1,9-Dithiophenalenyl System

Robert C. Haddon,* Fred Wudl,* Martin L. Kaplan, James H. Marshall, Rudolf E. Cais, and Fitzgerald B. Bramwell[†]

Contribution from Bell Laboratories, Murray Hill, New Jersey 07974, and the Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, New York 11210. Received November 17, 1977

Abstract: The 1,9-dithiophenalenylium cation has been prepared as a stable hexafluorophosphate salt, by reaction of 9-ethoxyphenalenone with phosphorus pentasulfide. The compound has been fully characterized and a MINDO/3 SCF MO calculation of the ground-state structure is reported. The compound is shown to undergo three one-electron reduction steps (without decomposition) the first two of which are reversible. Moderately highly conducting charge transfer salts are obtained with TCNQ derivatives. The 1,9-dithiophenalenyl radical has been prepared in solution by electrochemical and chemical reduction of 1,9-dithiophenalenylium hexafluorophosphate. The compound has been subjected to ESR, mass, and electronic spectral examination. The radical is found to be monomeric in solution in the temperature range between 18 and -95 °C. The observed ESR hyperfine splittings are consistent with the removal of spin density from the phenalenyl nucleus by disulfide substitution.

Odd alternant hydrocarbons are unique in their ability to form stable cations, radicals, and anions¹ which are of very similar molecular geometry.² They may therefore be of interest in the development of organic metals, where such characteristics have been suggested to be important.^{2–4} The chief obstacle to their utilization in this respect is the propensity of the neutrals radicals for dimerization—in fact we are not aware of any *planar* carbon-based radical which is wholly monomeric in solution and/or the solid state. The phenalenyl (PLY) (**1b**)



radical, while particularly stable, is known to dimerize at low temperatures in solution.^{5,6} We therefore sought to stabilize the triad of oxidation states and particularly the radical in a way which would not seriously perturb the desirable electronic properties of the PLY nucleus or inhibit intermolecular interactions in the solid state.

The 1,2-dithiolyl system also provides a number of accessible oxidation states.⁷ Thus the 3,5-diphenyl-1,2-dithiolylium cation (2a) has been shown to undergo three reduction steps;⁷ again the neutral radical (2b) is found to be in equilibrium with



the dimer.⁷ We therefore sought to combine these two components (1 and 2) in the 1,9-dithiophenalenyl system (DTPLY) (4). We felt that this species might be interesting in its own



right, as well as providing some insight into the effectiveness of incorporating sulfur into the PLY nucleus.

† City University of New York.

Results and Discussion

Synthesis and Characterization of the 1,9-Dithiophenalenylium Cation (4a) and 1,9-Dithiophenalenyl (4b). Our initial efforts to obtain 4a began with 9-hydroxyphenalenone (5),8-10 to which we applied the standard reagents for conversion of a β -hydroxy ketone into a 1,2-dithiolylium salt.^{11,12} Presumably as a result of the very strong hydrogen bonding in this compound,¹⁰ the material was found to be inert to the usual procedures, except under particularly forcing conditions from which no characterizable products could be recovered. Disruption of the hydrogen bonding, however, did allow preparation of 4a from the 9-hydroxyphenalenone skeleton, by use of phosphorus pentasulfide. As shown in Scheme I, 2,3-dihydro-9-hydroxyphenalenone $(6)^9$ leads to the desired product in low yield, in which the last reaction step is presumably a dehydrogenation. Complete removal of the hydrogen bonding, however, as in 9-ethoxyphenalenone (7),¹³ considerably improved the yield of product under much milder conditions. The hexafluorophosphate salt of $4a^{14}$ proved to be a stable, orange solid giving rise to yellow solutions. The cation gave rise to a

Scheme I



reaction sequence:

