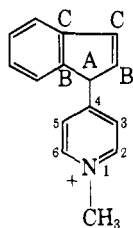


For the list of parameters, the pyridine ring is numbered in conventional fashion. The five-membered ring present in most of the compounds is numbered by calling A the carbon atom through which attachment is made to the heterocyclic ring. The two carbon atoms of the five-membered ring attached to A are both called B, and the two attached to B (and to each other) are called C. For example



For the *pyridinium conjugate acids* (62–78) the following parameters were used in the Hückel and ω -calculations: $h_N = 1.50$; h for C_2 and C_6 of the pyridine ring = 0.40; all other h -values = 0.00. For all the resonance integrals of the pyridinium ring, k was taken as 1.00; for the internuclear bond (*i.e.*, C_2 -A C_4 -A) in the conjugate acids of the anhydro bases, $k = 0.90$; for formally single bonds A-B, B-C, or C-C, $k = 0.90$; for formally double bonds A-B, $k = 1.06$. In all others, $k = 1.00$. For the internuclear bond (*i.e.*, N-A) in the conjugate acid of pyridinium cyclopentadienide (76, 77, and 78), $k = 0.75$.

For the bases, $k = 1.06$ for all formal carbon-carbon double bonds, 0.90 for carbon-carbon single

bonds, 0.75 for carbon-nitrogen single bonds, and 1.00 for carbon-nitrogen double bonds. The aromatic carbon-carbon double bonds in benzo rings and all the bonds in the five-membered ring of pyridinium cyclopentadienide (43) were given $k = 1.00$. For the oxygen compounds 49 and 50, $h_O = 1.00$; k for the carbon-oxygen double bond = 1.00; all other parameters were assigned as in the case of the anhydro bases.

Dipole moments (Table I) were calculated as vector sums from the charge distributions obtained from the ω -calculations and a molecular geometry assigned with reference to reasonably analogous substances of known geometry. Since the moments are not very sensitive to small changes in geometry, the precise values used are not reproduced here. The ω -calculations (A) themselves were carried out with all initial $\beta_{rs} = \beta_0$, *i.e.*, with $k = 1$. The off-diagonal elements of the secular determinant in the N th cycle were given by the equation³³

$$\log \beta_{rs} = \log \beta_0 + 0.224p_{ij} - 0.149$$

where p_{ij} is the bond order between atoms r and s in the $(N - 1)$ th cycle. The modifying terms vanish (*i.e.*, $\beta_{rs} = \beta_0$) when p_{ij} has the benzene π -bond order 0.667. About seven or eight cycles were required for convergence. Calculation B was carried out as described above for the results of Table III.

(33) Cf. H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc. (London)*, **A251**, 172 (1959).

Nitrogen Analogs of Sesquifulvalene. III. Theoretical Correlation of Excited-State Properties^{1a,2}

Earl M. Evleth, Jr.,^{1c} Jerome A. Berson,^{1b} and Stanley L. Manatt

Contribution from the IBM Research Laboratory, San Jose, California, Department of Chemistry, University of Southern California, Los Angeles, California, Department of Chemistry, University of Wisconsin, Madison, Wisconsin, and the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California. Received December 23, 1964

The experimental energies and intensities of the electronic absorption bands of a series of nitrogen analogs of sesquifulvalene are compared with the results of three kinds of theoretical treatment. Although the Hückel theory and its variant, the ω -method, are satisfactory in cor-

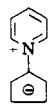
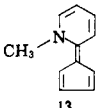
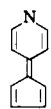
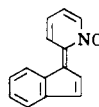
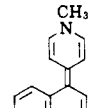
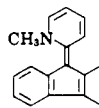
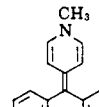
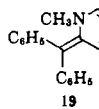
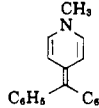


relating much of the data, they fail to account for the major observed difference in behavior between the members of the 2- and 4-series, namely, the occurrence of two strong, long wave length bands in the 2-series but of only one in the 4-series. Treatment of the data by first-order perturbation theory, using the series of anions phenylcyclopentadienide, phenylindenide, and phenylfluorene, gives better results. The transition energies are correlated with the values calculated from perturbation theory with a correlation coefficient of 0.953; the value of the resonance integral β , obtained from the slope of the correlation, is -47.6 kcal./mole.

