

action mixture was allowed to stir at 0° for 24 hr, during which time the mixture turned orange. At the end of this period the reaction mixture was extracted with 10 ml of H₂O, the aqueous layer was back extracted with three 25 ml portions of pentane, and the combined organic fraction was dried over MgSO₄. The solvents (pentane and cyclohexene) were slowly distilled off at atmospheric pressure through a small Vigreux column. The residue was vacuum distilled yielding two fractions, a forecut 1.1 g, bp 65–80° (45 mm), and a main fraction, 2.8 g, bp 81–83° (45 mm). The forecut was found to contain by gc on column A solvent (mostly cyclohexene) and 19% of the desired products whereas the main cut contained 90% of the desired products (*tert*-butyl vinyl ether and adduct) and 10% of solvent, for an overall yield of 2.7 g (82%) of carbene products. In such a small scale preparation it was impossible to obtain solvent free products by distillation alone without substantial loss in yield.

Preparative Scale Reaction of Triflate 7b with Ethyl Vinyl Ether. To a 100-ml round-bottom flask equipped with a magnetic stirring bar was added 3.5 g (0.031 mol) of *t*-BuOK and 70 ml of ethyl vinyl ether. This reaction mixture together with 5.1 g (0.025 mol) of the pure triflate 7b in a 10-ml addition funnel was allowed to cool to –20° in a cold room. After temperature equilibration the triflate was added to the solvent mixture over a period of 15–20 min during which time the entire mixture turned light yellow and viscous. The mixture was allowed to warm to 0°, stirred for 16 hr and then washed with about 7 ml of cold water. The water was back extracted with two 15-ml portions of ether and the combined organic portion dried over MgSO₄. After removal of solvent through a small Vigreux column at atmospheric pressure the residue was vacuum distilled yielding two fractions, a forecut, 1.2 g, bp 50–61° (50 mm), and a main fraction, 2.4 g, bp 62–67° (50 mm). Gas chromatography (column A at 75°) showed the forecut to be 66.6% solvent and 33.3% product and the maincut to be 88% products (*tert*-butyl vinyl ether and adduct) and 12% solvent for an

overall yield of 2.5 g (79%). Once again due to the small scale nature of the reaction it proved to be impossible to obtain solvent free products by distillation alone without substantial loss in yield.

Reaction of Triflate 7b with *t*-BuOD. To a 10-ml round-bottom flask equipped with a magnetic stirring bar were added 0.168 g (1.5 mmol) of *t*-BuOK and 0.75 g (10 mmol) of *t*-BuOD (90% D by nmr). The stoppered flask was allowed to cool to –20°; then 0.408 g (2.0 mmol) of triflate 7b in 5.0 ml of pentane was added and the solution stirred at 0° for 48 hr. At the end of this period both the unreacted triflate as well as the product *tert*-butyl vinyl ether were collected by preparative gc on column B at 80° and analyzed for deuterium content by both nmr and mass spectroscopy. The recovered triflate was found to contain no deuterium (<1%) within the limits of detection of nmr and mass spectroscopy, whereas the product *tert*-butyl vinyl ether (CH₃)₂C=CH(D)O-*t*-Bu was found to contain 55% H (45% D) by nmr integration and 43.8% D by mass spectroscopy.

Reaction of (CH₃)₂C=CHO-*t*-Bu with *t*-BuOD. To a 5-ml round-bottom flask equipped with a magnetic stirring bar was added 0.084 g (0.75 mmol) of *t*-BuOK and 0.375 g (5.0 mmol) of *t*-BuOD (99% D by nmr) in 1.5 ml. of dry pentane. The flask was cooled to –20° and 0.13 g (1.0 mmol) of *tert*-butyl isobutenyl ether in 1.0 ml of dry pentane was added. The solution was stirred at 0° for 48 hr. At the end of this period the ether was reisolated by preparative gc on column B at 80°. The recovered ether was found to contain no deuterium (<1%) within the limits of detection of nmr and mass spectroscopy.