- 1. $P_4S_{10}/reflux$ in (a) xylene, (b) carbon disulfide
- 2. solvent removal

3.4 N HCl/reflux

- 4. filtration
- 5. $NaPF_{6}/addition$ of solution to filtrate

compd	Eple	$E_{\rm pla}$	E_{p2c}	E_{p2a}	E _{p3c}	E _{p3a}	ref
2a ClO ₄ -	-0.27 $2a \rightarrow 2b$	-0.20 2b \rightarrow 2a	-1.07 $2b \rightarrow 2c$	-0.35 2d \rightarrow 2b	-1.75 2d $\rightarrow 2e$	-1.65 $2e \rightarrow 2d$	b
4 a PF ₆ -	-0.25 $4a \rightarrow 4b$	-0.19 $4b \rightarrow 4a$	-0.81 $4b \rightarrow 4c$	-0.74 $4c \rightarrow 4b$	-1.63 $4c \rightarrow 4e$ or 4f	-1.48 4e or 4f \rightarrow 4c	
	1	$E_1^{R}(R\cdot/R^+)$	$E_2^{\mathrm{R}}(\mathrm{R}^-/\mathrm{F})$	<u>۲</u> .)	$E_3^{R}(R^{2-}/R^{-})$	ΔE_{2-1}	
1a BF ₄ ⁻ 2a ClO ₄ ⁻ 4a PF ₆ ⁻		0.7 -0.23 -0.22	-0.9 -1.04 -0.77	ţd 7	-1.70 -1.55^{d}	-1.6 -0.80 -0.55	c b

Table I. Cyclic Voltammetry^a

 ${}^{a}E_{plc}$ = peak potential of first reduction wave, etc; with assignment of redox couple underneath. E_{I}^{R} = half-cell potential for first reduction, etc. Potentials are given in volts vs. SCE, and were determined in acetonitrile with 0.1 M (*n*-Bu)₄NBF₄ as supporting electrolyte. b Reference 7. c Irreversible. D. J. Beames, R. C. Haddon and R. L. Martin, unpublished data. d Irreversible; see text. E_{pc} + 30 mV.



Figure 1. Room temperature electronic spectrum of 4a and 4b in acetonitrile.

particularly simple ¹H NMR spectrum with all the resonances lying in the range δ 8.1–8.9. Insofar as we are aware, **4a** provides the first example of a 1,2-dithiolylium system fused to an aromatic ring, although a carbocation¹⁵ isoelectronic with **4a** has been reported.

The 1,9-dithiophenalenyl radial $(4b)^{14}$ was prepared by reduction of $4a PF_6^-$ using a variety of chemical and electrochemical techniques of which coulometry proved to be the most efficient. The radical gave rise to orange solutions and the electronic spectra of 4a and 4b are compared in Figure 1. A solution of 4b was evaporated in a mass spectrometer probe and gave rise to a parent ion at $m/e 227 (C_{13}H_7S_2^+ assigned to 4a)$ with an isotope distribution ratio characteristic of two sulfur atoms.

Electrochemistry. The results of cyclic voltammetric studies of **4a** PF_6^- in acetonitrile are shown in Table I, together with data on related materials. The separations of our peak potentials indicate that the couples $4 \cdot / 4^+$ and $4^- / 4^{-}$ for **4a** are reversible one-electron processes at a silver electrode. The same behavior was found⁷ for the couple $2 \cdot / 2^+$ but not $2^- / 2^{-}$ in the electrochemistry of **2a**. In this latter case the data were interpreted in favor of **2b** for the first reduction product of **2a** with **2c** being the immediate product of the second reduction step.⁷ Under all conditions, however, it was found⁷ that **2c** rapidly underwent sulfur-sulfur bond scission to produce **2d**. It therefore seems reasonable to assume that the first reduction of **4a** gives rise to **4b** (see ref 14) and that this in turn is reduced to **4c**, which on the time scale of our experiment is not converted to **4d**. On the basis of these considerations and the results presented in Table I (particularly the ΔE values), it would seem that sulfur substitution in the PLY nucleus has enhanced the relative stabilities of both the oxidized and reduced forms of the neutral radical in these systems.

Further reduction of 2d was reported⁷ to lead to 2e and a reduction at similar potential was observed for 4c which could lead to the production of either 4e or 4f. The peak separation for the third wave of 4a (150 mV) is not much larger than that of 2a (100 mV), and the latter was found to be reversible.⁷ This value for 4a is considerably smaller than the peak separation of the second wave for 2 (720 mV), which does involve cleavage and formation of a sulfur-sulfur bond.⁷ Therefore, the species produced in the third reduction of 4a cannot be ascertained at this time, beyond the likely involvement of 4e and/or 4f.

