THE ELECTRONIC SPECTRA AND ELECTRONIC STRUCTURES OF THE BENZYL CATION AND ITS METHYL DERIVATIVES

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Abstract—The electronic absorption spectra and NMR spectra of the benzyl cation and its methylderivatives were measured at room temperature and also at low temperatures. The π -electronic structure of the benzyl cation was studied theoretically by a method combining Roothaan's LCAO-SCF procedure with Pariser-Parr's approximation. The configuration interaction was considered for both singly and doubly excited configurations. Furthermore, concerning methyl substituted benzyl cation, the hyperconjugation effect of methyl groups was taken into account by the configurational interaction among the ground, charge-transfer and locally excited configurations.

From these experimental and theoretical studies, it was concluded that the electronic absorption spectra of the α, α -dimethylbenzyl-, $\alpha, \alpha, 2, 4, 6$ -pentamethylbenzyl-, 2,4,6-trimethylbenzyl- and 2,3,4,5,6pentamethylbenzyl-cations commonly show two absorption peaks in 300 and 400 m μ regions. These two bands were shown to be the intramolecular charge-transfer bands which are accompanied by a great amount of electron-transfer from the occupied orbitals of the benzene ring to the $2p\pi$ orbital of the carbon atom of the CH₃ or C(CH₃)₃ group. The observed absorption intensity of the shorter wavelength band was found to be six or seven times stronger than that of the longer wavelength band, completely satisfying the present theoretical expectation. The benzyl and α -methylbenzyl cations were found to be unstable even at low temperature and their spectra could not be observed.

CARBONIUM ions play an important role as intermediates in some organic reactions.¹ Some are stable under certain conditions (usually in strongly acidic solutions) and their electronic structures have been studied from both theoretical and experimental points of view.

Grace and Symons² showed that the electronic spectra of the benzyl cation has an absorption band at 470 m μ in concentrated sulfuric acid. Williams³ also studied the electronic absorption spectra of a number of carbonium ions in sulfuric acid. Deno *et al.*⁴ studied spectrophotometrically the equilibrium of some aryl carbonium ions. Williams and also Deno *et al.*, however, could not obtain reliable results for the benzyl cation itself.

Longuet-Higgins and Pople⁵ studied theoretically the π -electronic structure of the benzyl cation and showed that it may have an electronic absorption band at 460 m μ . Bingel⁶ calculated the electronic structure of the benzyl cation by the Hückel method and also by the free electron model with the result that two bands appear in the 400 m μ and 300 m μ regions.

- ¹ J. E. Leffler, The Reactive Intermediates of Organic Chemistry. Interscience, N.Y. (1956).
- ² J. A. Grace and M. C. R. Symons, J. Chem. Soc. 958 (1959).
- * J. F. A. Williams, Tetrahedron 18, 1487 (1962).
- ⁴ N. C. Deno, P. T. Groves, J. J. Jaruzelski and M. N. Lugasch, J. Amer. Chem. Soc. 82, 4719 (1960).
- ⁴ H. C. Longuet-Higgins and J. A. Pople, Proc. Phys. Soc. 68, 591 (1955).
- ^e W. Bingel, Z. Naturforsch. 10A, 476 (1955).

The main purposes of the present work were to determine:

(i) whether the benzyl cation is sufficiently stable to be detected, and whether its electronic spectrum shows the 470 m μ band observed by Grace and Symons;

(ii) by means of theoretical and experimental investigations whether the second absorption band of the benzyl cation and its derivatives as predicted by Bingel from theoretical considerations appears near 300 $m\mu$;

(iii) theoretically the hyperconjugation effect of the methyl group in the methylsubstituted benzyl cation on the electronic absorption spectrum of the benzyl cation.

EXPERIMENTAL

Materials. Aluminum chloride was obtained by one of the following two methods: (i) Commercial AlCl₂ was vapourized in a furnace under the flow of dry N_2 gas. The vapour flowed above the Al powder maintained at a temp slightly below its m.p. The FeCl₂ present in the AlCl₃ was removed as the AlCl₂ flowed out with N_2 gas as a white powder. This was collected in a glass tube and sealed off. The AlCl₃ thus obtained was further purified by sublimation in a vacuum system before use. (ii) Dry AgCl and Al powder were mixed and heated in a vacuum system. The AlCl₃ sublimed as a white powder and was collected in a sealed capsule.

