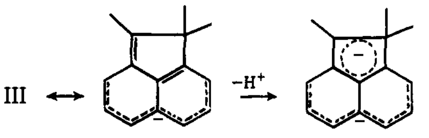
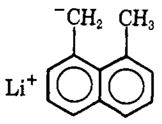
tive proton abstraction (eq 2, $k_2 \gg k_1$) would be expected to have[14] $k_H/k_D \cong 7$, while a simultaneous two-proton loss would require $k_H/k_D \cong (7)^2$. The conversion of II (12 mg in 5 ml of THF) to I at 0° using a tenfold excess of butyllithium (25% in hexane) was monitored by the increase of the 5800-Å band of I. Under these conditions the reaction was first order in II over 90% of its lifetime and had $k_H = 8.8 \times 10^{-4}$ sec^{-1}. A similar investigation using 1,1,2,2-tetradeuterioacenaphthene[15] gave $k_D = 10.1 \times 10^{-5}$ sec^{-1}. Accordingly, the deuterium isotope effect, $k_H/k_D = 8.7$, rules out eq 3 and supports monometalation of II (k_1 in eq 2) as rate determining.

To account for the greatly enhanced acidity of the protons in the monoanion I over those in the neutral hydrocarbon II, we stress the presence of the cyclopentadienoid character generated in monoanion III by charge delocalization, as illustrated in IIIa. Loss of the exceptionally acidic proton from IIIa produces dianion Ia, an auspicious combination of cyclopentadienyl and heptatrienyl anions, both well-established species.[16]

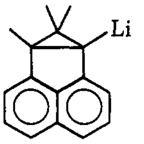


IIIa Ia

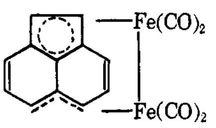
In support of IIIa we note that related compounds in which the cyclopentadiene ring is absent (as in 1,8-dimethylnaphthalene[6]) or is sterically inhibited (as in cycloprop[*a*]acenaphthene[17]) form only stable monoanions (V and VI, respectively) even when treated with a large excess of butyllithium for prolonged periods. Precedence for Ia is found in a binuclear, organometallic complex obtained from IV and $Fe_3(CO)_{12}$ which has been shown to have structure VII by an X-ray diffraction study.[18] The isolated cyclopentadienyl and allyl π systems of VII are readily extrapolated to the cyclopentadienyl–heptatrienyl π systems of Ia when the covalent iron atoms are replaced by ionic lithiums.



V

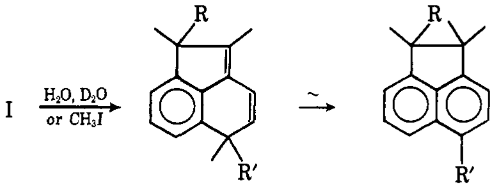


VI



VII

Protonation of I proceeds as predicted[19] and affords 1,5-dihydroacenaphthylene (VIII) in 95% yield. Similarly the 1,5-dideuterio (IX) and 1,5-dimethyl (X) analogs are obtained by quenching with D_2O and methyl iodide, respectively. Structural assignment for VIII–X is based on their nmr and uv spectra which closely parallel those for the known[20] trityl-substituted compound XI. The facile 1,5-H rearrangement of VIII, IX, and X to their thermodynamically favored acenaphthene isomers (II, XII, and XIII) is subject to a variety of catalytic effects and will be described in detail in a subsequent publication.



VIII, R = R′ = H
IX, R = R′ = D
X, R = R′ = CH_3
(XI, R = $(C_6H_5)_3C$; R′ = H)

XII, R = D; R′ = H or D
XIII, R = R′ = CH_3

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[15] Prepared by two exchanges of II in DMSO-d_6 (99.5%) containing potassium *tert*-butoxide. II-*1,1,2,2-d*$_4$ retained less than 1% of benzylic protons as shown by nmr and mass spectra.

[16] H. Kloosterziel and J. A. A. van Drunen, *Recl. Trav. Chim. Pays-Bas*, **88**, 1084 (1969), and R. B. Bates, *et al.*, *J. Amer. Chem. Soc.*, **91**, 4608 (1969), have prepared and characterized the heptatrienyl anion.

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Correlation between Multiple Charge-Transfer Bands and Radical Absorption as Exemplified with Pyridinium Compounds

Sir:

Multiple charge-transfer bands in donor–acceptor complexes have been assigned to transitions *from* two upper occupied levels in the donor[1] or *to* two lower unoccupied levels in the acceptor.[2,3] Isomeric complexes have also been postulated[4] but are difficult to justify.[3] In the case of the 1-alkylpyridinium iodides, the two charge-transfer bands observed in nonpolar solvents were once assigned to the formation of $^2P_{3/2}$ and $^2P_{1/2}$ iodine atoms in the excited state, on the basis that the separation between the two bands (ΔTE) corresponded exactly to that expected for the formation of iodine atom in two states in the case of 1-methylpyridinium iodide.[5] However, the marked variation in the magnitude of ΔTE with the position of substitution on the pyridinium ring was not easily explained in this way [$\Delta TE(4-) > \Delta TE(2-) = \Delta TE(\text{unsubsd}) > \Delta TE(3-)$].[5] Some parallelism between the variation in ΔTE values for dimethylaniline and iodide ion as donors to pyridinium ions led to the suggestion that two acceptor levels of the pyridinium ion were involved.[6] This idea has received strong support from the poor correlation of the ΔTE values with polarographic reduction potentials of pyridinium ions[7] in the face of

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[1] E. M. Voigt and C. Reid, *J. Amer. Chem. Soc.*, **86**, 3930 (1964).