(1) (a) For the support of part of this work, we are indebted to the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract No. AF49(638)-828, to the Office of Ordnance Research (now Army Research Office, Durham) under Contract No. DA-04-495-ORD-532, and to the Camille and Henry Dreyfus Foundation. This paper presents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS-7-100, sponsored by the National Aeronautics and Space Administration. (b) To whom inquiries should be directed at Madison. (c) This paper is taken from the dissertation presented by Earl Mansfield Evleth, Jr., in partial fulfillment of the requirements for the Ph.D. Degree at the University of Southern California, Jan. 1963.

(2) (a) Part I: J. A. Berson, E. M. Evleth, Jr., and Z. Hamlet, *J. Am. Chem. Soc.*, **87**, 2887 (1965); (b) part II: J. A. Berson, E. M. Evleth, Jr., and S. L. Manatt, *ibid.*, **87**, 2901 (1965).

In the preceding paper of this series,^{2b} we presented a correlation of molecular orbital theory with some of the experimentally determined^{2a} ground-state properties

Table I. Calculated and Observed^a Transition Energies and Intensities of Electronic Spectra^b

Compound	Exptl.		Hückel		Calcd.		Perturbation	
	$E_T,^c$	f	ΔE_H	f	ΔE_ω	ω -Method f	ΔE	μ_T^2
 43	56 ^d	0.38	0.815	...	0.744 0.750	0.392 0.086	0.708 0.808	2.39 0.159
 13	67 78	0.14 0.34	0.787 0.837	0.856 0.036	0.859 0.957	0.965 0.029	0.922 1.210	0.267 0.159
 15	67	0.66	0.799 0.830	1.21 0.04	0.860 0.938	1.31 0.026	0.816 0.840	0.159 2.39
 32	57 71	0.14 0.34	0.615 1.024	...	0.771 1.126	0.936 0.039	0.745 1.032	0.175 2.818
 33	62	0.62	0.638 1.035	1.42 0.00	0.764 1.120 1.293	1.37 0.073 <i>e</i>	0.816 1.099	2.818 0.445
 23	54 68	0.15 0.24	0.828 1.121	...	0.774 1.124	0.848 0.091	0.686 0.952	0.18 2.26
 24a	61 62	0.60	0.661 1.099	1.11 ...	0.774 1.155 1.179	1.37 0.106 <i>f</i>	0.810 0.886	1.23 2.26
 19	77	0.28 ^{g,h}	0.768 1.199	1.11
 20	79	0.58 ^{g,h}	0.775 1.227	1.74
 79	66 100	0.095 <i>j</i>			0.885 ⁱ 1.339 ⁱ	0.278 0.830
 80	62 89	0.018 0.050			0.808 0.909	0.119 0.730

^a See ref. 2a. ^b Transition energies are given in kcal./mole. ^c In dioxane unless otherwise noted. ^d In chloroform. ^e $\mu_T^2 = 0.19$. ^f $\mu_T^2 = 0.42$. ^g Calcd. from $4.32eh \times 10^{-9}$; see C. Sandorfy, "Electronic Spectra and Quantum Chemistry," Prentice-Hall, Inc., New York, N. Y., 1964, p. 108. ^h L. C. Anderson and N. V. Seeger, *J. Am. Chem. Soc.*, **71**, 343 (1949). ⁱ Calcd. for the π -electron system exclusive of the phenyl group. ^j Broad unresolved absorption at higher intensity than the long wave length band.

of a group of nitrogen analogs of sesquifulvalene. The present paper extends the theoretical treatment to the electronically excited states and correlates the experi-

mental data^{2a} on ultraviolet-visible spectra. Although the basis for the use of one-electron wave functions and for the neglect of configuration interaction in such