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Magnetic Circular Dichroism Studies. XXVII.¹ Electronic Structure of Ring-Halogenated Difluorophenylcarbenium Ions

Yoke K. Mo, Robert E. Linder, Günter Barth, Edward Bunnenberg, and Carl Djerassi*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. Received February 2, 1974

Abstract: The electronic structure of ring-halogenated difluorophenylcarbenium ions has been investigated by magnetic circular dichroism and absorption spectroscopy. The trends in the observed wavelength shifts for the two lowest excited states, some of which are quite large, are mostly accounted for by considering the benzyl cation self-consistent orbitals and assuming a first-order mesomeric effect.

Carbocations² are important intermediates in many organic chemical reactions, particularly isomerization, polymerization, surface catalytic reactions, and Friedel–Crafts reactions of hydrocarbons.

Early studies of carbocations were hindered by the fact that much of this work utilized concentrated sulfuric acid which, in addition to the carbocations, also produced decomposition products or allowed side reactions (sulfonation). By using highly acidic superacids and low nucleophilicity solvent systems (such as SO₂ and SO₂ClF) at low temperature, Olah and others³

have been able to measure the physical properties (nmr, ir, uv, Raman, and ESCA) of many carbocations, a series of studies which have produced significant contributions to the understanding of organic ion chemistry. Here we wish to focus attention on absorption spectroscopy, and its more selective counterpart magnetic circular dichroism (MCD) spectroscopy.⁴

Previous optical studies on carbocations^{3b} have been handicapped by the above mentioned experimental difficulties and by the fact that overlapping bands occur

(1) Part XXVI: G. Barth, R. E. Linder, E. Bunnenberg, and C. Djerassi, *J. Chem. Soc., Perkin Trans. 2*, in press.

(2) G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

(3) (a) G. A. Olah and P. v. R. Schleyer, Ed., "Carbonium Ions," Vol. 1, 1968, Vol. 2, 1970, Vol. 3, 1972, and Vol. 4, 1973, Interscience, New York, N. Y., (b) G. A. Olah, C. V. Pittman, and M. C. R. Symons in ref 3a, Vol. 1, p 153; (c) D. Bethell and V. Gold, "Carbonium Ions,

an Introduction," Academic Press, New York, N. Y., 1967; (d) G. A. Olah, *Chem. Eng. News*, **45**, 76 (March 27, 1967); *Science*, **168**, 1298 (1970); *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973).

(4) (a) C. Djerassi, E. Bunnenberg, and D. Elder, *Pure Appl. Chem.*, **25**, 57 (1971); (b) W. Voelter, R. Records, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 6163 (1968); (c) B. Briat, D. A. Schooley, R. Records, E. Bunnenberg, and C. Djerassi, *ibid.*, **89**, 6170 (1967).

for some carbocations, leading to ambiguous interpretations. Also, the relationship between structure and optical spectra is not straightforward because many effects can occur and because both ground and excited states must be considered in the analysis. Since significant advances⁵ have occurred in the analysis of optical spectra by the use of magnetic circular dichroism, we decided to apply this technique to a series of ring-halogenated difluorophenylcarbenium ions.

We select this particular class of ions because no systematic study of ring-substituted phenylcarbenium ions by absorption spectroscopy has been reported in the literature. Furthermore, the effects (both inductive and mesomeric) of halogen atoms in the carbocations are of particular interest.

Experimental Section

Materials. All of the halobenzotrifluorides were commercially available materials (Columbia Organic Chemicals, Columbia, South Carolina, or PCR Inc., Gainesville, Fla.). Antimony pentafluoride (Allied Chemicals, Morristown, N. J.) was purified by double distillation at atmospheric pressure in an all-glass apparatus. In a third distillation a constant-boiling fraction (bp 142–143°) was collected directly into a Teflon bottle. Fluorosulfuric acid (Organic/Inorganic Research Chemical Corp., Sun Valley, Calif.) was purified by double distillation at atmospheric pressure in an all-glass apparatus.

