Laboratories, for running the low-pressure liquid chromatography separations.

Registry No.—**5**, 59906-78-4; **8**, 59906-79-5; **9**, 59906-80-8; **10**, 59906-81-9; **11**, 59906-82-0; **12**, 59906-83-1; **13**, 59906-84-2; **14**, 59906-85-3; **15**, 10158-27-7; **16**, 59906-86-4; **18**, 4813-43-8; **19**, 3020-10-8; **20**, 59906-87-5; **21**, 59906-88-6; **22**, 58210-92-7; deoxycorticosterone, 64-85-7; benzenesulfonyl chloride, 98-09-9; nitrosyl chloride, 2696-92-6; acetic anhydride, 108-24-7; potassium acetate, 127-08-2.

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The He I Photoelectron Spectra of *N*-Methylisoindole and *N*-Methylindole

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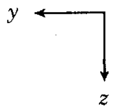
The He I photoelectron spectra of *N*-methylisoindole and *N*-methylindole are reported. The first three bands of the isoindole are assigned to $^2A_2$ (7.22 eV), $^2B_1$ (8.48 eV) and $^2A_1$ (9.51 eV) ionic states of the C_{2v} molecular geometry. Predictions of INDO, Hückel, and structure representation models for the indoles pyrrole and 1,4-dihydropyridine are compared.

The high reactivity of isoindoles has excited many previous experimental[1] and theoretical investigations.[1,2] We presently wish to report the results of our determination of the He I photoelectron spectra of *N*-methylindole (**3**) and *N*-methylisoindole (**4**) and a comparison of the predictions of INDO–SCF,[3] Hückel,[4] and structure representation[5] (SR) models for the ordering of the ionic states of these molecules.



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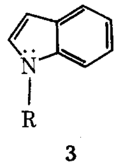

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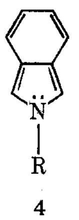


4

R = H, CH_3

N-Methylindole was prepared from *N*-methylindole-2-carboxylic acid by decarboxylation. *N*-Methylisoindole was prepared from *N*,*N*-dimethylisoindolinium bromide by treatment with phenyllithium.[6] It was isolated by an extraction under nitrogen and purified by sublimation under high vacuum (<0.05 Torr). Photoelectron spectra of this compound were recorded immediately after breaking open the sealed sublimation tube containing the purified material so that contact time of the sample with air was less than 2 min. A small amount of volatile impurity was evident in the initial spectra but disappeared after a short period in the vacuum chamber of the spectrometer. The spectrum of **4**, shown in Figure 1, is typical of those reproducibly obtained after the initial 30 min of pumping.[6a] The observed and calculated vertical ionization potentials for the series **1–4**, using several methods, are summarized in Table I.

The INDO–SCF method gives the first ionic configuration of **4** (C_{2v}) as $^2A_2$ and the second as $^2B_1$. The differences[11] in the energies of these ionic configurations and that for the ground state are 8.31 and 9.80 eV, respectively. The former

Table I. Observed and Calculated Vertical Ionization Potentials (eV)

Compd	Ion. sym	IP$_{(\mathrm{obsd})}$[a]	ΔE^{INDO} [b]	$-\epsilon^{\mathrm{INDO}}$ [c]	Hückel[d]	SR[e]	SR[f]
N-Methylisoindole	$^2A_2$	7.22	8.31	9.09	7.04	7.81	(7.36)
(C_{2v})	$^2B_1$	8.48	9.80	11.11	8.78	7.66	(8.46)
	$^2A_2$	9.51		14.71	9.53	10.01	(9.67)
Isoindole	$^2A_2$		8.45	9.16	7.04	7.81	
(C_{2v})	$^2B_1$		10.66	11.91	8.99	8.11	
	$^2A_2$			14.80	9.53	10.01	
N-Methylindole	$^2B(\pi)$	7.71			7.54	6.84	
(C_s)	$^2B(\pi)$	8.36			8.34	8.67	
	$^2B(\pi)$	9.76			9.68	10.13	
Indole	$^2B(\pi)$	7.87			7.66	7.13	
(C_s)	$^2B(\pi)$	8.48			8.41	8.68	
	$^2B(\pi)$	9.89			9.78	10.31	
N-Methylpyrrole	$^2A_2$	7.95[h]	10.19	11.09	7.93	9.01	
(C_{2v})	$^2B_1$	8.80[h]	9.93	11.34	8.64	7.81	
Pyrrole	$^2A_2$	8.22[h]	10.36	11.15	7.93	9.01	
(C_{2v})	$^2B_1$	9.22[h]	11.03	12.42	8.99	8.38	
N-Methyl-1,4-dihydro-							
pyridine	$^2B_1$	7.39			5.75	7.19	
(C_{2v})	$^2A_2$	9.77			8.99	9.77	
1,4-Dihydropyridine	$^2B_1$	7.46			6.22	(7.46)	
(C_{2v})	$^2A_2$	9.77			8.99	9.77	