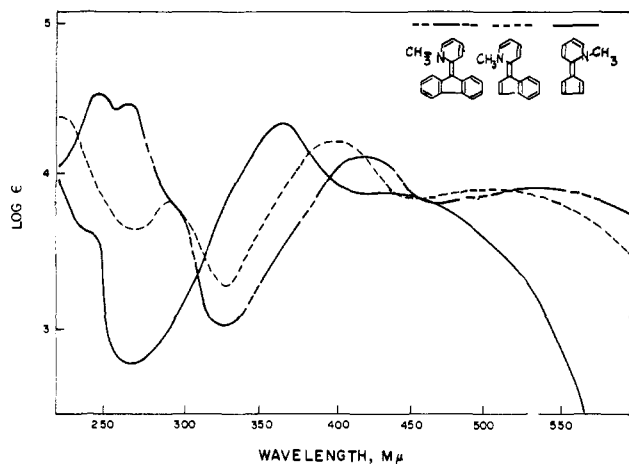


Figure 1. Ultraviolet-visible spectra of representative members of the 2-series of anhydro bases in isooctane.

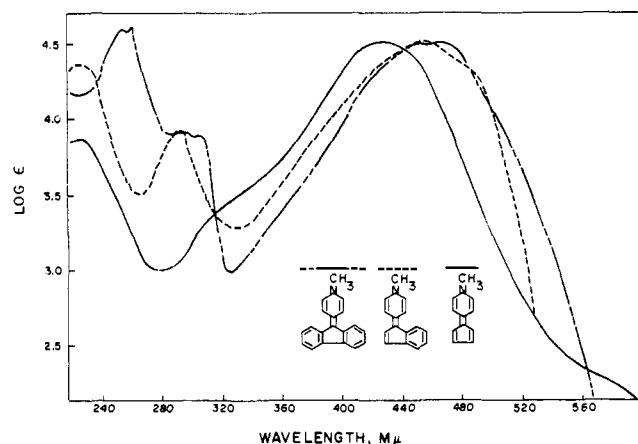


Figure 2. Ultraviolet-visible spectra of representative members of the 4-series of anhydro bases in dioxane.

correlations is largely empirical,³ we were encouraged to proceed by many previous successful applications^{3,4} and by the hope that some physical insight would emerge.

Table I gives (in units of the resonance integral β) the two lowest energy electronic transitions calculated for several of the anhydro bases as well as for pyridinium cyclopentadienide (**43**). The theoretical transition energies are obtained from the energies of the ground state and the two lowest lying excited states given by two of the methods previously described.^{2b} The oscillator strength (f) is obtained from the standard equation $f = 1.085 \times 10^{-6} \nu \mu_T^2$, where ν is the experimentally observed frequency at the maximum of the band in question, and μ_T is the transition moment calculated from an assumed approximate molecular geometry and the coefficients of the atomic orbitals in the LCAO representation of the energy levels involved in the transition.⁵ Also in Table I are experimental transition energies, corresponding to the frequencies at the absorption maxima, and experimental oscillator

(3) Cf. A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 8.

(4) Cf., *inter alia*, A. Zweig, J. E. Lehnsen, and M. A. Murray, *J. Am. Chem. Soc.*, **85**, 3933 (1963).

(5) Cf. R. Daudel, R. Lefebvre, and C. Moser, "Quantum Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter X.