G.R. grade 95% H₃SO₄ and oleum were used without further purification. Methylene chloride used as a solvent was refluxed for a day with AlCl₃ and a small amount of benzyl chloride for the purpose of removing impurities and then distilled twice with a 30 cm packed column. Other organic solvents were purified by standard methods.

Commercial benzyl chloride, benzyl alcohol, styrene, α -methylbenzyl alcohol and α -methylstyrene were dried over CaCl₂ and purified by distillation under red. press. α -Methylbenzyl chloride was prepared by passing HCl gas into styrene, the reaction vessel being cooled in an ice-salt bath and the product distilled under red. press. (b.p. 70° C/11mm Hg). α,α -Dimethylbenzyl chloride was prepared from α -methylstyrene in a similar manner (b.p. 82° C/11 mm Hg). 2,4,6-Trimethylbenzyl chloride was prepared by the method described in the literature,⁷ and distilled under red. press. (b.p. 110° C/60 mm Hg; m.p. 37°). 2,4,6, α,α -Pentamethylbenzyl alcohol was prepared by the method described by Newman and Deno,⁸ and recrystallized from pet. ether (m.p. 110°). *p*-t-Butylbenzyl alcohol was prepared by reducing *p*-t-butylbenzoic acid with LAH and distilled under red. press.

2,3,4,5,6-Pentamethylbenzyl chloride was prepared by the chloromethylation of pentamethylbenzene as described for 2,4,6-trimethylbenzyl chloride. The crystalline product was recrystallized from pet. ether and distilled under red, press. (m.p. 80°).

Preparation of solutions and measurement of the electronic absorption spectra

All the electronic absorption measurements were carried out with a Cary recording spectrophotometer model 14, quartz absorption cells with 1 cm and 1 mm optical path-lengths being used. The carbonium ion solutions in the conc H_sSO_4 were prepared according to Symons,^a i.e., the acetic acid solution of the respective benzyl compound was poured into ice-cooled H_sSO_4 . The spectrophotometric measurements for the H_sSO_4 solutions were made in the atmosphere.

The formation of carbonium ions from parent compounds (benzyl and methyl-substituted benzyl chlorides) and AlCl₃ was carried out both *in vacuo* and in the atmosphere. The design of the vacuum vessel is shown in Fig. 1. Purified CH_2Cl_2 used as a solvent was transferred by vacuum distillation into vessel A which contained a small amount of AlCl₃. Vessels C and E contain purified AlCl₃ and the weighed amount of parent compound respectively. The solvent was kept overnight in A and was distilled into E, where the organic chloride was dissolved in CH_2Cl_2 . Then, AlCl₃ was sublimed from C into B (during this procedure the solution in E was frozen by liquid N₃), the glass was sealed off at G and H and the solution allowed contact with AlCl₃ in vessel B. The solution which usually coloured rapidly was poured into cell F and the electronic absorption spectrum measured as soon as possible. The excess AlCl₈ was filtered off through the glass filter D.

The electronic absorption spectra of some carbonium ions were measured at low temperatures

⁷ Organic Synthesis coll. Vol. III, p. 557.

⁸ M. S. Newman and N. C. Deno, J. Amer. Chem. Soc. 73, 3644 (1951).

as follows: The parent compound was weighed and dissolved in purified CH₈Cl₈. The solution was cooled in a dry ice-EtOH bath and the purified AlCl₃ added. At this temp the solution did not colour, but without cooling, the solution gradually became warmer and at some temperature coloured rapidly. It was then returned to the dry ice-EtOH bath and the absorption spectrum was measured as soon as possible. The quartz Dewar vessel was used to measure the light absorption at the dry ice-EtOH temp. All measurements at low temperature were carried out in the atmosphere.



FIG. 1. The vacuum vessel

The concentration of the parent compound was $10^{-5} \sim 10^{-4}$ mol/l. and $10^{-4} \sim 10^{-3}$ mol/l. in the experiments carried out in the atmosphere and *in vacuo* respectively.

Nuclear magnetic resonance measurement

The sample for NMR measurement was prepared by adding AlCl₂ powder to the solution of the parent compound in CH₂Cl₂ (about $1 \sim 5\%$) at low temp ($\sim -70^{\circ}$ C). As the concn of the solute in the NMR measurement was much higher than in the electronic absorption measurements, the solution rapidly decomposed at room temp and, therefore, the measurement was carried out at low temp. Tetramethylsilane was used as the internal reference. The NMR measurements were carried out using a JNM C-60 NMR spectrometer at Japan Electron Optics Laboratory.