Preparation of Ions. Difluorophenylcarbenium ions (1–10) were prepared by treating the precursors (approximately 1 mg) with neat $\text{FSO}_3\text{H}-\text{SbF}_5$ (1:1 mol/mol) solution (ca. 1 ml) at the desired temperatures. In general, the concentrations of the solutions were approximately 10^{-3} M. All spectra were run in short path length (0.1 mm) quartz absorption cells. The spectrum of the $\text{FSO}_3\text{H}-\text{SbF}_5$ solution shows essentially no absorption above 215 nm (a weak absorption tail begins at 205 nm). MCD and uv spectra were immediately recorded in all cases, and shown to be reproducible.

Quenching of Ions. Quenching experiments of halogenated difluorophenylcarbenium ions (2–10) and halogenated diphenylfluorocarbenium ions (11) were accomplished by pouring the acid solution onto water-ice mixtures. The precipitates were collected by filtration and analyzed by mass and nmr spectrometry. The halogenated benzoic acids obtained from the quenching experiments show spectral properties identical with authentic samples in every respect. Similarly, the halogenated benzophenones (12) were also isolated and identified by nmr, ir, and mass spectrometry.⁶

Instrumentation. A Japan Spectroscopic Co. spectropolarimeter (Durrum-JASCO Model ORD-UV-5) modified to allow CD measurements and to accept a superconducting magnet built by Lockheed Palo Alto Research Laboratories (Model OSCM 103) was used for MCD measurements. Room and low temperature absorption spectra were recorded on a Cary 14 recording spectrometer. The cell compartment of the spectrometer was equipped with a variable-temperature control unit cooled by a flow of nitrogen.

Results and Discussion

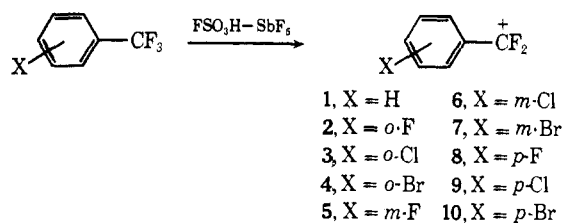
(A) Preparation of Halogenated Difluorophenylcarbenium Ions. Recently, Olah and coworkers⁷ reported the preparation and nmr study of a series of ring-halogenated difluorophenylcarbenium ions by treating the corresponding halobenzotrifluorides with antimony pentafluoride in SO_2ClF solution at -78° . Since SO_2ClF (or SO_2) has an ultraviolet absorption at 280 nm (λ_{max}), carbocations in these solvents are not

(5) (a) L. Seamans, Ph.D. Dissertation, University of Minnesota, 1971; (b) L. Seamans, A. Moscowitz, G. Barth, E. Bunnenberg, and C. Djerassi, *J. Amer. Chem. Soc.*, **94**, 6464 (1972); (c) D. J. Shieh, S. H. Lin, and H. Eyring, *J. Phys. Chem.*, **77**, 1031 (1973); (d) I. N. Douglas, R. Grinter, and A. J. Thomson, *Mol. Phys.*, **26**, 1257 (1973); (e) H. H. Dearman, *J. Chem. Phys.*, **58**, 2135 (1973).

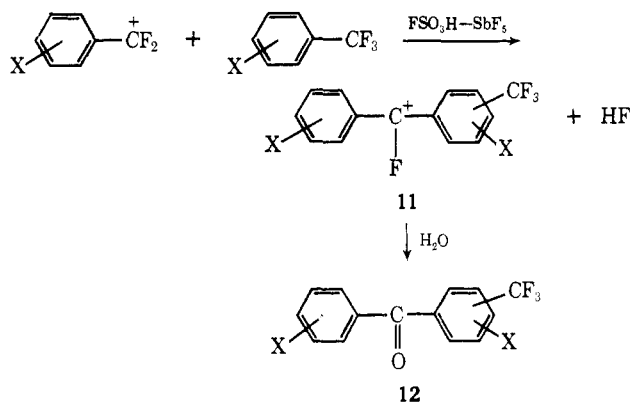
(6) Y. K. Mo and C. Djerassi, unpublished results.