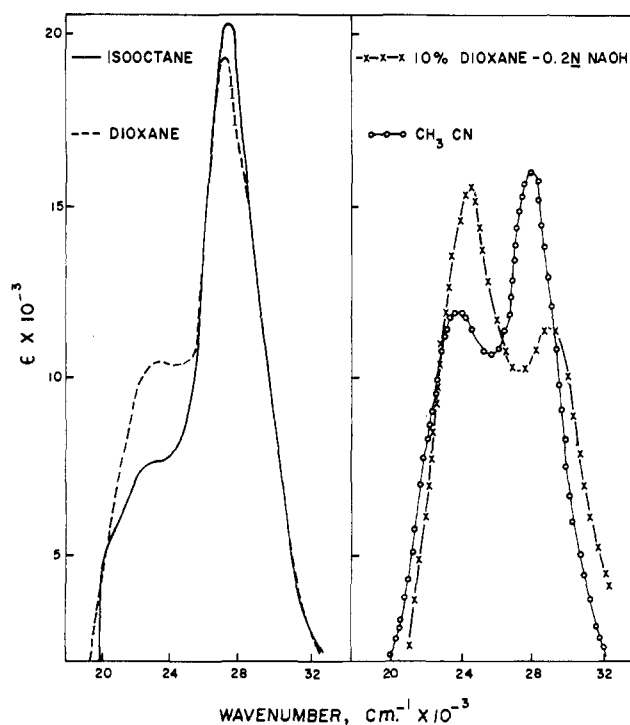


Figure 3. Effect of solvent on the long wave length absorption bands of 1-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (**13**).

strengths, obtained from $f = 4.31 \times 10^{-9} \int \epsilon d\nu$ by evaluating the integral as the area of the band envelope in a plot of molar extinction coefficient (ϵ) vs. ν .

Figures 1 and 2 give typical absorption curves for representative members of the 2- and 4-series. The compounds of the 2-series all exhibit two broad intense maxima in the region 360–550 $m\mu$ as well as short wave length selective absorption in the form of shoulders and/or maxima. The compounds of the 4-series show only a single broad maximum in this region in addition to rather richly detailed short wave length absorption. The apparently single long wave length band associated with the 4-compounds shows partially resolved fine structure in some solvents, but it is not clear whether this is of vibrational or electronic origin. Similar effects are observed with the two long wave length bands of N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (**13**), which are poorly resolved in isooctane and dioxane. These bands become more clearly separated in acetonitrile and 10% dioxane–90% 0.2 N aqueous sodium hydroxide (Figure 3). Accompanying the increasing separation is a reversal in relative intensity of the two bands; the short wave length band, which is the stronger in the nonpolar solvents, becomes the weaker. Furthermore, both bands are hypsochromically shifted by about 10–20 $m\mu$. As is shown in Table II, the total oscillator strength remains nearly constant throughout these changes of solvent, which thus merely effect a transfer of intensity from one absorption band to the other. Although the phenomenon requires further study, it seems possible that it may be describable in terms of solvent-dependent wave functions.

The Hückel theory, either in its naive form or in the slightly more sophisticated variant given by the ω -calculation, is only partly successful in accounting for

Table II. Measured Oscillator Strengths^a of the Two Long Wave Length Bands of 1-Methyl-2-cyclopentadienylidene-1,2-dihydropyridine in Various Solvents

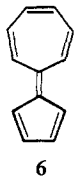
Solvent	f_1^b	f_2^c	f_{total}
Isooctane	0.11	0.39	0.50
Dioxane	0.17	0.37	0.54
Acetonitrile	0.20	0.27	0.47
10% dioxane-0.2 N aq. NaOH	0.29	0.19	0.48

^a Calculated as described in the text. ^b For the longer wave length band. ^c For the shorter wave length band.

the spectroscopic properties of the series of anhydro bases. For example, the calculations of Table I predict a strong transition to the first excited state and a weak one to the second in both series, and thus fail to predict the principal observable difference between the 2- and 4-compounds, which is the occurrence of two low-energy bands of high and approximately equal intensity in the 2-series and apparently of only one in the 4-series.⁶ Further discussion of this point is deferred to the section on perturbation theory.

Nevertheless, many of the other spectroscopic details are successfully correlated. In the 4-series, where distortions due to intramolecular overcrowding probably are not serious, the Hückel and ω -calculations predict correctly that annelation of the cyclopentadienylidene **15** to the indenylidene **33** should produce a shift to lower energy of the $N \rightarrow V_1$ band. The slight upturn in energy predicted for further annelation (indenylidene **33** \rightarrow fluorenylidene **24a**) should have amounted to only about 0.3 kcal./mole, if the ratio of the predicted and experimental values ($\Delta E_\omega/\Delta E_T$) for the **15** \rightarrow **33** case is assumed to apply also to **33** \rightarrow **24a**. This would not have been experimentally detectable with the broad bands observed, so that the near-equality of ΔE_T for **33** and **24a** may be considered to be in accord with theory.

