Electronic Spectra of Lithium Salts of Substituted Fluorenes. Evidence for the π-Inductive Effect of Unshared Pairs[1]

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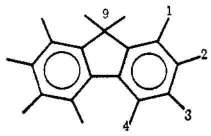
Electronic absorption spectra have been recorded for lithium salts of twelve substituted fluorenes in cyclohexylamine. The compounds include 2-fluorofluorene, 2-dimethylaminofluorene, the five isomeric methylfluorenes, and the five methoxyfluorenes. Relative to lithium fluorenyl itself, salts bearing a substituent at the 1, 2, or 4 position show a hypsochromic shift, whereas those substituted at the 3 or 9 position show a bathochromic shift. Coulson's treatment correctly predicted the direction of the spectral shift for all five methylfluorenyl anions, but on the basis of σ-inductive effects it failed for every anion bearing a lone-pair substituent. The results provide evidence for the electron-repelling π-inductive effect of lone-pair substituents, recently proposed by Clark, Murrell, and Tedder.

The spectral shifts produced when hydrogen is replaced by methyl in an aromatic hydrocarbon have been studied extensively. In even-alternant hydrocarbons (those which have no odd-membered rings), substitution of methyl for hydrogen invariably results in a shift to longer wavelength. In contrast, in the nonalternant hydrocarbon azulene, the direction of the spectral shift for the absorption in the visible region depends on the position at which the methyl is introduced. A methyl group at position 1 or 5 produces a shift to longer wavelength, but methyl at 2, 4, or 6 results in a shift to shorter wavelength.[2]

By comparison to the wealth of reports on stable hydrocarbon compounds, the electronic spectra of hydrocarbon ions have received little attention; until recently the literature contained almost no information about the effect of substituents on the spectra of these ions. Studies of allyl and benzyl cations have shown that introduction of methyl into an odd-alternant hydrocarbon cation can result in either a bathochromic or a hypsochromic shift, depending on the position of the substituent,[3] just as in the case of the neutral species azulene. Waack and Doran recorded spectra of a number of methyl-substituted allyl and benzyl anions and found the direction of the spectral shift to be position dependent.[4] Thus, the effect of methyl substituents on electronic spectra has been examined in neutral hydrocarbon compounds of the even and nonalternant types and in odd-alternant hydrocarbon cations and anions, but studies of this kind on nonalternant hydrocarbon ions have not previously been done.

Streitwieser and his coworkers reported electronic absorption spectra for lithium and cesium salts of a number of nonalternant hydrocarbon anions. These included salts of fluorene, the three benzfluorenes, and 9-methyl-, 9-phenyl-, and 9-benzylfluorene, as well as salts of several other hydrocarbons,[5] but did not include any fluorene derivatives substituted in the 1, 2, 3, or 4 position. This study deals with the relation of spectral shift to position of substitution for lithium salts of twelve substituted fluorenes, with cyclohexylamine as solvent, and substituents including methyl and three groups of the lone-pair type, fluoro, dimethylamino, and methoxy.



The effect of lone-pair substituents on the spectra of even alternants is, like the effect of methyl, well documented. Substitution of halogen, –OR, –SR, or $-NR_2$ for hydrogen on either ethylene or benzene causes a decrease in electronic transition energy.[6] Only a few examples in odd and nonalternant systems have been reported. Halogen at the 1 or 3 position of azulene[7] and amino, dimethylamino, methoxy, or chloro at the *ortho* or *para* position of triphenylmethyl cation[3c] produces all bathochromic shifts. Our search of the literature uncovered only one example of a hypsochromic shift caused by a lone-pair substituent; substitution of chlorine for *meta* hydrogen in triphenylmethyl cation shifts λ_{max} from 431 to 412 mμ.[3c] Clark, Murrell, and Tedder hypothesized that a major and previously unrecognized effect of lone-pair groups is electron donation by a π-inductive mechanism,[8] and suggested that decisive evidence for their hypothesis would be observation of increases in electronic transition energy produced by lone-pair substituents in nonalternant systems. A major objective of our study of spectra of the five isomeric methoxyfluorenyl anions was to provide this test for the π-inductive effect.