(7) (a) G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **91**, 2955 (1969); (b) G. A. Olah and Y. K. Mo, *J. Org. Chem.*, **38**, 2686 (1973).

suitable for MCD or absorption spectroscopic studies. In addition, we also had experimental difficulty in recording low-temperature MCD spectra through short path length cells (0.1 mm).⁸ Consequently, we have prepared the ions in antimony pentafluoride-fluorosulfuric acid solution and recorded their spectra at room temperature.



Unfortunately, the ions 2–4 and 7 were not stable under these experimental conditions but dimerized to the corresponding halogenated diphenylfluorocarbenium ions, 11. We believe that dimerization of benzo-



trifluorides in superacid solutions involves alkylation reactions of benzotrifluorides with difluorophenylcarbenium ions. Evidence for the dimerization was obtained from the quenching experiments of these solutions in ice-water mixtures to give the corresponding halogenated benzophenones (12). The nmr (^1H and ^{19}F) spectra as well as the MCD and absorption spectra of these solutions also indicate the formation of ions 11.⁶

The other difluorophenylcarbenium ions (1, 5, 6, 8–10) are sufficiently stable at room temperature for spectral measurements. These ions have identical nmr spectra with those reported by Olah and coworkers.⁷ However, they also gradually dimerized in $\text{FSO}_3\text{H}-\text{SbF}_5$ solution at room temperature over a longer period of time (e.g., 24 hr). Detailed discussion of these alkylation (dimerization) reactions will be reported in a forthcoming paper dealing with preparative aspects of this reaction.

(B) Interpretation of the Spectra. The MCD and absorption spectra of the parent ion (1) and the para-substituted halogenated difluorophenylcarbenium ions (8–10) are presented in Figure 1. The positive MCD peak at lower energy (340–400 nm) can be identified with a weak absorption band in ions 1 and 8 (band I in Figure 1). For ions 9 and 10, band I is hidden in absorption, but is clearly identifiable with the positive MCD peak. The negative MCD peak (290–350 nm) is correlated with the strong absorption band (band II).

(8) At this path length $\text{FSO}_3\text{H}-\text{SbF}_5$ has essentially no absorption above 215 nm (see Experimental Section).