This behavior on annelation is quite different from that observed for simple alkyl fulvene derivatives, where annelation shifts the long wave length electronic absorption band to higher energies,⁹ as predicted by Hückel-type molecular orbital theory.¹⁰ Sesquifulvalene (**6**) derivatives behave spectroscopically like ordinary fulvenes on annelation,¹¹ despite the formal analogy between the conjugated system of **6** and those



of the anhydro bases of Table I. The difference em-

(6) Compare a superficially similar set of relationships in the case of 2-pyridones vs. 4-pyridones.^{7,8}

(7) J. A. Berson, *J. Am. Chem. Soc.*, **75**, 3521 (1953).

(8) S. F. Mason, *J. Chem. Soc.*, 1253 (1959).

(9) For a summary, see E. D. Bergmann in "Progress in Organic Chemistry," Vol. 3, J. W. Cook, Ed., Academic Press Inc., New York, N. Y., 1955, p. 103.

(10) B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie, Paris, 1952, p. 496, and references therein cited.

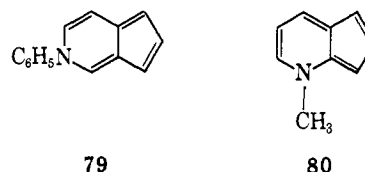
(11) H. Prinzbach and W. Rosswog, *Tetrahedron Letters*, No. 19, 1217 (1963).

phasizes again the previous conclusion^{2b} that these heterocycles, though structural analogs of **6**, are not necessarily reliable as guides to its properties. The bathochromic annelation effect observed with the 4-cyclopentadienylidene anhydro base **15** is the same predicted¹² for cyclopentadienide ion, which should¹² have its long wave length band at higher energy than that of indenide or fluorenyl ion. This sequence is actually observed¹³ in the isoelectronically corresponding series pyrrole $>$ indole $>$ carbazole, where the transition energies decrease in the indicated order.

The ω -calculation also correctly predicts that pyridinium cyclopentadienide (**43**) should absorb at lower energy than the 2- or 4-cyclopentadienylidene anhydrobases **13** or **15**. This result represents an improvement over the Hückel calculation, which gives the order incorrectly (Table I).

The zwitterion **43** is unique in the series in that the ω -calculation predicts *two* near-degenerate low-energy transitions at 0.744β and 0.750β , with an intensity ratio of 46:1. Although only one long wave length band is observed¹⁴ in a variety of solvents, some slight resolution into two bands does appear in heptane.¹⁴ It would be unjustified at present to take this as more than merely suggestive. The ω -treatment also works particularly well in this case in predicting intensity, the calculated oscillator strength of 0.48 (the sum of the two energetically near-degenerate weak and strong predicted intensities) being less than that for **13** or **15**, in agreement with experiment.

The ω -treatment also gives a rather satisfactory account of the spectra of the azulene analogs 2-phenyl-2-pyridine (**79**)^{15a} and 1-methyl-1-pyridine (**80**).^{15b} Neglecting conjugation of the nitrogen with the phenyl



group in **79**, the calculation predicts a wider spacing of the first two excited-state energy levels in the 2-pyridine system (**79**) than in the 1-pyridine case (**80**). This seems to be in accord with experiment (Table I), although there is some question about the assignment of the $N \rightarrow V_2$ transition.¹⁶ According to the calculation, the relative intensities of the first two transitions in both cases should be about the same, with the shorter wave length band being the stronger. The first part of this prediction is difficult to test because of the lack of resolution in the second absorption of **79**, but the remainder is in accord with the observations. The weaker intensity of the long wave length bands of

(12) Ref. 10, p. 644.

(13) Cf. R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951, spectra no. 1, 2, 192, 193, 338, 339, and 340.