In fact the stability of the sulfur-sulfur bond toward cleavage on reduction of 4a is not at all surprising in view of the results of our ESR measurements and SCF MO calculations (see later). Both of these techniques indicate that the molecular orbitals which the reducing electrons populate in

	Tab	ole I	Ι.	Hy	perfine	Proton	Cou	oling	Constants	of	Phenalen	yl l	Radical
--	-----	-------	----	----	---------	--------	-----	-------	-----------	----	----------	------	---------

		coupling constan	nts of radical, G			
	3 2					
positions	obsd ^a	calcd	obsd ^a	obsd ^b	calcd	
2,8	1.820	1.794	1.754	1.49	0.71	
3,7	6.304	6.044	6.089	5.06	4.83	
4,6	6.304	6.044	6.089	5.45	5.50	
5	1.820	1.794	1.754	1.49	1.47	

^a Solution in carbon tetrachloride; g = 2.0027. Reference 6. ^b Solution in dichloromethane; g = 2.0042, line width = 0.115 G. The 3,7/4,6 assignment was made on the basis of the calculations.



Figure 2. Room temperature ESR spectrum of 4b in dichloromethane.

 $4a^+$ have rather small coefficients at the sulfur atoms (although, of course, antibonding with respect to the sulfur-sulfur bond), in comparison to those of $2a^+$. A further consideration applies to the structural rigidity of the sulfur atoms of 4 which are forced to lie in close proximity irrespective of the presence of a sulfur-sulfur bond. This is not the case in 2, where rotation about one of the partial carbon-carbon double bonds or flexing of the backbone of the molecule allows the sulfur atoms to move away from one another.

Electron Spin Resonance Spectroscopy. The ESR spectrum of 4b in dichloromethane is shown in Figure 2. Essentially identical spectra were obtained when 4b was generated by chemical (Zn) or electrochemical reduction of 4a PF_6^- in a variety of solvents including methylene chloride, toluene, dimethoxyethane, carbon disulfide, and mixtures thereof. The spectrum was successfully computer simulated by assuming one set of three equivalent protons and two sets of two equivalent protons. Efforts to experimentally resolve the ESR spectrum further, particularly the quartet assigned to three equivalent protons, were unsuccessful. The results of the spectral analysis are shown in Table II along with previously published data for 1 and an alkylated derivative of 1. Comparison of the observed hfs found for 4 with those for 1 indicates that an appreciable amount of spin density is removed from the phenalenyl nucleus on disulfide substitution (approximately 20%). Solutions of 4b prepared in a variety of solvents showed no detectable change in concentration of monomer (as measured by the integrated intensity of the ESR signal) in the temperature range 19 to -95 °C. We therefore conclude that under these conditions, 4b provides the first example of a monomeric, coplanar, carbon-based free radical. This observation stands in marked contrast to the behavior noted for solutions of 1b in which ESR signals are not observed at temperatures below -25 °C.⁶ The explanation for such



Figure 3. MINDO/3 calculated geometries for 1a, dithiolylium cation, and 4a.

differences may stem in part from a decrease in the statistical enhancement for dimerization of **1b** (with six equivalent coupling sites, the forward step of reaction 1 is kinetically enhanced by a factor of 6^2). In the case of **4b**, dimerization would be statistically enhanced by a factor of 2^2 for dimers involving **8** alone or 4^2 for equally favored dimers among **8** and **9**. Although dimers involving **10** would seem to be energetically



unfavorable, such dimers have been shown to occur in the 1,2-dithiolyl system⁷ (reaction 2). For **2f**, the *dissociation* is totally suppressed, whereas for **2b**, dimerization was shown to be essentially complete at -30 °C.⁷

Calculations. The MINDO/3¹⁶ SCF MO equilibrium geometries of **1a**, **4a**, and the 1,2-dithiolylium cation¹⁷ (optimized in D_{3h} , C_{2v} , and C_{2v} symmetry, respectively) are given in Figure 3. The MINDO/3 structure for the 1,2-dithiolylium cation is in good agreement with crystallographic studies;¹⁸ the largest error is associated with the sulfur-sulfur bond, which is overestimated in length by approximately 0.1 Å. It may be seen that disulfide substitution is found to exert a relatively minor effect on the geometry of the PLY⁺ nucleus at this level of approximation.

