11 (CH₂) and 8.93 (CH₃): the methylene peak is a triplet ($J = 0.6$ c./sec.), indicating a small spin-spin coupling with the β -ring proton (the peak for which was itself broad) (cf. mesitylene⁷).

In the isobutyl compound (No. 16), CH₂ is found at τ 6.92 (doublet, $J = 7.5$ c./sec.) and CH₃ at 8.95 (doublet, $J = 7.0$ c./sec.); the (at least 9-line) patterns for the methine protons were not identified.

⁷ Hoffman, *Mol. Phys.*, 1958, **1**, 326.

[1964]

Lloyd and Wade.

1649

Experimental.—Spectra were obtained at 40 Mc./sec. on a Perkin-Elmer permanent-magnet spectrometer with sample spinning. Shifts are given on the τ scale (SiMe = 10 p.p.m.) against tetramethylsilane as internal standard.

We thank Imperial Chemical Industries Limited (Pharmaceuticals Division), for financial assistance.

INSTITUTE OF ATOMIC PHYSICS, BUCHAREST, RUMANIA (A. T. B.).
CHEMICAL LABORATORY, CAMBRIDGE (G. R. B., A. R. K.).

[Present address (A. R. K.): SCHOOL OF CHEMICAL SCIENCES,
UNIVERSITY OF EAST ANGLIA, NORWICH.]

[Received, August 29th, 1963.]