Experimental Section

Materials Used.—Several of the compounds used were obtained from the Aldrich Chemical Co. The ones which melted below the literature values were purified by recrystallization from isooctane (spectranalyzed). These samples had the following melting points:[9] 2-fluorofluorene, mp 99.0–100.0°

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(1) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) P. A. Plattner, *Helv. Chim. Acta*, **24**, 283E (1941); P. A. Plattner and E. Heilbronner, *ibid.*, **30**, 910 (1947).

(3) J. A. Grace and M. C. R. Symons, *J. Chem. Soc.*, 958 (1959); (b) J. Rosenbaum and M. C. R. Symons, *ibid.*, 1 (1961); (c) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954).

(4) R. Waack and M. A. Doran, *J. Phys. Chem.*, **68**, 1148 (1964).

(5) (a) A. Streitwieser, Jr., and J. I. Brauman, *J. Amer. Chem. Soc.*, **85**, 2633 (1963). (b) A. Streitwieser, Jr., J. I. Brauman, J. H. Hammons, and A. H. Pudjaatmaka, *ibid.*, **87**, 384 (1965).

(6) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 175–177 and 248–252.

(7) E. Heilbronner in "Non-benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N.Y., 1959, pp 237, 244.

(8) D. T. Clark, J. N. Murrell, and J. M. Tedder, *J. Chem. Soc.*, 1250 (1963); D. T. Clark, *Chem. Commun.*, 390 (1966).

(9) Melting points were taken on a Thomas-Hoover apparatus, and are uncorrected.

(lit.[10] mp 98°); 1-methoxyfluorene, mp 85.0–86.0° (lit.[11] mp 85–86°); 2-methoxyfluorene, mp 109.5–110.5° (lit.[12] mp 110°); 3-methoxyfluorene, mp 83.0–84.0° (lit.[13] mp 84–85°); 4-methoxyfluorene, mp 77.0–78.0° (lit.[14] mp 76.5–77.5°). Melting points of three additional samples[15] were as follows: 1-methylfluorene, mp 84.0–85.0° (lit.[16] mp 85°); 2-methylfluorene, mp 100.5–102.5° (lit.[12] mp 101.5–102.5°); 2-dimethylaminofluorene, 179.5–180° (lit.[17] mp 180.0–180.5°).

The method of DeTar and coworkers[18,19] was used to prepare 3-methyl-9-fluorenone; 1.6 g of this ketone was reduced by the Huang-Minlon modification[20] of the Wolff-Kishner reaction to yield 1.4 g (94%) of 3-methylfluorene, mp 83–85°. Recrystallization from isooctane raised the melting point to 87.5–88.5° (lit.[21] mp 88°). Preparation of 4-methylfluorene was accomplished by a five-step sequence. Commercial 9-fluorenone-4-carboxylic acid (Aldrich Chemical Co.) was reduced to fluorene-4-carboxylic acid by the method of Morrison.[22] The acid was converted to the acid chloride by treatment with thionyl chloride, and the unpurified acid chloride was reduced in the usual way with lithium aluminum hydride to yield 4-hydroxymethylfluorene (75.3% yield from the acid) of mp 126.5–128.5° (lit.[23] mp 129–130°). Treatment with thionyl chloride coverted the alcohol to 4-chloromethylfluorene,[23] and the chloride was reduced to 4-methylfluorene with lithium hydride and lithium aluminum hydride by the method of Streitwieser and Langworthy,[24] mp 70.0–72.0° (lit.[25] mp 69–70°). Preparation of 9-methylfluorene was accomplished by reaction of 9-fluorenone with methylmagnesium iodide, and reduction of the resulting 9-methyl-9-fluorenol with zinc dust and palladium in acetic acid,[26] mp 45.0–46.0° (lit.[27] mp 46–47°). 9-Methoxyfluorene was prepared by lithium aluminum hydride reduction of 9-fluorenone, conversion of 9-fluorenol into 9-bromofluorene with hydrobromic acid in acetic acid, and reaction of the bromide with silver nitrate in methanol,[28] mp 43.0–44.0° (lit.[28] mp 43.5°).