THEORETICAL

The SCF calculation on the benzyl cation

The π -electronic states of the benzyl cation were calculated* by a method^{9.10} combining Roothaan's SCF procedure¹¹ with Pariser and Parr's approximation.¹² The geometrical configuration and numbering of the atoms of the benzyl cation are shown in Fig. 2. All the carbon-carbon distances were assumed to be 1.39 Å. The resonance integral between the adjacent carbon $2p\pi$ AO's was assumed to be -2.39 eV which is the value determined by Pariser and Parr for benzene. The one-center electronic repulsion integral was determined from the relation:

$$(pp \mid pp) = I_p - A_p$$

where I_p and A_p are the valence state ionization potential and electron affinity of the carbon $2p\pi$ AO respectively. The two-center repulsion integrals were also calculated following Pariser and Parr's method.

* The numerical calculation was carried out by a FACOM-202 electronic computer at our nstitute. The computer programs for the SCF calculation and for the transition moment calculation were written by one of the authors, and the program for solving secular equations were written by Mr. Suchiro Iwata and Mr. Hidechika Takahashi to whom the presnet authors' thanks are due.

- ¹⁰ J. A. Pople, Trans. Faraday Soc. 49, 1375 (1953).
- ¹¹ C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).
- ¹⁸ R. Pariser and R. G. Parr, J. Chem. Phys. 21, 466, 767 (1953).

^{*} H. Kon, Bull. Chem. Soc. Japan 28, 275 (1955).

The configurational interaction calculation

The calculated result of the electronic states of the benzyl cation should be improved if the configurational interaction is introduced into the SCF results. In this study, the singly-excited configurations, the excitation energies of which are below 9 eV were introduced. The effect of some doubly-excited configurations were also examined.



FIG. 2. The numbering of the carbon atoms and the assumed geometrical structure of the benzyl cation

The hyperconjugation effect of the methyl group in the substituted benzyl cation was calculated by dividing it into the benzyl cation and the methyl groups, and by considering the configurational interaction among the ground, locally-excited and charge-transfer configurations.* We considered the CT configuration in which an electron is replaced from the pseudo π type MO of a methyl group into the lowest vacant MO of the benzyl cation. The pseudo- π MO φ of the methyl group was determined in the case of the t-butyl cation¹³ as follows:

$$\varphi = 0.5505 \,\chi_{\rm H} + 0.8348 \,\chi_{\rm C} \tag{1}$$

$$\varepsilon = -13.245 \,\mathrm{eV} \tag{2}$$

where $\chi_{\rm C}$ is the $2p\pi$ AO of the carbon atom in the methyl group, $\chi_{\rm H}$ is the pseudo π AO constructed from three is AO's of the hydrogen atoms and ε denotes the orbital energy of φ .

The diagonal element of the CT configuration was calculated from the relation:

$$\langle \text{CT} | \text{H} | \text{CT} \rangle = I \text{ (methyl)} - A \text{ (benzyl)}$$
 (3)

Here I(methyl) is the ionization potential for removing an electron from the pseudo- π MO φ of the methyl group, and is equal to $-\varepsilon$. That is to say,

$$I(methyl) = -\varepsilon$$

= 13.245 eV. (4)

A(benzyl) is the electron affinity of the benzyl cation and was assumed to be equal to the ionization potential of the benzyl radical. Its experimental value is 7.76 e V^{14} . A small correction due to the electrostatic interaction between the benzyl and methyl groups was

[•] The charge-transfer configuration will hereafter be abbreviated to 'CT'. The excited configuration within the π -electron system of the benzyl cation will be abbreviated to 'LE' (locally-excited configuration).

¹⁸ I. Hanazaki, H. Hosoya and S. Nagakura, Bull. Chem. Soc. Japan 36, 1673 (1953).

¹⁴ J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing, J. Chem. Phys. 22, 1948 (1954).

neglected. The off-diagonal elements between the CT configurations and ground configuration, and between the CT configurations and LE configurations were evaluated in the usual manner^{13,15,16} assuming the zero-differential-overlap approximation.

The oscillator strength was calculated from the equation

$$f = 1.08 \times 10^{-5} \sigma G R^2 \tag{5}$$

where σ , G and R denote the transition energy (in cm⁻¹), degeneracy factor and transition moment vector (in Å) respectively.