Table III. NMR	. Chemical Shifts and	Calculated Charge	Densities for $DTPLY^+$ (4a)
----------------	-----------------------	-------------------	------------------------------

				calculated charge densities					
		¹ H NMR,	¹³ C NMR,		П	t	otal		
	position	δ	δ	STO-3G	MINDO/3	STO-3G	MINDO/3		
	3		167.45	0.134	0.233	-0.041	0.257		
	5	8.719	141.28 <i>ª</i>	0.172	0.196	0.021	0.166		
Å,	7	8.74	136.47 <i>ª</i>	0.144	0.165	0.008	0.138		
	1		134.70 <i>^b</i>	0.055	0.053	0.035	0.079		
()	8	8.23	131.43	-0.018	-0.027	-0.060	-0.045		
	6		129.46	-0.059	-0.083	-0.014	-0.071		
ss.	4	8.444	124.01 <i>ª</i>	-0.073	-0.088	-0.073	-0.103		
	2		122.52 ^b	-0.100	-0.138	-0.035	-0.160		
	9			0.211	0.133	0.267	0.049		

^{*a,b,c*} Interchangeable. Assigned on the basis of the calculations.

In addition, a single ab initio STO-3G¹⁹ calculation was carried out on **4a** (at the MINDO/3 geometry), and the charge densities from the calculations are compared with the observed ¹³C NMR chemical shifts in Table III. If one accepts the uncertain assignments, then there appears to be a rather good correlation between these quantities (with the exception of the total charge densities from the ab initio calculation). It may be seen that some remnants of the pairing theorem still apply in **4a** as the largest charge densities are still associated with the active positions of the PLY⁺ nucleus.^{2c}

Charge Transfer Complexes. Mixture of equimolar acetonitrile solutions of 4a PF_6^- and $(n-Bu)_4N^+$ TCNQ⁻ gave rise to a black solid of 1:1 stoichiometry with a compaction specific resistivity of 100 ohm cm. A benzotetracyanoquinodimethane (BTCNQ) complex which was prepared in like manner showed a specific resistivity of 70 ohm cm. The only previous charge transfer salt containing a 1,2-dithiolylium cation for which conductivity data are available²⁰ involved a complex between 2a and 11 which gave specific resistivities of 10⁷-10⁸ (com-



paction)^{20a} and 6×10^{12} ohm cm (single crystal).^{20b} Under the same conditions the organic metal TTF TCNQ has a compaction resistivity of about 1 ohm cm.²¹ It is interesting to note that the DTPLY BTCNQ complex has a slightly higher conductivity than that of the DTPLY TCNQ complex, which is a reversal of the usual order of TCNQ complexes. We believe that this behavior can be accounted for by reference to the cell emf's for the redox reactions of the components of the various complexes, as shown in Table IV. Although all processes are endothermic as shown, it is clear that the highest conductivity is associated with the most closely matched half-cell potentials (all other things being equal).

Experimental and Calculational Section

HMO wave functions were obtained with the parametrization^{7,22,23} $\alpha_{\rm s} = \alpha + 1.2 \beta$, $\beta_{\rm cs} = 0.65 \beta$, and $\beta_{\rm ss} = 0.7 \beta$. The spin densities were calculated with the McLachlan procedure using $\lambda = 1.1$. Theoretical coupling constants ($a_{\rm H}$) were derived from the calculated spin densities ($\rho_{\rm H}$) by use of the relationship $a_{\rm H} = Q_{\rm H}\rho_{\rm H}$ with $Q_{\rm H} = 27 \ {\rm G}^{.7,22,23}$

 $(\rho_{\rm H})$ by use of the relationship $a_{\rm H} = Q_{\rm H}\rho_{\rm H}$ with $Q_{\rm H} = 27~{\rm G}^{.7,22,23}$ The cyclic voltammetry on 4a PF₆⁻ was carried out in acetonitrile with 0.1 M *n*-Bu₄NBF₄ as supporting electrolyte, with a platinum working electrode and silver/silver chloride reference electrode using an ESA sweep generator. The results in Table I are corrected (-0.02 V) to the SCE scale. The peak separations for the cathodic and anodic waves for the first two reductions of 4a were in the range 60-70 mV at sweep rates from 500 to 50 mV/s, whereas the third reduction wave had peak separations of 150-200 mV over the same range of sweep rates. Within the precision of our experiment the cathodic and anodic currents were equal for all waves.