The cyclohexylamine used (Eastman Kodak Co.) was purified by fractional distillation, bp 134.2–134.8° (760 mm). *n*-Butyllithium (Foote Mineral Co.) was approximately 1.6 *M* in heptane.

Spectra.—The solutions were prepared in Pyrex vessels having the following features: (1) a straight-bore stopcock and outer joint at the top for connection to a vacuum system, (2) a side arm with a straight-bore stopcock for injection of butyllithium, and (3) a side arm with a rectangular Pyrex absorption cell. Path lengths of the cells on the three reactors used were calibrated with standard solutions of K_2CrO_4–KOH and found to be 9.97 mm, 10.02 mm, and 1.02 mm (10-mm Pyrex cell with 9.0-mm silica spacer). A quantity of a hydrocarbon was weighed on a Cahn Model M-10 electrobalance, dissolved in isooctane (spectranalyzed), and introduced into the weighed vessel with a syringe. The vessel was attached to a vacuum system and the isooctane was removed. About 5 ml of dry cyclohexylamine was transferred under vacuum into the vessel directly from a stock solution of lithium cyclohexylamide in cyclohexylamine. The vessel was charged to atmospheric pressure with argon and removed from the vacuum line. A syringe was used to inject 0.1 ml of butyllithium solution through a rubber septum and the adjacent stopcock. The volume of the solution was determined from the weight of solution added and the known density of cyclohexylamine.

Preliminary scans of the spectra were made on a Beckman DB recording spectrophotometer. The λ_{max} and ϵ_{max} values reported were determined from more precise measurements on a Beckman DU instrument which had previously been adjusted for maximum accuracy of wavelength calibration. Absorbances were corrected for absorbance by the cell and solvent.

Results

All of the fluorene derivatives used in this study were readily soluble in cyclohexylamine containing lithium cyclohexylamide, giving solutions of substituted fluorenyl anions which absorbed in the region 400–600 mμ; the range below 400 was not examined, as solutions of lithium cyclohexylamide in cyclohexylamine are known to absorb below about 375.[5a] The stability of the anion solutions was evident from the fact that repeated scans showed no change in absorption over periods as long as 10 days. At least two runs were made for each salt, and ϵ_{max} values were reproduced to better than 10% in every case except those of 2-methylfluorenyl and 9-methoxyfluorenyl anions, for which two runs gave results differing by 12 and 14%, respectively. The three extinction coefficients found for lithium fluorenyl and the three for lithium 9-methylfluorenyl were approximately 7% lower than the values reported by Streitwieser and Brauman.[5a] Solutions of fluorene and 9-methylfluorene (as well as those of a number of other fluorene derivatives) in lithium cyclohexylamide–cyclohexylamine are known[5a] to obey Beer's law, indicating that the reaction in eq 1 goes to

$$RH + C_6H_{11}NHLi \longrightarrow RLi + C_6H_{11}NH_2 \qquad (1)$$

completion. Solutions of 3- and 4-methylfluorene and 1-, 2-, 3-, and 4-methoxyfluorene in this medium proved to obey Beer's law; the concentration ranges used with the remaining hydrocarbons were too small to permit any conclusion about the relation between concentration and absorbance.

As the data in Table I show, all of these lithium fluorenyl salts have three maxima between 435 and 555 mμ, spaced from 20 to 40 mμ apart. In every case the middle one is the most intense, with ϵ_{max} values ranging from 937 to 1780, and the long wavelength one is the least, with ϵ_{max} values lying between 591 and

TABLE I

Lithium salt of	λ_{max}, mμ (ϵ_{max})
Fluorene	454 (1040), 480 (1220), 514 (788) 452 (1080), 477 (1300), 510 (827)[a]
1-Methylfluorene	449 (1210), 472 (1500), 503 (1020)
1-Methoxyfluorene	440 (1470), 461 (1620), 489 shoulder (979)
2-Methylfluorene	450 (910), 476 (982), 505 shoulder (592)
2-Methoxyfluorene	441 (974), 461 (1030), 489 shoulder (643)
2-Fluorofluorene	443 (805), 470 (973), 501 (591)
2-Dimethylaminofluorene	439 (928), 462 (937), 490–495 shoulder
3-Methylfluorene	461 (1070), 489 (1210), 522 (773)
3-Methoxyfluorene	475 (1070), 497 (1260), 528 (838)
4-Methylfluorene	441 (1260), 465 (1480), 496 (958)
4-Methoxyfluorene	428 shoulder (1450), 448 (1780), 474 (1250)
9-Methylfluorene	482 (848), 514 (1080), 553 (706) 480 (905), 512 (1130), 551 (785)[a]
9-Methoxyfluorene	487 shoulder (972), 513 (1100), 542 shoulder (758)