Coefficient [®]								
ε(eV)ª	0	1	2	3	4	5	6	
-20.8100	0-3088	0.5760	0.3984	0.3021	0.2698	0.3021	0.3984	
- 17.8095	- 0·3795	-0.4652	- 0 ·0126	0.4049	0.5579	0.4049	-0.0126	
-17.1332	0	0	-0.5174	-0.4820	0	0.4820	0.5174	
-9.1525	-0.7305	0-0603	0-3909	-0.0233	-0.3950	-0.0233	0-3909	
- 5·7024	0	0	0-4820	-0.5174	0	0.5174	-0.4820	
5·2517	-0.4472	0.5580	-0·2139	- 0·2531	0.5188	-0·2531	-0.2135	
-2·6138	0.1645	- 0·3698	0.3776	-0.4245	0.4368	-0·4245	0.3776	

TABLE 1. THE RESULT OF THE SCF CALCULATION OF THE BENZYL CATION

^a Orbital energy

^b The numbers in each row give the coefficients of the atomic orbitals in the LCAO-MO expression. The numbers given in the first row correspond to the numbering shown in Fig. 2.

RESULTS AND DISCUSSION

The result of the SCF calculation of the benzyl cation is summarized in Table 1. The results of the configuration interaction calculation are shown in Tables 2 and 3. Table 3 includes the results of the benzyl cation and its methyl derivatives. From the present theoretical study, the first band is expected to appear at $400 \sim 500 \text{ m}\mu$ and the second band near $300 \text{ m}\mu$ for all the carbonium ions under consideration. Furthermore, it is to be noticed in connection with the experimental results described that the calculated oscillator strength value for the $300 \text{ m}\mu$ band is six or seven times larger than that for the $400 \text{ m}\mu$ band. These expectations from the theoretical consideration seem to be conclusive and are not altered even if the doubly-excited configurations are included in the configuration-interaction calculation in addition to the singly-excited configurations.

Some typical examples of the electronic spectra of the benzyl and methyl-substituted benzyl compounds in sulfuric acid and aluminum chloride-methylene chloride solutions measured at room temperature are shown in Figs 3, 4, 5 and 6. The results at room temperature are tabulated in Table 4.*

* In the AlCl₂-CH₂Cl₂ solution, the absorption bands in the 400 m μ and 300 m μ regions disappeared when moist air was bubbled into the solution. This fact indicates that these two bands are attributable to some unstable species. No change in these two bands could be detected by bubbling dry O₂, N⁵, and CO₂ gases. Therefore, the unstable species is sensitive to moisture. In most cases, a shoulder appeared in the 260 m μ region. This band increased gradually as the bands in the 300 m μ and 400 m μ region disappeared during the bubbling of moist air. The new band had a very sharp single peak and was not identical with the band of the parent substance.

¹⁶ S. Nagakura and J. Tanaka, J. Chem. Phys. 22, 236 (1954); S. Nagakura, Ibid. 23, 1441 (1954); Mol. Phys. 3, 105 (1960).

¹⁰ J. N. Murrell, Quart. Revs. 15, 191 (1960).

			Wave fu	nction ^b		
E(eV) ^a	0	3 → 5	2 → 4	2 6	1 -	→ 4
0	1	0	0	0		0
4.2774	0	0.3243	0.9259	-0.0991	_ 0 ∙	1667
6.1674	0	0.262	-0·1049	-0.3635	5 O·	7331
6-4914	0	0.6681	-0.3630	-0.1368	3 -0.	6350
7.5710	0	0.3591	0.0043	0.9162	<u> </u>	1780
Antisy	mmetric:					
			Wave f	unction		
E(eV)	3		$3 \rightarrow 6$	3 → 7	2→5	
3.0036	0-	9870	-0.0274	0.0052	-0.1585	
6·0396 0		1215	0.7731	-0.0135	0.6224	
7-2337	0.	1053	- 0 ·6320	-0.0882	0.	7626
8.6468 0.0058		0058	-0.0454	0-9960	0-	0768
I. with singly- Symmetric:	and doubly-e	excited config	rurations			
			Wave fu	inction		
<i>E</i> (eV.)	0	3 → 5	2 → 4	2 → 6	1→4	$3^{3}_{3}^{4}_{4}$
-0·0199	0·9987	-0.0046	-0.0026	0-0006	-0-0059	-0.02
4·2582	0.0070	0.3403	0.9216	- 0 ·1030	-0.1361	0.0753
5-8299	0.0249	0.4525	-0.1121	-0.2488	0.7651	0.3671
6.4812	-0.0035	0.7356	-0·3680	-0·2011	-0.5294	0-0518
7-4744	0.0145	0.2683	-0·0173	0.9234	0.0073	0.2736
8-4813	0.0412	-0.2574	-0.0484	-0.1856	-0.3402	0.8829
Antisymmetr	ic:					
			Wave fu	nction		
					2 4	3 4