Table I. MCD and Absorption Parameters of Difluorophenylcarbenium Ions^a

Substituent	Parameter ^b	Position isomer								
		Ortho			Meta			Para		
		Band I	Band II	Band III	Band I	Band II	Band III	Band I	Band II	Band III
F	$\lambda_{\max}^{-60^\circ}(\epsilon)$	393 (5200)	292 (12,900)	221 (4000)	398 (1900)	303 (19,600)	227 (6000)	340 (3600)	303 (36,600)	210 (4900)
	$\lambda_{\max}^{\text{RT}}(\epsilon)$		<i>c</i>		400 (2300)	303 (20,700)	228 (6900)	340 (3300)	302 (35,000)	210 (2400)
	$\lambda_{\max}^{\text{RT}}([\theta]_{\text{M}} \times 10)$		<i>c</i>		410 (1.05)	302 (-2.98)	228 (0)	350 (2.36)	298 (-5.98)	210 (2.63) ^f
Cl	$\lambda_{\max}^{-60^\circ}(\epsilon)$	415 (4700)	300 (9900)	237 (2100)	415 (1900)	312 (17,100)	239 (11,100)	(360) ^d	330 (37,000)	223 (5700)
	$\lambda_{\max}^{\text{RT}}(\epsilon)$		<i>c</i>		415 (2400) ^e	310 (15,000)	236 (9100)	(360) ^d	330 (33,000)	223 (4300)
	$\lambda_{\max}^{\text{RT}}([\theta]_{\text{M}} \times 10)$		<i>c</i>		425 (0.60)	310 (-2.40)	235 (-0.24)	360 (3.12)	328 (-6.20)	217 (1.43) ^f
Br	$\lambda_{\max}^{-60^\circ}(\epsilon)$	423 (3900)	298 (10,400)	220 (8100)	428 (1700)	315 (12,000)	248 (11,700)	(374) ^d	352 (28,600)	241 (5600)
	$\lambda_{\max}^{\text{RT}}(\epsilon)$		<i>c</i>			<i>c</i>		(374) ^d	353 (29,000)	238 (6400)
	$\lambda_{\max}^{\text{RT}}([\theta]_{\text{M}} \times 10)$		<i>c</i>			<i>c</i>		374 (4.81)	342 (-5.92)	238 (-0.03) ^f
H	$\lambda_{\max}^{-60^\circ}(\epsilon)$	385 (3000)	292 (23,600)	218 (5600)						
	$\lambda_{\max}^{\text{RT}}(\epsilon)$	392 (6200)	298 (16,200)	218 (4000)						
	$\lambda_{\max}^{\text{RT}}([\theta]_{\text{M}} \times 10)$	406 (1.12)	295 (-3.43)	218 (0)						

^a In $\text{FSO}_3\text{H-SbF}_5$ solution (see Experimental Section). ^b Wavelength in nm; RT = room temperature. ^c Dimerization at room temperature; see text. ^d Since only one absorption maximum is identifiable in these species, the wavelengths were taken from the positive maxima in the MCD spectra (Figure 1). ^e Some dimerization took place under these experimental conditions; see text. ^f Two absorption bands exist in this region; see Figure 1.

In cases where room temperature MCD spectra could not be obtained (ions 2-4, 7), absorption measurements at low temperature (-60°) showed that the absorption peak corresponding to band I is well separated from that of the stronger band II. A third band (band III) is also identifiable in the uv and MCD spectra (210-250 nm) in all of the ring-halogenated difluorophenylcarbenium ions. The MCD (at room temperature) and absorption (both at -60° and room temperature) spectral parameters are summarized in Table I.

The wavelength shifts of the absorption bands of the halogenated difluorophenylcarbenium ions from those of the parent ion are given in Table II. Comparison of

Table II. Band Frequency Shifts in Halogenated Difluorophenylcarbenium Ions from Their Parent Ion, $\Delta\nu^a$ (cm^{-1})

	Ortho		Meta		Para		Mono shifts ^b	
	I	II	I	II	I	II	¹ L _b	¹ L _a
F	529	-577	658	667	-3438	447	230	1149
Cl	1878	+237	2164	1412	-2597	3367	1037	3036
Br	2333	+113	2826	2223	-1704	5261	1093	3208

^a A red shift is denoted by positive values of $\Delta\nu$. ^b The shifts observed for the halobenzenes⁹ are given for comparison purposes.

the magnitudes of these spectral shifts with those observed in halobenzenes (Table II) shows that the substituent effects observed for the ions are unusually large for both bands I and II.

An attempt to interpret the spectral shifts in terms of the Petruska-Platt model for substituted benzenes^{9b} led to contradictory results. First, most of the shifts are in the same order (F < Cl < Br) as the mesomeric

(9) (a) A. Buraway and A. R. Thompson, *J. Chem. Soc.*, 4314 (1956); (b) L. Seamans, Ph.D. Dissertation, University of Minnesota, Minneapolis, Minn., 1971.