[a] Values of Streitwieser and Brauman.[5a]

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(10) E. D. Bergmann, S. Berkovic, and R. Ikan, *J. Amer. Chem. Soc.*, **78**, 6037 (1956).

(11) E. K. Weisburger and J. H. Weisburger, *J. Org. Chem.*, **18**, 864 (1953).

(12) J. D. Dickinson and C. Eaborn, *J. Chem. Soc.*, 2337 (1959).

(13) N. Ishikawa and M. Okazaki, *Yuki Gosei Kagaku Kyokai Shi*, **16**, 610 (1958); *Chem. Abstr.*, **53**, 3168*b* (1959).

(14) H. L. Pan and T. L. Fletcher, *J. Org. Chem.*, **25**, 1106 (1960).

(15) These compounds were generously supplied by Professor A. Streitwieser, Jr.

(16) F. H. Howell and D. A. H. Taylor, *J. Chem. Soc.*, 3011 (1957).

(17) T. L. Fletcher, M. E. Taylor, and A. W. Dahl, *J. Org. Chem.*, **20**, 1021 (1955).

(18) H. J. Scheifele and D. F. DeTar, *Org. Syn.*, **32**, 8 (1952).

(19) D. F. DeTar and T. E. Whitely, *J. Amer. Chem. Soc.*, **79**, 2498 (1957)

(20) Huang-Minlon, *ibid.*, **68**, 2487 (1946).

(21) A. Sieglitz and J. Schatzkes, *Chem. Ber.*, **54**, 2070 (1921).

(22) D. C. Morrison, *J. Org. Chem.*, **23**, 1772 (1958).

(23) R. Quelet and J. Barge [*Compt. Rend.*, **251**, 1019 (1960)] reported the preparation of 4-hydroxymethylfluorene by lithium aluminum hydride reduction of methyl fluorene-4-carboxylate.

(24) A. Streitwieser, Jr., and W. C. Langworthy, *J. Amer. Chem. Soc.*, **85**, 1757 (1963).

(25) R. D. Haworth and P. B. Tinker, *J. Chem. Soc.*, 911 (1955).

(26) Experiments were by Mr. J. E. Tear.

(27) W. Wislicenus and A. Densch, *Chem. Ber.*, **35**, 759 (1902).

(28) A. Kliegl, *ibid.*, **62**, 1327 (1929).

1250. In a few cases one or the other of the side peaks appears only as a shoulder. The maxima are broad and cannot be located with an accuracy greater than ±1 or 2 mμ. The three λ_{max} values found for the fluorenyl anion and the three for 9-methylfluorenyl differ slightly from those given by Streitwieser and Brauman, all of them being shifted 2–4 mμ to longer wavelength from the earlier values. Several of the salts showed end absorption in the 400–415-mμ region.

Substitution of methyl or methoxy for hydrogen at the 3 position results in a shift of λ_{max} (for the middle of the three peaks) to longer wavelength by 9 and 17 mμ, respectively. At the 9 position these substituents also produce a bathochromic shift, but the effect is more pronounced; the shifts are 34[5a] and 32 mμ. In contrast, methyl or methoxy at position 1 or 4 causes a shift to shorter wavelength; the shifts are as follows: 1-methyl-, 8; 1-methoxy-, 19; 4-methyl-, 15; and 4-methoxy-, 32 mμ. Similarly, all four 2-substituted salts show hypsochromic shifts relative to lithium fluorenyl itself: 2-methyl-, 4; 2-methoxy-, 19; 2-fluoro-, 10; and 2-dimethylamino-, 18 mμ. The hypsochromic shifts found for 2-fluoro-, 2-dimethylamino-, and 1-, 2-, and 4-methoxyfluorenyl anions appear to be the first known examples of increases in transition energy produced in a nonalternant hydrocarbon system by a lone-pair substituent.