TABLE 2.	Тне	RESULT	OF THE	CONFIGURATION-INTERACTION	CALCULATION
			OF TH	HE BENZYL CATION	

 $3^{-1}4$ **3** → 7 3 5 E(eV.) 3 --- 4 3 --- 6 2 **→** 5 0.9740 2.8399 -0.0132 0.0293 -0.1435 -0.0471 0.1656 0-7497 5.9766 0.0791 0.0212 0.6373 -0.11240.1113 0.1115 -0.6250 -0.12280.7082 7.1367 -0.2339 -0.1317 7.7764 -0.1283-0.20190.6654 0.1023 -0.0398 0.6986 8.5659 0.0759 -0.0740 0.0251 0.2421 0.9634 0.0359 0.0295 0.7294 9.4273 0.1017 0.0206 0.0256 -0.6735

* The state energy

^b The numbers in the given row give the coefficients of the configurations in the expression of the state wave function in terms of the configurational wave functions cited in the first row. The abbreviated notation "O" denotes the ground configuration and " $i \rightarrow k$ " denotes the excited configuration in which an electron in MO φ_i is excited to MO φ_k . Similarly $\stackrel{"i}{j} \rightarrow \stackrel{k"}{l}$ denotes the doubly-excited configuration in which two electrons in φ_i and φ_j are excited to φ_k and φ_i respectively.

		-		~				
	SE ^b			DE				
	Ed	f.	СТ%′	Δ^{i}	E	f	ст%	Δ
-	0			_	0			
phC+H ₂	3.004	0-078	_		2.860	0-065	_	
-	4.277	0-465	_		4.278	0-425		
<u> </u>	0	_	5.0	0.301	0	_	5.0	0.319
phC⁺H(Me)	3.305	0.080	0.0		3·159	0.067	0.0	
-	4.426	0.551	8 ∙1		4.436	0.522	7∙6	
	0	_	8.9	0-580	0	_	8.8	0.596
phC ⁺ (Me) _a	3.584	0.083	0.0		3.436	0.069	0.0	
• • • •	4.619	0.593	9·6		4.631	0.570	9.3	
2,4,6-(Me) ₂ -phC+H ₂ "	0		4.4	0.262	0		4.4	0.280
	2-963	0·105	9.8		2.840	0-095	8-8	
	4.295	0.593	14.0		4·289	0.547	14-2	
2,4,6-(Me) _a -phC ⁺ (Me) _a ^a	0	_	11.2	0.789	0	_	11.1	0.805
	3.490	0.114	9.8		3.364	0.099	8.8	
	4-558	0.706	22.5		4.568	0.686	22·2	
2,3,4,5,6-(Me)5-phC+H2'	0	_	4.4	0.262	0		4.4	0.281
	2.849	0.100	12.6		2.733	0.086	11.4	
	4.067	0.510	24.1		4.056	0-462	24.0	

TABLE 3. THE LOWER EXCITED STATES OF THE BENZYL CATION AND ITS METHYL DERIVATIVES⁶

^a The ground and lower two excited states are shown.

^b The results of the configuration interaction including eight singly-excited configurations.

• The result of the configuration interaction including eight singly-excited and four doubly-excited configurations.

^d Transition energy (in eV).

Oscillator strength.

¹ The percentage of the CT configuration in the state.

• 2,4,6-trimethylbenzyl cation.

* 2,4,6,α,α-pentamethylbenzyl cation.

¹2,3,4,5,6-pentamethylbenzyl cation.

¹ The ground state depression by the methyl substitution (in eV).

As is seen from Table 4 and Fig. 5, the electronic absorption spectra of the α, α -dimethylbenzyl compounds in strong acid are in good agreement with the theoretical expectation in that the two absorption bands appear in 300 m μ and 400 m μ regions, and the former is several times stronger than the latter. Therefore, it may be said that the observed absorption spectrum is due to the α, α -dimethylbenzyl cation.