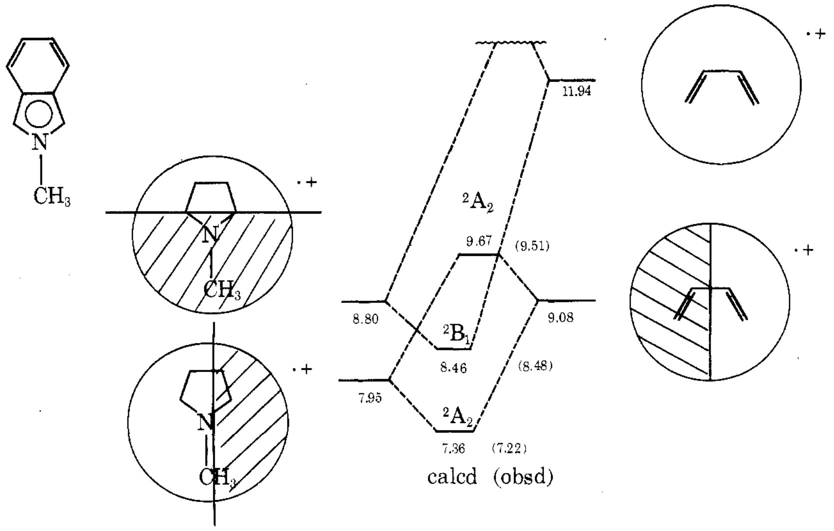
[a] Experimental values. [b] $E^{\cdot +}{}_{\mathrm{g.s.}}$, doublet configuration calculated as in ref 11. [c] INDO–Koopmans approximation. [d] Hückel model, $h_N = 1$, $k_{CN} = 1$, relation of Eland.[4] [e] Structure representation using ionic structures derived from 1–4. Parameters from ref 9. [f] Structure representation results from **4a.** [g] Literature value 7.88, ref 12. [h] Data of ref 13.

value is close to that (8.40 eV) reported by Dewar and coworkers[7] for the parent isoindole by PPP–SCF methods. The symmetry of the lowest ionic state suggests that its energy should not be much affected by N-methylation. The observed shifts on N-methylation of indole and pyrrole are small so that the first ionization potential of isoindole itself should not be much higher than that reported here for the *N*-methyl compound. The observed ionization potentials are thus considerably lower than semiempirical SCF calculations predict. The INDO–Koopmans'[8] approximation method produces the same assignments but the numerical aggreement with the observed ionization potentials is very poor (Table I).

The same assignments for the spectrum of 4 are produced using the simple Hückel model ($h_N = 1$, $k_{CN} = 1$). In fact, the empirical correlation of Eland[4] (IP = 6.22 + 2.77*m*) produces very good numerical agreement with the experimental values. This method correlates the observed ionization potentials of the entire pyrrole-related series of compounds (2–4) very well. All of the molecular orbital methods are thus in agreement for the assignments of symmetries of the first two π ionic states of 4 as $^2A_2$ (7.22 ± 0.04 eV), $^2B_1$ (8.48 ± 0.05 eV). The Hückel method indicates that the third band is also π ($^2A_2$, 9.51 ± 0.03 eV) and gives the best numerical agreement with experiment.

The good correlation between observed and calculated ionization potentials from the simple Hückel method does not extend to the dihydropyridines (1). Our previous investigations[9] showed that the SR method, using ionic structures derived from a single localized representation of the ground state, could easily rationalize the band positions for 1. This analysis yielded the parameters needed to predict the spectra of 2 and 4 (Table I) considering ions derived from the localized structures. These predictions are in very poor agreement with experiment for the pyrrole and isoindole series and the symmetry ordering is not the same as that given by the molecular orbital methods. Such discrepancies are just what is expected if the pyrrole derivatives are delocalized such that the ionic structures, formed from a *localized* ground state (structure