Discussion

The fact that these lithium fluorenyl salts all have the same π system suggests that their spectra all involve the same electronic transition or transitions. This suggestion receives strong confirmation from the extremely close similarity of the λ_{max} and ϵ_{max} values and the general shapes of the spectra.

Attempts were made to resolve each of the experimental curves into three overlapping Gaussian curves centered near the observed absorption maxima. In each case good agreement was obtained at the long wavelength end, but discrepancies at the short wavelength end were substantial, and agreement in this region could be accomplished only by inclusion of one or two more Gaussian curves (see Figure 1 for comparison of the observed and calculated spectra of 9-methylfluorene). The resolved curves were spaced at intervals of approximately 1350 cm^{-1}, the intervals being slightly larger at the high-frequency end and smaller at the low-frequency end. These results strongly support the suggestion of Streitwieser and Brauman[5a] that the spectra of lithium fluorenyl salts result from a single electronic transition, with vibronic interaction involving several vibrational levels of the electronic excited state. All 13 salts show very nearly the same spacing, 1400 ± 60 cm^{-1}, between the two Gaussians at the high-frequency end, indicating that the same vibrational mode produces the fine structure in each spectrum.

The transition which produces absorption in the visible range for the fluorenyl anion may be assumed to be promotion of an electron from the highest filled π molecular orbital to the lowest empty one. This transition is allowed by symmetry.

The intensities for the substituted fluorenes show a moderate dependence on the position and nature of the substituent. These effects would be expected to arise from three principal causes. (1) Substituents cause shifts in frequency of absorption and intensity is directly dependent on the frequency. (2) Substituents cause small perturbations in the molecular orbitals at each of the atoms in the π system, thereby affecting the dipole strength, which in turn affects the intensity. (3) The atomic orbitals of the substituent may contribute slightly to the molecular orbitals of the π system and thus make a contribution to the dipole strength. None of these factors correlated the observed changes in even a qualitative way with Hückel wave functions, however; rationalization of the changes in terms of molecular orbital theory would appear to require more refined calculation methods.

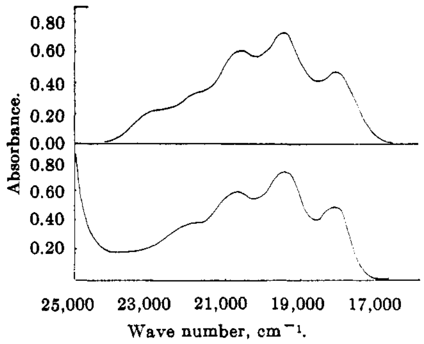

Figure 1.—The upper curve was generated by summation of five Gaussian curves. All five curves were assumed to have the same width at half-height. Taken in order from lower to higher wavenumber, the relative intensities are 1.0, 1.5, 1.2, 0.6, and 0.4, and the maxima of the individual curves are spaced 2.8, 2.4, 2.4, and 2.3 units apart. If the parameter of width at half-height is also varied, slightly better agreement can be obtained, especially at the low wavenumber end. The pronounced difference between the experimental and calculated curves around 25,000 cm^{-1} suggests the occurrence of a second electronic transition (probably either the $\psi_6 \rightarrow \psi_8$ or the $\psi_7 \rightarrow \psi_9$ transition), which is not taken account of in the calculated curve. The lower curve represents the spectrum of lithium 9-methylfluorenyl.

The Methylfluorenyl Salts.—Coulson[29] treated substituent effects on transition energies in π-system hydrocarbons by perturbation methods, and derived an expression for the inductive effect of a substituent at atom r (see eq 2), where c_{ir} and c_{fr} are the coefficients

$$h\Delta\nu = (c_{fr}^2 - c_{ir}^2)\delta\alpha_r \qquad (2)$$

of atomic orbital of atom r in MO's i and f (MO i is the one *from* which the electron is promoted, and MO f is the one *to* which it is promoted), and $\delta\alpha_r$ is the effective change in the Coulomb integral of atom r as a result of the inductive effect of the substituent. The quantity $\delta\alpha_r$ is positive for substituents which are electron donating relative to hydrogen, and negative for those which are electron withdrawing. Application of this expression to the substitution of methyl for hydrogen in azulene correctly predicts the direction of the shift in the visible spectrum for all five isomers; the quantitative correlation, however, is mediocre, no doubt due at least in part to the limitations of the Hückel eigenfunctions.