Solutions of the radical 4b were prepared under argon by coulo-

Table IV. Standard Cell Emf's

		C	ella				<i>E</i> °, V <i>^b</i>
TTF TTF DTPLY ⁺ DTPLY ⁺	+ + + +	TCNQ BTCNQ TCNQ- BTCNO-	$ \begin{array}{c} \uparrow \\ \uparrow $	TTF ⁺ TTF ⁺ DTPLY DTPLY	+ + + + +	TCNQ- BTCNQ- TCNQ BTCNO	-0.13 -0.29 -0.41 -0.25

a DTPLY = 1,9-dithiophenalenyl; BTCNQ = benzo TCNQ. b In acetonitrile.

metric reduction of **4a** PF_6^- at -0.4 V (relative to SCE) in acetonitrile using a PAR Model 380 controlled potential coulometry system with a platinum working electrode. The radical was then separated from the electrolyte via carbon disulfide extraction. The solvent was subsequently removed under an inert atmosphere to give a black solid. This solid was used to prepare solutions of **4b** in various solvents.

Radical concentrations were determined in toluene, carbon disulfide, and a mixed solvent composed of CH₂Cl₂/toluene (1:3), using the double integral of the first derivative ESR spectra. The concentrations were found indirectly by reference to a standard solution of 2,2,6,6-tetramethyl-4-hydroxypiperidinyl-1-oxyl. A plot of log [4b] vs. 1/T showed zero slope over the temperature range 173–292 K at radical concentrations of 1.85×10^{-6} . 2.65×10^{-5} , and 3.06×10^{-4} M. The spectra were obtained with a Varian x-band ESR spectrometer utilizing 100-kHz field modulation.

¹³C NMR spectra were obtained with a Bruker WH-90 spectrometer (22.62 MHz) at 50 °C in acetonitrile- d_3 . The primary internal reference was hexamethyldisiloxane (δ 1.99), and chemical shifts were measured from the nitrile carbon resonance as a secondary standard (δ 118.15).

Preparation of 9-Hydroxyphenalenone (5). The synthesis followed a slight variant of the original method,⁸ which obviates the need to isolate the intermediate 1-cinnamoyl-2-methoxynaphthalene.8 2-Methoxynaphthalene (158.5 g) and cinnamoyl chloride (144 mL) were dissolved in 1500 mL of dry 1,2-dichloroethane. The reaction vessel was cooled in an ice bath and 135 g of aluminum trichloride was slowly added while the solution was mechanically stirred. After 30 min (at which time the reaction mixture had come to room temperature) a further 135 g of aluminum trichloride was added, and the reaction taken to reflux. After about 1 h solid started to form which had to be mechanically broken up during the course of the reaction. The reaction was quenched after about 2 h by pouring into an ice/hydrochloric acid mixture. The aqueous mixture was repeatedly extracted with methylene chloride to give a total volume of about 5 L. The organic extracts were dried over MgSO4 and taken down on a rotary evaporator to give a yellow solid, crude yield 103 g (52%), mp 193-200 °C. The compound can be purified by sublimation and/or recrystallization from benzene, methanol, or acetonitrile to give golden plates, mp 199-200 °C (lit. mp 198-199,²⁴ 199-200,^{9,10} 200-201 °C⁸).

2,3-Dihydro-9-hydroxyphenalenone (6). The compound was prepared by hydrogenation of 5 at 4 atm pressure in acetic acid with palladium on charcoal as catalyst.⁹ Recrystallization from methanol gave yellow needles, mp 137-138 °C.

9-Ethoxyphenalenone (7). Reaction of 5 with ethyl iodide and silver oxide in chloroform gave 7^{13} as an oil which was used without further purification.

1,9-Dithiophenalenylium Hexafluorophosphate (4a PF_6^{-}). 9-Ethoxyphenalenone (7, 4.26 g) was dissolved in 75 mL of carbon disulfide and 8 g of phosphorus pentsulfide (twice recrystallized from carbon disulfide by the Soxhlet method) was added. The mixture was held at reflux for 30 min and then the carbon disulfide removed by evaporation. HCl (4 M, 50 mL) was added to the residue and the mixture was refluxed for 15 min and then filtered. A solution of sodium hexafluorophosphate (4 g in 40 mL of water) was added to the filtrate, and the precipitate isolated by filtration. The solid was dried, dissolved in acetonitrile, and recrystallized by addition of ether to give 1.28 g of orange solid (18%).