Scheme I



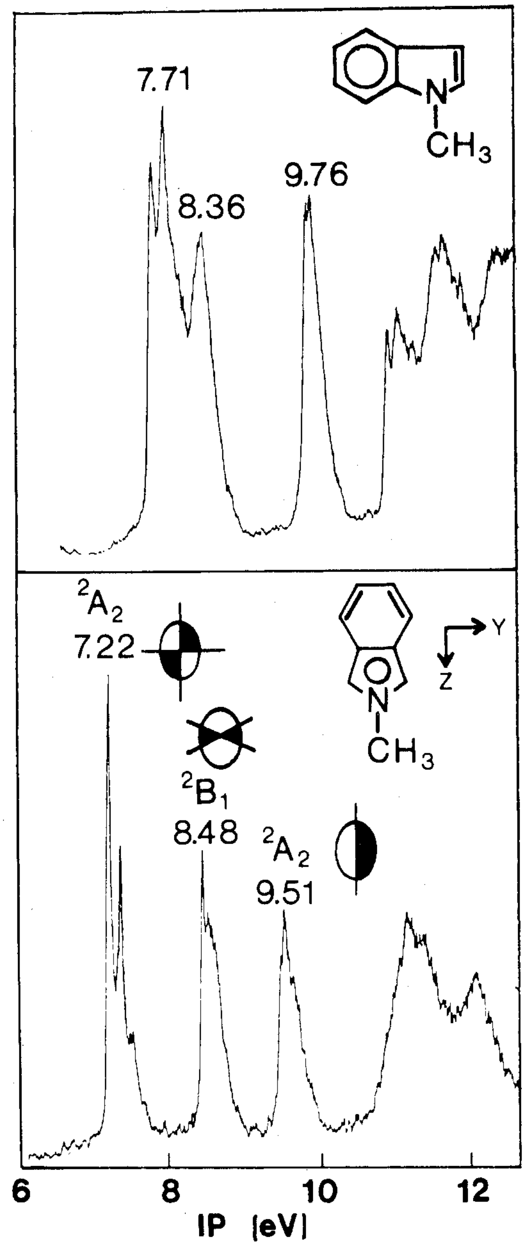


Figure 1. Observed He I photoelectron spectra of N-methylindole and N-methylisoindole. The numbers indicate our estimates of vertical ionization potentials. The first peak in the first band of the N-methylindole spectrum is assigned to a vibrational effect.

2 or 4), are an insufficient basis for the stationary states of the ion. The Hückel method is superior for delocalized species but fails for localized structures such as **1** while the SR procedure works best on systems for which the ground state can be represented by a single structure.

SR method does give good numerical agreement (Table I, last column) with experiment for isoindoles if the ionic basis functions are derived from **4a** rather than **4** where the circle in the pyrrole ring of **4a** indicates complete delocalization. The hydrocarbon ring behaves as a perturbing diene unit on the aromatic pyrrole moiety. The interactions are shown as Scheme I.

Taking structure **4a** as the best representation of the ground state indicates that the high reactivity and orientation of N-methylisoindole, in Diels–Alder reactions,[6,10] is determined by the stabilization of the transition state rather than the ground state. The former gains the stabilization of the benzene ring at the expense of the pyrrole ring.

Experimental Section

The photoelectron spectra were obtained using a Perkin-Elmer PS-18 photoelectron spectrometer and calibrated vs. Xe/Ar mixtures. N-Methylindole was prepared by the decarboxylation of N-methylindole-2-carboxylic acid as previously described.[14]

***N*-Methylisoindole.** This compound was prepared according to the method of Wittig.[6] To a suspension of N,N-dimethylisoindolinium bromide (0.20 g, 0.87 mmol) in dry ether (10 ml), a solution of phenyllithium in ether (2 ml, 0.81 mM) was added dropwise with stirring over a period of 0.5 h. The mixture, which became homogeneous after a time, was stirred under N_2 for 2 h. Water (10 ml) was then added and the two phases were mixed by stirring. The ether layer was removed by a transfer needle to a N_2 filled sublimer, and the solvent evaporated with a stream of N_2. It is very important to keep the N-methylisoindole under N_2, since exposure to air causes decomposition to a nonvolatile brown resin. The compound was sublimed at room temperature (0.025 Torr), and the crystals (white needles) were washed into an NMR tube, under N_2. N-Methylisoindole for the PE measurements was repeatedly sublimed using a heat gun and collected in a narrow tube fitted for the PE spectrometer. Transfer of the compound to the spectrometer was made in the air in less than 2 min; ^1H NMR ($CDCl_3$) 3.92 (s, 3 H), 6.82–7.68 ppm (m, 6 H).

Acknowledgments. We are grateful to the National Science Foundation for financial support of this work.

Registry No.—N-Methylisoindole, 33804-84-1; isoindole, 270-69-9; N-methylindole, 603-76-9; indole, 120-72-9; N-methylpyrrole, 96-54-8; pyrrole, 107-97-7; N-methyl-1,4-dihydropyridine, 33666-44-3; 1,4-dihydropyridine, 3337-17-5.

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