The method is equally successful for the methylfluorenyls examined in the present work. The assumption that the electron is promoted from ψ_7 to ψ_8, together with the use of the appropriate HMO coefficients, leads to the prediction that methyl at C-3 or C-9 will

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[29] C. A. Coulson, *Proc. Phys. Soc.* (London), **A65**, 933 (1952).

lower the transition energy; methyl at C-1, C-2, or C-4 is predicted to raise the energy. The predictions are in agreement with experimental observation for all five isomers.[30] As is apparent from the data in Table II, the correlation is not quantitative, and the use of MO's obtained by the ω technique gives little improvement. It would be interesting to apply Coulson's method, making use of eigenfunctions obtained by less approximate MO techniques, especially those which take electron repulsion into account.

TABLE II

Substituent	ν_{max},[a] cm^{-1}	$c_{fr}^2 - c_{ir}^2$, HMO[b]	$c_{fr}^2 - c_{ir}^2$, ω technique[c]
H	19,430		
1-Methyl	19,760	+0.022	+0.025
1-Methoxy	20,340		
2-Methyl	19,600	+0.108	+0.088
2-Methoxy	20,340		
3-Methyl	19,070	−0.087	−0.065
3-Methoxy	18,780		
4-Methyl	20,050	+0.137	+0.112
4-Methoxy	20,980		
9-Methyl	18,060	−0.347	−0.290
9-Methoxy	18,120		

[a] The frequency given here is that of the maximum of the longest wavelength Gaussian curve, as obtained by resolution of the experimental curve into individual Gaussians. The estimated uncertainty is ±50 cm^{-1}. Because all eleven salts show virtually the same spacing between the two longest wavelength Gaussians, essentially the same shifts can be obtained directly from the λ_{max} values for the middle, or most intense, maximum for each salt. [b] Values calculated from data in A. Streitwieser, Jr., and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol. 1, Pergamon Press Inc., New York, N. Y., 1965, pp 247–250. [c] We thank Mr. J. Gatewood and Mr. J. Fahnestock for writing the computer program used for these calculations.

The complete qualitative success of this approach for the nonalternant methylfluorenyl anions is in striking contrast to the observations of Waack and Doran[4] on methyl-substituted allyl and benzyl anions. The direction of the spectral shift in these odd-alternants is incorrectly predicted in three of the four ions studied, 1-methylallyl, 2-methylallyl, and 4-methylbenzyl. The predicted direction is correct for α-methylbenzyl anion, but the low magnitude of the shift, 3 mμ, is in complete disagreement with the very large decrease in charge density at the α position, 0.57 unit. In view of the fact that Hückel wave-functions are generally less accurate for nonalternants than for odd-alternants, it is remarkable that Coulson's treatment works for the former in the two systems studied to date, methylazulenes and methylfluorenyl anions, and not for the latter. That the shift is correctly predicted for nonalternants in ten cases out of ten suggests that the agreement is not fortuitous.

The Methoxyfluorenyl Salts.—Coulson's approach dissects the total effect of a substituent into an inductive and a conjugative contribution. If the inductive effect predominates, the direction of the shift is dependent both on the position of the group and its electronegativity. As the σ-inductive effect of methoxy is electron withdrawal relative to hydrogen, $\delta\alpha_r$ will be negative. The term $c_{fr}^2 - c_{ir}^2$ is negative for positions 3 and 9, and positive for 1, 2, and 4. Thus, the transition is predicted to shift to higher energy for substitution of methoxy at C-3 or C-9, and to lower energy for methoxy at C-1, C-2, or C-4. In fact, the 3 and 9 isomers show shifts to lower energy, and the 1, 2, and 4 isomers show shifts to higher energy; the direction of the change in transition energy is incorrectly predicted for all five isomers. The effect is not limited to the methoxy group; two other lone-pair substituents, fluoro and dimethylamino, also produce an increase in transition energy at the 2 position, again contrary to the expected result.