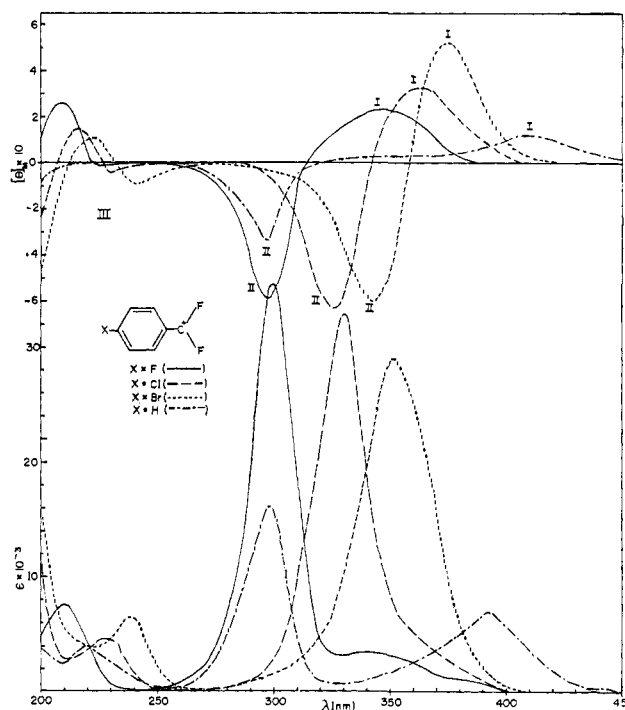


Figure 1. The MCD (top curves) and absorption spectra (bottom curves) of *p*-(halo)difluorophenylcarbenium ions.

effect in benzene. However, the Petruska-Platt model predicts that mesomeric effects are additive, except for the ¹L_a band of the para isomers. The shifts of the monosubstituted compounds in Table II, when compared with those in the disubstituted benzenes, clearly show that the spectral shifts are *not* additive.

It is possible to analyze these spectra in terms of

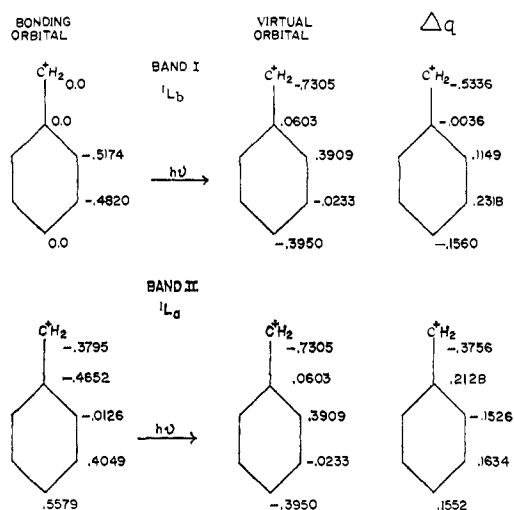


Figure 2. Bonding and virtual orbitals and charge migration in the first two excitations of benzyl cation.

Hanazaki and Nagakura's¹⁰ self-consistent molecular orbitals and state wave functions for the benzyl cation. The spectrum predicted for the benzyl cation agrees rather well with that observed for the difluorophenylcarbenium ion both with regard to band intensities as well as energies [predicted (experimental) values are: parallel band, 290 (297) nm, $f = 0.465$ (0.289) and perpendicular band, 412 (385) nm, $f = 0.078$ (0.060)]. Also, the MCD of the lowest energy band, band I, is positive. This is in agreement with the conclusions of Foss and McCarville¹¹ and Seamans^{9b} for the perpendicularly polarized 1L_b band of benzene derivatives with electron-accepting substituents. The spectral shifts may be interpreted by considering the principal one-electron excitations (expansion coefficient greater than 0.9) contributing to the two lowest excited states. The bonding and virtual orbitals, as well as the concomitant charge migration, for these two excitations are given in Figure 2.