4a PF_6^- : mp 261.3-261.7 °C dec; ¹H NMR (δ , CD₃CN) absorption range 8.1–8.9, AB pattern (intensity 4), δ_A 8.44, δ_B 8.71 (J_{AB} = 9 Hz), AB₂ pattern (intensity 3), δ_A 8.23, δ_B 8.74 (J_{AB} = 8 Hz); IR (cm⁻¹, CsI) 3060 (w, br), 1611 (s), 1584 (s), 1548 (s), 1474 (m), 1407 (vs), 1354 (w), 1316 (s), 1307 (s), 1289 (s, sh), 1243 (s), 1199 (m), 1172 (s), 1160 (m), 1127 (s), 1087 (vw), 1063 (w), 991 (w), 940 (vw), 900-800 (vs, br), 796 (m, sh), 676 (s), 554 (vs), 497 (w), 478 (m), 387 (vw), 362 (m), 298 (vw); UV [nm (e), CH₃CN] 213 (32 600), 226 (31 800), 258 (7400, sh), 281 (9400), 343 (5600), 420 (21 600, sh), 439 (30 800). Anal. Calcd for C13H7S2PF6: C, 41.94; H, 1.90; S, 17.23. Found: C, 42.14; H, 1.71; S, 17.42. Semiquantitative X-ray spectrochemical analysis gave an S:P ratio of about 2:1.

Acknowledgments. The authors would like to thank S. H. Glarum for permitting us the use of his ESR equipment, D. J. Freed and A. M. Mujsce for their cooperation in obtaining the mass spectral data, and S. M. Vincent for X-ray spectrochemical analysis. F. B. Bramwell also wishes to acknowledge the partial support of the National Science Foundation in the form of Grant SMI77-17390.

References and Notes

- (1) (a) V. Boekelheide and C. E. Larrabee, J. Am. Chem. Soc., 72, 1245 (1950);
 (b) R. Pettit, Chem. Ind. (London), 1306 (1956); (c) D. H. Reid, *ibid.*, 1504 (1956); (d) R. Pettit, J. Am. Chem. Soc., 82, 1972 (1960).
 (2) (a) R. C. Haddon, Nature (London), 256, 394 (1975); (b) Aust. J. Chem., 28, 1972 (1960).
- 2333 (1975); (c) ibid., 28, 2343 (1975).
- (3) H. Gutfreund, B. Horovitz, and M. Weger, J. Phys. C. 7, 383 (1974); Phys. Rev. B, 9, 1246 (1974); Solid State Commun., 33, 305 (1974).
- (4) M. J. Rice, C. B. Duke, and N. O. Lipari, Solid State Commun., 17, 1089

(1975); C. B. Duke, N. O. Lipari, and L. Pietronero, Chem. Phys. Lett., 30, 415 (1975); N. O. Lipari, C. B. Duke, R. Bozio, A. Girlamdo, and C. Pecile, ibid., 44, 236 (1976); M. J. Rice, Phys. Rev. Lett., 37, 36 (1976); M. J. Rice and N. O. Lipari, ibid., 38, 437 (1977).