Comparison with substituent effects in the azulene system[31] is instructive. For four groups which are electron withdrawing both inductively and by resonance ($-COOH$, $-COOC_2H_5$, $-COCH_3$, and $-NO_2$), the direction of spectral shift is correctly predicted on the assumption of a dominating inductive effect. For Cl and Br, substituents of the unshared-pair type, which are inductively electron withdrawing and electron donating by resonance, the same assumption results in incorrect prediction of the direction of the shift. A possible explanation of these observations is that spectral shifts caused by lone-pair substituents result from a predominating conjugative effect.

Coulson's discussion shows that for a substituent of electronegativity similar to that of aromatic carbon, such as vinyl, an overriding conjugative effect should invariably lead to a red shift. Much evidence from solution chemistry demonstrates that the resonance effect of methoxy does override the opposing inductive effect when the group is located in a conjugating position. Thus, extension of Coulson's argument to the methoxyfluorenyl anions suggests that the spectra of all five isomers will be shifted to lower frequency relative to fluorenyl. In fact, three of the five are shifted to higher frequency. Despite these incorrect predictions based on perturbation theory, it is difficult to rule out unequivocally the possibility that the observed blue shifts are caused by a predominating conjugative effect. Introduction of a methoxy group into a π system can actually result in an increase in the calculated transition energy. Our calculations, done by the Hückel method with $\alpha_O = \alpha_C + 2\beta_{CC}$ and $\beta_{CO} = 0.8\beta_{CC}$,[32] gave the following transition energies: 1-methoxy, 0.981β; 2-methoxy, 1.013β; 3-methoxy, 0.961β; 4-methoxy, 1.014β; 9-methoxy, 0.877β (the value for the parent anion, fluorenyl, is 0.993β). Thus, decreases in transition energy are predicted and observed for 3- and 9-methoxy, and increases are predicted and observed for 2- and 4-methoxy. Of the five isomers, the direction of the spectral shift is incorrectly predicted only for 1-methoxyfluorenyl.

A number of lines of argument indicate that the success of these calculations is apparent rather than real. From the standpoint of theory, there is no assurance that the Hückel eigenvalues are an accurate reflection of the molecular energy levels. The calculated transition energies would be expected to be quite sensitive to the parameters chosen for the oxygen atom and to the approximations involved in the calculation method. Furthermore, the magnitudes of the calcu-

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[30] Streitwieser and Brauman[5a] have already pointed out the success of this treatment for the case of lithium 9-methylfluorenyl.

[31] See ref 7, pp 237 and 244.

[32] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N.Y., 1961, p 123.

lated blue shifts are much too small. If β is assigned a normal spectroscopic value of 50 to 60 kcal, an increase of Δm from 0.993 to 1.013 or 1.014 corresponds to a shift of about 400 cm^{-1}; the observed shifts for 2- and 4-methoxyfluorenyl anions are 910 and 1550 cm^{-1}, respectively. Moreover, the discrepancy becomes greater when the opposing σ-inductive effect of methoxy is taken into account. Many kinds of evidence, such as Hammett σ_m constants, acidities of appropriate α-substituted acetic acids, chemical shifts in nuclear magnetic resonance, and the like, demonstrate that relative to hydrogen, methoxy is more effective in withdrawing electrons inductively than methyl is in donating electrons. Thus, the σ-inductive perturbation produced by methoxy should cause a red shift at least as large in magnitude as the opposing blue shift which the calculations suggest may result from conjugation. The net effect on the observed spectrum would then be either no shift at all or a small red shift.

More significant than these theoretical considerations are the experimentally observed effects of lone-pair substituents in spectra of even-alternant hydrocarbons. In compounds of this class, such as ethylene and benzene, inductive effects produce little change in the positions of absorption maxima; the spectrum of anilinium ion is virtually superimposable on that of benzene.[6] Spectral shifts produced by substituents in these systems result from a predominating conjugative effect, and for a variety of lone-pair groups, including methylamino, amino, hydroxy, methoxy, and four halogens, the shift is in every case to lower frequency.[6] Amino derivatives of naphthalene, anthracene, 1,2-benzanthracene, and pyrene are all red shifted relative to the parent hydrocarbons.[33] In view of the fact that the conjugative effect of lone-pair substituents in even-alternant hydrocarbons invariably causes a decrease in transition energy, it is not unreasonable to conclude that it will cause a similar decrease in nonalternant hydrocarbon systems.