2,3,4,5,6-Pentamethylbenzyl chloride in aluminum chloride-methylene chloride and in concentrated sulfuric acid show two absorption bands in the 500 m μ and 300 m μ regions. The intensity of the 300 m μ band is several times larger than the 500 m μ band. This also agrees well with the theory.

The absorption spectrum of $\alpha, \alpha, 2, 4, 6$ -pentamethylbenzyl alcohol in sulfuric acid also agrees with the theoretical expectation for the $\alpha, \alpha, 2, 4, 6$ -pentamethylbenzyl cation.*

* The positions of the two absorption bands of the $\alpha, \alpha, 2, 4, 6$ -pentamethylbenzyl cation may shift to longer wavelengths if two α -methyl groups are not coplanar with the ring plane because of the steric hindrance of the methyl groups at *ortho*-positions.



FIG. 3. The electronic absorption spectra of the benzyl compounds in acidic media. A: phCH₃Cl-AlCl₅-CH₄Cl₄ at low temp. B: phCH₃OH-H₃SO₄ C: phCH₂Cl-AlCl₅-CH₄Cl₃ at room temp, *in vacuo*.



FIG. 5. The electronic absorption spectra of the α,α-dimethylbenzyl compounds in acidic media. A: phC(Me)₂Cl-AlCl₃-CH₃Cl₃ at low temp B: phC(Me)₂Cl-AlCl₃-CH₂Cl₂ at room temp, *in vacuo* C: α-methylstyrene in H₃SO₄



FIG. 4. The electronic absorption spectra of the 2,4,6-trimethylbenzyl compounds in acidic media. A: at low temp. B: after 2 hr C: at room temp, *in vacuo*. See footnote d in Table 5 concerning a shoulder at 380 mµ of Curve A,



FIG. 6. The electronic absorption spectra of the 2,3,4,5,6-pentamethylbenzyl chloride in acidic media. A: 2,3,4,5,6-(Me)₁phCH₂Cl-AlCl₂-CH₂Cl₂ at low temp. B: after 2 hr (kept at room temp) C: 2,3,4,5,6-(Me)₅-phCH₂Cl in H₂SO₄ at room temp. See footnotes g and d in Tables 4 and 5 respectively concerning shoulders at 400 m μ of curves A, B and C.

Although the spectra of the α -methylbenzyl and 2,4,6-trimethylbenzyl compounds in sulfuric acid and aluminum chloride-methylene chloride solutions show two bands in the 400 m μ and 300 m μ regions, the observed intensity ratio of the 300 m μ bands to the 400 m μ bands is very small in comparison with the theory. In the case of the benzyl compounds, no band can be observed in 300 m μ region. This is also incompatible with the theory.

It is, therefore, very doubtful whether the bands of the benzyl, α -methylbenzyl and 2,4,6-trimethylbenzyl compounds observed at room temperature in strong acid

System*		Probable ion	λ•(ε)•	Conclusion of the existence of the cation
phCH ₁ Cl	A,V	phC+H ₂	426(1800)*	
phCH ₃ OH	S,V	phC+H ₃	445(450)	non existent at
p-t-Butyl·phCH₂OH	S,N	p-t-Butyl·phC+H _a	440(4000)	P
phCH(Me)Cl	A,N	phC+H(Me)	445(800) 329(1350)	probably non
phCH(Me)OH	S,N	phC+H(Me)	442(2860) 298(4000)	existent at
phCH=CH ₂	S,N	phC ⁺ H(Me)	427(—) 306(—)•	room temp
phC(Me),Cl	A,N	phC ⁺ (Me) _a	419() 324()'	
• • • •	A,V	phC ⁺ (Me) _z	410(650) 317(4500)	stable existence
	S,N	$phC^{+}(Me)_{1}$	390(150) 320(1400)	
phC(Me)—CH ₃	S,N	phC ⁺ (Me) ₁	400(150) 320(1300)	
2,4,6-(Me) ₈ -phCH ₈ Cl	A,V	2,4,6-(Me) ₈ - phC+H ₂	470(5800) 325(7400)	unstable at room temp
	S,N	2,4,6-(Me) ₈ - phC+H ₂	465(4000) 330(3700)	The second se
2,4,6-(Mc) ₃ - ph(Mc) ₃ OH	A,V	2,4,6-(Me) ₃ - phC ⁺ (Me) ₃	440() 360()	stable existence
	S,N	2,4,6-(Me),- phC ⁺ (Me),	450(1930) 355(12700)	
	A,N	2,4,6-(Me) ₃ - phC ⁺ (Me) ₂	450(2780) 360(14600)	
2,3,4,5,6-(Me) ₅ - phCH ₂ Cl	A,N	2,3,4,5,6-(Me) ₅ - phC ⁺ H ₂	520(2100) 340(17200)*	stable existence
-	S,N	2,3,4,5,6-(Me) _s - phC ⁺ H ₁	~500(1900) 332(13900)*	