- (5) D. H. Reid, Tetrahedron, 3, 339 (1958); D. H. Reid, Q. Rev., Chem. Soc., 19, 274 (1965).
- (6) (a) F. Gerson, Helv. Chim. Acta, 49, 1463 (1966); (b) F. Gerson, E. Heilbronner, H. A. Reddock, D. H. Paskovich, and N. C. Das, ibid., 50, 813 (1967).
- (7) K. Bechgaard, V. D. Parker, and C. Th. Pedersen, J. Am. Chem. Soc., 95, 4373 (1973).
- (8) C. F. Koelsch and J. A. Anthes, J. Org. Chem., 6, 558 (1941).
 (9) J. D. Loudon and R. K. Razdan, J. Chem. Soc., 4299 (1955).
 (10) Y. Demura, T. Kawato, H. Kanatomi, and I. Murase, Bull. Chem. Soc. Jpn., 48, 2820 (1975).
- (11) G. Duguay and H. Quiniou, Bull. Soc. Chim. Fr., 1918 (1970).
- (12) H. Hartmann, K. Fabian, B. Bartho, and J. Faust, J. Prakt. Chem., 312, 1197 (1970).
- (13) K. D. Franz and R. L. Martin, Tetrahedron, in press. We are grateful to the authors for a preprint of this manuscript
- (14) Preliminary communication: R. C. Haddon, F. Wudl, M. L. Kaplan, J. H. Marshall, and F. B. Bramwell, J. Chem. Soc., Chem. Commun., 429 (1978).
- (15) I. Murata, K. Yamamoto, and Y. Kayane, Angew. Chem., Int. Ed. Engl., 13, 808 (1974).
- (16) R. C. Bingham, M. J. Dewar, and D. H. Lo, J. Am. Chem. Soc., 97, 1285, 1294 (1975); M. J. S. Dewar, D. H. Lo, and C. A. Ramsden, *ibid.*, 97, 1311 (1975).
- (17)The status of carbocation calculations has been reviewed by L. Radom, D. Poppinger, and R. C. Haddon, "Carbonium Ions", Vol. 5, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1976, Chapter 38.
 A. Hordvik and E. Sletten, Acta Chem. Scand., 20, 1974 (1966); A. Hordvik
- and R. M. Baxter, *ibid.*, **23**, 1082 (1969); A. Hordvik and H. M. Kjoge, *ibid.*, **23**, 1367 (1969); H. C. Freeman, G. H. W. Milburn, C. E. Nockolds, R. Mason, G. B. Robertson, and G. A. Rusholme, *Acta Crystallogr., Sect. B*, **30**, 886 (1974); R. Mason, G. B. Robertson, and G. A. Rusholme, *ibid.*, **30**, 894, 906 (1974).
- (19) W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys., 51, 2657 (1969).
- (20) (a) N. Loayza and C. Th. Pedersen, J. Chem. Soc., Chem. Commun., 496 (1975); (b) O. Simonsen, N. Loayza, and C. Th. Pedersen, Acta Chem. Scand., Ser. B, **31**, 281 (1977).
- (21) Single crystal studies are reported by J. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973); L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Commun.*, **12**, 1125 (1973).
- (22) F. B. Bramwell, R. C. Haddon, F. Wudl, M. L. Kaplan, and J. H. Marshall, J. Am. Chem. Soc., 100, 4612 (1978).
- (23)R. C. Haddon, M. L. Kaplan, and J. H. Marshall, J. Am. Chem. Soc., 100, 1235 (1978).
- (24) H. Silberman and S. Silberman, Aust. J. Sci., 18, 115 (1956).

Ion Pairing in Excited States of Carbanions. 2. Emission of Fluorenyl and Fluoradenyl Alkali Salts in Aprotic Media

T. E. Hogen-Esch*1 and J. Plodinec

Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611. Received March 8, 1978

Abstract: The UV/visible absorption and emission and excitation spectra of alkali salts of fluorene (FIH) and fluoradene (FdH) were measured in a series of low dielectric constant ethereal solvents in or without the presence of crown ethers. For a series of tight ion pairs the absorption and emission wavelength maximum increased and decreased, respectively, with increasing cation radius. The spectroscopic results for LiFl/THP, NaFl/THF, and NaFd/THF are consistent with the existence of an equilibrium between contact and solvent-separated ion pairs in the first excited state. The fraction of separated ion pairs in the first excited states was found to increase as THP < THF < DME similar to the ground states. The proportion of separated ion pairs was also invariably found to be higher in the first excited state than in the ground state. It was found that the relative stabilities of the two ion pairs in ground state and first excited states could be quantitatively related through a Förster cycle. Dissociation of contact ion pairs into free ions could be easily observed in emission and excitation spectra of the NaFl/ THF and NaFd/THP systems. Cation and solvent effects on lifetime of these salts were also examined. Na, K, and Rb contact ion pairs of Fl-* in THP were shown to have similar lifetimes and emission intensities whereas the Cs ion pair is shorter lived presumably owing to a heavy atom effect. Separated ion pairs and free ions were shown to be longer lived and to emit most intenselv.

Introduction

Over the last few years there has been a considerable interest in the photochemistry of ionic intermediates.² Much experimental work has been done but not much is known regarding the detailed nature of the postulated ionic intermediates. The behavior of excited-state carbanions has been described by Burley and Young,³ Vander Donckt et al.,⁴ Vos et al.,^{5,6} and