Clearly both excitations involve extensive charge rearrangement, particularly by electrons migrating to the carbenium carbon atom (C^+) during excitation. The orbital coefficients may be used to predict spectral shifts. First we observe that the spectral shifts are, in most cases, in the order $F < Cl < Br$, the order of the mesomeric effect in the Petruska-Platt model. If we consider the benzyl cation as the basic chromophore, this indicates an additional charge-transfer state involving the halogen atom. We assume that this state is an excitation from the halogen to the ring orbital given in Figure 2. The spectral shift for a substituent in a given position will be approximately proportional to the coefficient of the bonding orbital and will be in the order $F < Cl < Br$. Finally, we note that the mesomeric effect of the halogen to ring charge-transfer state leads to either a red shift or no shift for each band. The trends are given in Table III and agree well with the predictions except in the case of band I for the para isomers. In this case, a fluorine substituent gives the greatest shift, and it is a blue shift. Both of these ob-

(10) I. Hanazaki and S. Nagakura, *Tetrahedron*, **21**, 2441 (1965).

(11) J. G. Foss and M. E. McCarville, *J. Chem. Phys.*, **44**, 4350 (1966). Also see ref 5c for further experimental and interpretive work.

Table III. Predicted and Observed Spectral Shifts of Ring-Halogenated Difluorophenylcarbenium Ions from Their Parent Ion

	Orbital coefficient	Predicted shift		Obsd shift
Band I				
Ortho	-0.5174	Red	$F < Cl < Br$	Red $F < Cl < Br$
Meta	-0.4820	Red	$F < Cl < Br$	Red $F < Cl < Br$
Para	0	None		Blue $Br < Cl < F^a$
Band II				
Ortho	-0.0126	None		None
Meta	0.4049	Red	$F < Cl < Br$	Red $F < Cl < Br$
Para	0.5579	Red	$F < Cl < Br$	Red $F < Cl < Br$

^a In terms of absolute energy, band I in the para isomers appears in the same order as in the other isomers ($\lambda^F < \lambda^{Cl} < \lambda^{Br}$).

servations are indicative of an inductive effect,^{9b} but since the first-order inductive effect is proportional to Δq , the values given in Figure 2 are not consistent with an inductive interpretation. However, there is experimental evidence (${}^{19}F$ nmr studies of C^+F_2 resonance for all three isomers)⁷ that indicates substantial ground-state charge rearrangement on substitution, showing that the changes in chemical shifts of the C^+F_2 fluorine atoms are appreciable in all the isomers. Since the order of the effect is the same for both the nmr chemical shifts and for the blue shift of band I for the para isomers ($F > Cl > Br$), it is tempting to assume a common explanation for both effects. However, at this time, we have no basis for such an assumption and the blue shift of band I on para substitution must be considered anomalous.

Conclusions

We have measured the absorption and MCD spectra of the halogenated difluorophenylcarbenium ions, and find regular spectral shifts in the series. These shifts, as well as the spectrum of the parent ion, have been shown to be consistent, for the most part, with the predictions inherent in Hanazaki and Nagakura's¹⁰ self-consistent state wave functions. The explanation for the anomalous blue shift of band I in the para-substituted ions will probably require detailed calculations, either in terms of the localized orbital model¹² or in terms of self-consistent wave functions for the ground state of each ion, both of which are beyond the scope of this preliminary investigation.

More generally, we have shown that the electronic spectra of the difluorophenylcarbeniums ions are unusually sensitive to substituent effects. Thus the MCD and absorption spectra of these ions and, presumably, other phenylcarbeniums ions, can be utilized to advantage in exploring their electronic properties. Then, inasmuch as an accurate description of the ground state is required before the excited states become understandable, an improved understanding of all properties is possible.

Acknowledgment. We thank Mrs. Ruth Records for technical assistance and an anonymous donor for interim financial help.

(12) M. Godfrey and J. N. Murrell, *Proc. Roy. Soc., Ser. A*, **278**, 7, 64, 71 (1964).