(14) E. M. Kosower and B. C. Ramsey, *J. Am. Chem. Soc.*, **81**, 856 (1959).

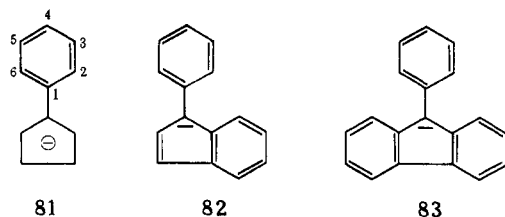
(15) (a) A. G. Anderson, Jr., W. F. Harrison, R. G. Anderson, and A. G. Osborne, *ibid.*, **81**, 1255 (1959); A. G. Anderson, Jr., W. F. Harrison, and R. G. Anderson, *ibid.*, **85**, 3448 (1963); (b) C. B. Reese, *ibid.*, **84**, 3978 (1962).

(16) The reported spectrum^{15a} of **79** shows the two longest wave length maxima lying at 432 and 286 $m\mu$, but there is a broad shoulder in the region 310-340 $m\mu$ that may correspond to $N \rightarrow V_2$. For the complete spectrum of **80**, from which the f numbers of Table I were calculated, we are indebted to Dr. C. B. Reese.

79 and 80 parallels a similar feature of the isoelectronic hydrocarbon azulene.^{15a}

First-Order Perturbation Treatment of the Electronic Spectra. Although the ω -calculation gives a generally satisfactory account of many aspects of the spectra, it fails to cope with one of the major experimental observations, the occurrence of two, strong, low-energy bands in the 2-series but of only one in the 4-series. This is undoubtedly attributable to the use of single-configuration wave functions, a crudity of the Hückel treatment that the ω -method does not correct. Nevertheless, an improved physical insight into the problem is provided by the even cruder procedure of treating the heterocycles as first-order perturbations of an all-hydrocarbon system. A discussion by Mason⁸ of the spectra of pyridones as perturbations of benzyl anion has served a similar purpose.

The transition energies between the two highest occupied and the two lowest unoccupied energy levels for phenylcyclopentadienide ion (**81**), phenylindenide ion (**82**), and phenylfluorenylide ion (**83**) are shown in Table III. These levels are obtained by recycling the



Hückel bond orders and charge densities to self-consistency as described elsewhere.^{2b} The energy of any level of the heterocyclic system obtained by sub-

Table III. Calculated Spectroscopic Properties of Hydrocarbon Anions and Heterocycles

Transition	μ_T^2	$\Delta E_{ij}, \beta$	Heterocycle ($\Delta E_T, \beta$)		
			$r =$ C-2	$r =$ C-4	$r =$ C-1
Anion 81					
N \rightarrow V ₁	2.39	1.236	1.220	0.840	0.708
N \rightarrow V ₂	0.267	1.290	0.922	1.444	1.360
N \rightarrow V ₃	0.159	1.364	1.210	0.816	0.808
N \rightarrow V ₄	0.000	1.418	0.912	1.418	1.418
Anion 82					
N \rightarrow V ₁	2.82	1.030	1.032	0.816	0.706
N \rightarrow V ₂	0.175	1.139	0.745	1.257	1.145
N \rightarrow V ₃	0.445	1.151	1.227	1.099	0.985
N \rightarrow V ₄	0.821	1.462	0.821	1.15	...
Anion 83					
N \rightarrow V ₁	2.26	0.880	0.952	0.886	0.766
N \rightarrow V ₂	1.23	1.048	1.082	0.810	0.672
N \rightarrow V ₃	0.18	1.070	0.686	1.202	1.072
N \rightarrow V ₄	1.075	1.85	1.199	1.207	1.077

stituting N+R for CH of **81**, **82**, or **83** is then given by eq. 1 in first-order perturbation theory, where E_i^*

$$E_i^* = E_i + \sum_r q_r d\alpha_r + \sum_{r>s} p_{rs} d\beta_{rs} \quad (1)$$

is the energy of the i th level of the heterocycle, E_i is the eigenvalue of the corresponding level of the hydrocarbon anion, q_r is the electron density on atom r ,