TABLE 4. THE ELECTRONIC ABSORPTION SPECTRA OF THE BENZYL COMPOUNDS AND ITS METHYL DERIVATIVES IN ACIDIC MEDIA AT ROOM TEMPERATURE

• A and S denote the AlCl₃-CH₃Cl₃ solution and H₅SO₄ solution respectively. V and N show that the measurement was carried out *in vacuo* and in the atmosphere respectively.

• Peak position (mµ).

^c Apparent molar extinction coefficient. That is, the molar extinction coefficient is calculated assuming that the parent substance is completely changed to the ion.

^d See text for details.

• The ratio of the extinction coefficient of the 306 m μ band to that of the 427 m μ band is 1.14.

⁷ The ratio of the extinction coefficient of the 324 m μ band to that of the 419 m μ band is 3.46.

* Another weak band appears at \sim 400 m μ which may correspond to some impurities or protonated ion.

are those of the corresponding benzyl-type carbonium ions, though they are attributable to some unstable species.

In this connection, we carried out the absorption spectrum measurements of benzyl chloride, α -methylbenzyl chloride, α,α -dimethylbenzyl chloride, 2,4,6-trimethylbenzyl chloride and 2,3,4,5,6-pentamethylbenzyl chloride at low temperature in aluminum chloride-methylene chloride solution. The results are summarized in Table 5. The absorption curves are shown in Figs 3, 4, 5 and 6. The 2,4,6-trimethylbenzyl chloride in aluminum chloride-methylene chloride solution shows a very strong band in the 300 m μ region at low temperature, and the intensity of this band becomes several times larger than that of the 400 m μ band. This is in good agreement with the theoretical expectation. When the solution of the 2,4,6-trimethylbenzyl chloride-aluminum chloride-methylene chloride system prepared at low temperature was kept at room temperature, the band in the 300 m μ

System	Probable ion	λ(ε)	Conclusion on the existence of the cation	
phCH₄Cl phCH(Me)Cl	phC ⁺ H ₂ phC ⁺ H(Me)	420° 450(900) 327(1400)	non existent probably non existent	
phC(Me)₃Cl 2,4,6-(Me)₅-phCH₂Cl 2,3,4,5,6-(Me)₅-phCH₂Cl	phC+(Me) <u>s</u> 2,4,6-(Me)s-phC+Hs 2,3,4,5,6-(Me)s-phC+Hs	405(1300) 333(17500) 480(2400) 325(26700) ⁴ 520(1900) 340(16300) ⁴	stable existence stable existence stable existence	

Table 5. The electronic absorption spectra of the benzyl compounds and its methyl derivatives in acidic media at low temperature^{4,3}

^a See the footnotes of Table 4 for notations.

* All experiments were carried out in the system AlCl₈-CH₂Cl₂ in the atmosphere.

• The apparent molar extinction coefficient was ~600 when the absorption spectra was measured soon after the solution was coloured. The band developed up to $\varepsilon \sim 3000$ and the peak position shifted to 430 m μ on standing.

^d See footnote g of Table 4.

region gradually decreased its intensity and the peak position of the band in the 400 m μ region gradually shifted to the shorter wavelength (489 m $\mu \rightarrow$ 440 m μ , see Fig. 4). These changes were not reversible. These facts seem to indicate that the 2,4,6-trimethylbenzyl cation is stable at low temperature but it undergoes some further reactions at room temperature.

In the case of the α, α -dimethylbenzyl chloride in strongly acidic media, there is no appreciable difference between the spectra obtained at low temperature and at room temperature. The band in the 300 m μ region decreases only slightly in intensity when the solution is kept at room temperature. This is also the case for 2,3,4,5,6pentamethylbenzyl chloride in aluminum chloride-methylene chloride. Therefore, it may be concluded that the α, α -dimethylbenzyl and 2,3,4,5,6-pentamethylbenzyl cations are stable at room temperature as well at low temperature.