If the spectral shifts observed for the five isomeric methoxyfluorenyl anions cannot be convincingly rationalized in terms of conjugation or of the electron-withdrawing σ-inductive effect of methoxy, they can be readily accounted for on the basis of an electron-repelling π-inductive effect. Clark, Murrell, and Tedder[8] proposed that for an electronegative substituent with an unshared pair, while the σ electrons are attracted to the electronegative atom because of the increased nuclear charge, the π electrons may well be repelled by the unshared pair more strongly than they are attracted by the nuclear plus charge. With respect to properties which would be expected to depend markedly on distribution of the σ electrons, such groups would have a net inductive effect of electron withdrawal, but for properties dependent primarily on the π electrons, such as energies of $\pi \rightarrow \pi^*$ transitions, the net inductive effect would be an electron-repelling one. In Coulson's expression for the inductive perturbation, a predominating π-inductive effect corresponds to a positive sign for the quantity $\delta\alpha_r$. When the appropriate HMO coefficients are substituted into the equation, hypsochromic shifts are predicted for methoxy at C-1, C-2, and C-4, and bathochromic shifts are predicted for methoxy at C-3 and C-9. As Table II shows, all five of these predictions are correct. The hypsochromic shifts observed for 2-fluoro- and 2-dimethylaminofluorenyl anions also cannot be rationalized in terms of conjugation or a σ-inductive effect, but are successfully explained by the π-inductive model. If this effect predominates, one can draw the general conclusion that at a given position of an odd- or nonalternant system methyl and lone-pair groups should cause spectral shifts in the same direction. Few examples have been reported, but the generalization does hold for 1-halogenated azulenes[7] and *meta-* and *para*-chlorinated triphenylmethyl cations.[3c]

The observed shifts for 1-, 2-, 3-, and 4-methoxyfluorenyl anion are about two to three times larger than the shifts for the corresponding methyl anions. The similar pattern of magnitudes suggests that the shifts result from the same cause; for methyl the cause seems clearly to be an inductive perturbation, and the implication is that the hypsochromic shifts produced by methoxy at C-1, C-2, or C-4 should be attributed to the π-inductive effect and not to conjugation. The 9 isomers fit the pattern less neatly, as methyl and methoxy at C-9 produce nearly identical shifts. However, scale models show that the hydrogens at C-1 and C-8 force the 9-methoxy group out of the plane of the fluorenyl system.[34] Because of the lack of coplanarity, both the conjugative and the π-inductive effects are probably reduced, and the red shift is less than expected.

Comparison of the blue shifts observed for 2-methoxy- and 2-dimethylaminofluorenyl anions provides further support for the π-inductive effect. Dimethylamino is a far better conjugative electron donor than methoxy, and produces much larger red shifts in benzenoid hydrocarbons.[6] If the blue shifts observed for these 2-substituted fluorenyl anions resulted from a predominating conjugative effect, the perturbation ought to be much greater for the dimethylamino group. In fact the two groups produce virtually identical shifts.

In our judgment, the effects of lone-pair substituents on the electronic spectrum of fluorenyl anion cannot be satisfactorily explained in terms of conjugation; the results constitute solid evidence for the π-inductive effect.

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(33) See ref 6, pp 303–337.

(34) Scale models indicate that if the methoxy carbon lies in the plane of the fluorenyl system, the steric interference between the methyl and the C-1 hydrogen is about as severe as the interaction in 1-acetylazulene which would occur between the methyl and the C-8 hydrogen, if the methyl group were directed toward the seven-membered ring. 1-Acetylazulene is believed to have a structure in which the carbonyl group lies on the side toward the hydrogen at the 8 position, so that steric strain is minimized. See E. Heilbronner and R. Gerdil, *Helv. Chim. Acta*, **39**, 1996 (1956).