and p_{rs} is the bond order between atoms r and s in the i th level of the anion. The quantities $d\alpha_r$ and $d\beta_{rs}$ are the changes in the Coulomb parameter α and the resonance integral β that result from the substitution, the changes being summed over all the atoms replaced by heteroatoms and over all the affected bonds. We neglect changes of bond order, so that the spectroscopic transition energy for the perturbed system is given by

$$\Delta E_T^* = \Delta E_{ij} + \Sigma \Delta q_r d\alpha_r \quad (2)$$

for an electronic excitation from level j to level i . In eq. 2, Δq_r is the increment of q_r between levels j and i of the unperturbed system. The Coulomb term $d\alpha_r$ is taken as 2.0β .

Table III shows that perturbation shuffles the order of the transitions predicted for the anions. For example, the two lowest energy transitions, N \rightarrow V₁ and N \rightarrow V₂, for anion **81** are predicted to be separated by 0.06β -unit and to have an intensity ratio of about 9, with the N \rightarrow V₁ band being the stronger. Perturbation of the phenylcyclopentadienide anion **81** to the 2-cyclopentadienylidene anhydro base **13** produces a drastic reordering of the energy levels: the two lowest energy transitions of the perturbed system now correspond to the N \rightarrow V₂ and N \rightarrow V₄ transitions of the anion **81**, but the latter transition has identically zero probability, since the corresponding transition moment (between levels 5 and 8) vanishes. Consequently, the two lowest energy allowed excitations of **13** correspond to N \rightarrow V₂ and N \rightarrow V₃ of **81**; they are predicted to have $\Delta E_T = 0.922$ - and 1.210β -units and should have intensities that differ by less than a factor of 2.

A pronounced difference between the 2- and 4-compounds **13** and **15** now becomes evident. The two lowest energy transitions for **15** correspond to N \rightarrow V₃ and N \rightarrow V₁ of **81**. They differ by only 0.024β -unit and have an intensity ratio of 15. These relationships would produce two closely overlapping bands for **15**, one of which would be so weak relative to the other that it might well be buried. The perturbation calculation thus distinguishes well between **15** and **13**, whereas the Hückel and ω -calculations (Table I) do not. Similarly, the perturbation calculation qualitatively predicts the observed distinctions in the spectra of the fluorenylidene anhydro bases **23** and **24a**. The 2-fluorenylidene compound, **23**, shows two well-separated bands, the lower energy one being somewhat weaker, while the 4-compound, **24a**, shows two strong bands lying very close together. Again the other two methods of calculation do not give correct predictions. Only with the 4-indenylidene anhydro base **33** does the perturbation treatment fail to improve upon the other two calculations.

A quantitative comparison of the correlative abilities of the ω -treatment and the perturbation method in treating the spectroscopic data is given by Figures 4 and 5, in which observed transition energies are plotted as a function of calculated values in β -units. (The plot for the simple Hückel treatment shows such severe scatter that it has not been included here.) Clearly the perturbation treatment (Figure 5) is superior; its correlation coefficient is 0.953 for the indicated least-squares regression line. The ω -calculation has a correlation coefficient of only 0.771. The slopes of the

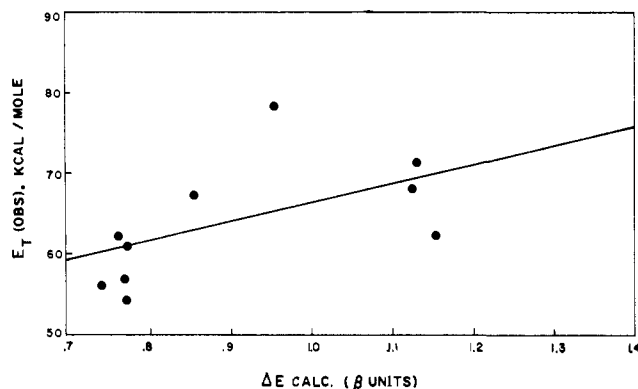


Figure 4. ω -Treatment correlation of experimental (E_T obsd.) and calculated (ΔE calcd.) transition energies. The calculated values are in units of β .

plots give correlative evaluations of the resonance integral β ; that of the perturbation correlation, 47.6 kcal./mole, is in the region frequently encountered for "spectroscopic" β -values,³ while the value from the ω -treatment, 23.2 kcal./mole, is not.