[2] S. Iwata, J. Tanaka, and S. Nagakura, *ibid.*, **88**, 894 (1966).

[3] R. Foster, "Organic Charge-Transfer Complexes," Academic Press, New York, N. Y., 1969, pp 67–72.

[4] H. Cauquis, O. Chalvet, and Y. Thibaud, *Bull. Soc. Chim. Fr.*, 1015 (1971).

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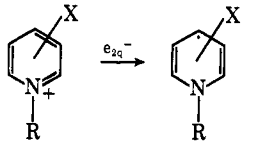
Table I. Pyridinyl Radical Absorption and ΔTE Values

Pyridinyl radical (substn)	λ_{max}, nm	L, kcal/mol	D,[c] kcal/mol	$L/\Delta TE$	ΔTE, kcal/mol	1-Alkylpyridinium iodide (substn)
1-CH_3	750	38	16	1.7	21.8[a]	1-CH_3
					21.5[b]	1-CH_3
1-CH_3-2-$CONH_2$	900	32	11	1.5	21.1[a]	1-CH_3-2-$COOC_2H_5$
					21.2[b]	1-CH_3-2-CN
1-CH_3-3-$CONH_2$	1250	23	8	1.5	15.9[a]	1-CH_3-3-$COOCH_3$
					14.0[b]	1-CH_3-3-CN
1-CH_3CH_2-4-$CONH_2$	650	44	16	1.6	28.6[a]	1-CH_3CH_2-4-$COOCH_3$
					27.0[b]	1-CH_3CH_2-4-CN

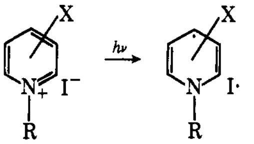
[a] Reference 5. [b] Reference 7. [c] $D = L - \Delta TE$.

excellent correlation of such potentials with the position of the longest wavelength charge-transfer bands of pyridinium iodides.[7,8] We now report the correlation of ΔTE values with the position of the longest wavelength pyridinyl radical absorption, and thus provide considerable support for the two acceptor level interpretation.[6,7]

Pyridinyl radicals were produced by reduction of the corresponding pyridinium ions with solvated electrons or $\dot{C}OO^-$ radicals[9] generated on pulse radiolysis[10] of an oxygen-free aqueous 0.1 M sodium formate–0.01 M sodium phosphate (pH 6.8) medium using 0.5–5-μsec pulses of 10 MeV electrons. The dose was adjusted so as to convert about 10% of the pyridinium ions to radicals (eq 1). The changes in transmitted light in the visible region were monitored with a double monochromator and a EMI 9558a photomultiplier, and that from 700–1400 nm with a single monochromator, an appropriate filter, a Hammamatsu R196 photomultiplier, or a Philco Ford L4521 photodiode. The longest wavelength maxima of the pyridinyl radicals produced are listed in Table I.



(1)



(2)

The transformation produced by the charge-transfer light absorption is illustrated in eq 2. Pyridinyl radical absorption in the visible and near-infrared region can be assigned as a transition from the highest occupied orbital to the lowest unoccupied orbital, with a transition energy of L kcal/mol. The relationship of L to ΔTE is easily seen in the qualitative level diagram in Figure 1. These quantities are included in Table I.

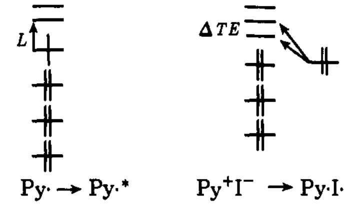


Figure 1.

The correlation between L and ΔTE values is quite evident in the values compiled in Table I. The difference in the magnitudes of L and ΔTE promise further insight into certain features of the excited states of both complexes and the related radical species. In the present case, a plausible explanation for the greater magnitude of L is that the pyridinyl radical excited state geometry resembles the pyridinium ion more than that of the ground-state radical (*i.e.*, consider it as $Py^+ + e^-$). The first vertical transition in the complex should be at higher energies than the zero–zero transition because the upper state includes a pyridinyl radical with an equilibrium distance greater than that of the pyridinium ion. The second vertical transition in the complex should be close in energy to the zero–zero transition since the upper state resembles the excited state of the pyridinyl radical. The difference (ΔTE) must thus be smaller than L.

It would be important to examine the spectrum of the 1,2,4,5-tetracyanobenzene radical anion for which similar considerations predict a low intensity maximum between 800 and 1000 nm, based on the ΔTE values reported by Nagakura, *et al.*[2] Only the intense portion of the spectrum has been examined.[11]

The present results provide substantial support for the revised[6,7] interpretation of pyridinium ion charge-transfer bands. In addition, we expect that useful estimates may be made of the lowest energy electronic transitions of radicals from charge-transfer data. Conversely, the locations of the second charge-transfer bands of some complexes might be estimated from knowledge of longest wavelength absorption of the appropriate radical. Systematics of the relationship between L and ΔTE values might prove useful in achieving a qualitative understanding of the geometric relationships of the various states involved in these electronic transitions.

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(12) Grateful acknowledgment is made for support from the National Institutes of Health, the Petroleum Research Fund and the Army Research Office (Durham).