 α -Methylbenzyl chloride in aluminum chloride-methylene chloride solution gives a rather weak band in the 300 m μ region, i.e. its intensity does not increase at low temperature compared with that at room temperature. The benzyl chloride-aluminum chloride-methylene chloride system shows no absorption band in the 300 m μ region even at low temperature. These facts indicate that the cations of these two compounds are not stable even at the temperature of dry ice-ethanol.

The NMR measurement at low temperature also supports this conclusion (Fig. 7). α, α -Dimethylbenzyl chloride in aluminum chloride-methylene chloride shows two signals ($\tau = 7.96$ and 2.38) which correspond to the protons of α -methyl groups and the ring protons. The intensity ratio (6.13:5.00) is also in good agreement with the expected value (6:5) for the α, α -dimethylbenzyl cation.

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2,3,4,5,6-Pentamethylbenzyl chloride in aluminum chloride-methylene chloride shows three peaks at $\tau = 7.50$, 7.05 and 4.02. The signal at $\tau = 7.50$ is attributable to the methyl protons at *meta* positions. The signal $\tau = 7.05$ may be attributable to the sum of the methyl protons at *ortho* and *para* positions. The signal at $\tau = 4.02$ may be attributable to the protons in the methylene group even though they appear in overlap with the solvent signal ($\tau = 4.2 \sim 4.7$).



FIG. 7. The NMR spectra of the methyl-substituted benzyl cations at low temperature A: phC(Me)₂Cl in CH₂Cl₃; B: phC(Me)₂Cl-AlCl₃-CH₄Cl₃; C: 2,4,6-(Me)₃phCH₂Cl₂ in CH₃Cl₃; D: 2,4,6-(Me)₅phCH₂Cl-AlCl₅-CH₂Cl₃; E: 2,3,4,5,6-(Me)₅phCH₂Cl in CH₂Cl₃; F: 2,3,4,5,6-(Me)₅phCH₂Cl-AlCl₅-CH₂Cl₂ (The relative intensity is shown in parenthesis.)

In the case of the 2,4,6-trimethylbenzyl chloride in aluminum chloride-methylene chloride, the intensity ratio between the signals corresponding to the ortho- and para- methyl groups (6.33:3.00) is in good agreement with the expectation. However, the intensity (0.55) of the signal corresponding to the ring protons is smaller than the expected value (2.00). This result suggests that a reaction occurs at the meta position, although the solute may exist chiefly as the 2,4,6-trimethylbenzyl cation. The CH₂ signal is uncertain because it is covered by the slope of the strong solvent signal. This result indicates that the high concentration of the solution used in NMR measurements may promote further reactions of the ion whereas the low temperature and low concentration used in the measurement of the electronic absorption spectra is suitable for the stable existence of the ion. The solution of benzyl chloride in aluminum chloride-methylene chloride shows three signals at $\tau = 8.19$, 4.62 and 2.44. The higher field signal ($\tau = 8.19$) may be attributable to some reaction product.

The percentage of the CT configurations mixed in the ground and lower excited states is shown in Table 3. The charge densities of the benzyl cation are shown in Fig. 8 for the ground configuration obtained by the SCF calculation. As is shown in Table 3, the stabilization of the ground state by introducing a methyl group into the α -position is very large in comparison with the stabilization obtained by introducing a methyl group into the ring. This fact is related to the neutralization of the charge on the carbon atom C₀ by the electron transfer from the methyl group. The percentage of CT configuration mixed into the ground state of the α -substituted ion is



FIG. 8. The charge distribution of the benzyl cation.

rather large so that the charge on C_0 may be considerably neutralized by the hyperconjugation from the methyl group and the ion may be stabilized. In the case of the methyl-substituted benzyl cations in which the ring hydrogens are replaced by methyl groups, this effect seems to be weak.

As is clearly seen from the result in Table 2, the main components of the excited states corresponding to the bands in the 400 and 300 m μ regions are the antisymmetric configuration $\phi_3 \rightarrow \phi_4$ and the symmetric configuration $\phi_2 \rightarrow \phi_4$ respectively. This means that the 300 m μ and 400 m μ bands may be assigned to the CT bands, the transitions of which are accompanied by a great amount of electron transfer from the occupied MO's ϕ_3 and ϕ_3 of benzene respectively to the vacant $2p\pi$ AO of C⁺.

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