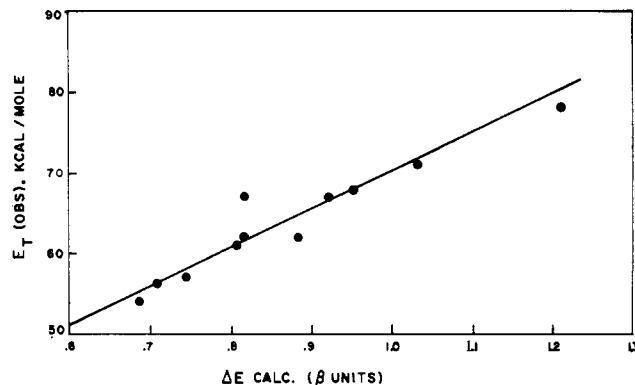


Figure 5. Perturbation treatment correlation of experimental (E_T obsd.) and calculated (ΔE calcd.) transition energies. The calculated values are in units of β .

The results are of a familiar (and, by now, no longer disconcerting) type. In theoretical treatments using one-electron wave functions, there is no readily predictable relationship between the degree of theoretical sophistication or refinement of the calculations and their success in correlating experimental data.

Mass Spectrometry in Structural and Stereochemical Problems. LXX.¹ A Study of the Fragmentation Processes of Some Five-Membered N-Alkylactams and N-Alkylsuccinimides²

A. M. Duffield,³ H. Budzikiewicz, and Carl Djerassi

Contribution from the Department of Chemistry of Stanford University, Stanford California. Received February 20, 1965

Deuterium labeling has enabled mechanistic interpretations to be presented for the principal ions formed in the mass spectrometric fragmentation of N-alkyl-2-pyrrolidones and N-alkylsuccinimides (alkyl = n-propyl or n-butyl). The most abundant ion in the mass spectrum of both N-alkylsuccinimides involves a double hydrogen transfer from the alkyl chain, and the sites from which these transfers originate in this and other rearrangement ions were demonstrated by deuterium labeling. High-resolution mass spectrometry established the composition of many of the peaks in the low-resolution spectra of the compounds studied.

Recently we described the mass spectrometric fragmentation behavior of some five- and six-membered lactams and their N-methylated derivatives⁴ and, as an

extension of this study, we now wish to report the processes occurring subsequent to electron impact in N-n-propyl- and N-n-butyl-2-pyrrolidone. These compounds were chosen in order to determine the effect of an N-alkyl chain on the fragmentation behavior particularly with regard to possible hydrogen transfer from the alkyl chain. As will be demonstrated below, rearrangement ions were observed and the sites of hydrogen transfer from the alkyl chains were elucidated by deuterium labeling experiments.

It was of interest to study the effect of a second carbonyl group adjacent to nitrogen in these substituted 2-pyrrolidones, and the mass spectra of N-n-propyl- and N-n-butylsuccinimide were determined especially since imides have as yet not been subjected to mass spectral scrutiny. Whereas the base peak in the spectra of the five-membered lactams studied arose from simple α -cleavage to nitrogen (see below), in the N-alkylated succinimides the most abundant peak had its genesis from loss of the alkyl chain less two hydrogen atoms. Consequently deuterium labeling of the side chain was commenced to establish the sites from which hydrogen was transferred.

Convenient synthetic procedures have been described for the preparation of alkyl bromides labeled with

(1) Paper LXIX: F. Komitsky, Jr., J. E. Gurst, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 1398 (1965).

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(3) Postdoctoral Research Fellow 1963-1965.

(4) A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 5536 (1964).