

CCA-1364

YU ISSN 0011 1643

UDC 541:547.75

Original Scientific Paper

## Electronic Absorption and Fluorescence Spectra of Indole Derivatives. Quantitative Treatment of the Substituent Effects and a Theoretical Study\*

Jean-Jacques Aaron\*\* and Alphonse Tine

Département de Chimie, Faculté des Sciences, Université de Dakar,  
Dakar-Fann, Sénégal

Claude Villiers

Laboratoire de Chimie Solaire, C.N.R.S., 2—8, rue Henri Dunant,  
F-94320 Thiais, France

Cyril Párkányi\*\* and Danielle Bouin\*\*\*

Department of Chemistry, The University of Texas at El Paso,  
El Paso, Texas 79968, U.S.A.

Received August 30, 1982

The room-temperature absorption spectra of nine substituted indoles containing the acetyl, bromo, carboxy, cyano, formyl, methoxy, methyl, and nitro substituents have been measured in cyclohexane, methanol, ethanol, ethanol-water (1:9, vol.), and in 0.1 M NaOH ethanolic solution. The room-temperature excitation and emission fluorescence spectra of these compounds have been obtained in cyclohexane and ethanol. Satisfactory linear Hammett correlations have been established for the electronic absorption and fluorescence maxima wavenumbers of most of the indoles. PPP quantum-chemical calculations indicate a good agreement between the experimental and calculated electronic transitions and provide information about the distribution of  $\pi$ -electrons in the ground and the lowest excited singlet states of indole derivatives.

### INTRODUCTION

The indole ring constitutes the aromatic moiety of tryptophan, a biomolecule which is used as a fluorescent probe in the studies of the structure of proteins and enzymes and which plays an important photochemical and photobiological role in the photoreactions of proteins.<sup>1,2</sup> For these reasons, the fluorescence properties of indole derivatives have been extensively studied.<sup>3-31</sup> However, very little is known about the effect of substituents upon the electronic absorption and fluorescence spectra of indoles.<sup>11,32,33</sup> From this stand-

\* Presented at *The IUPAC International Symposium on Theoretical Organic Chemistry*, held in Dubrovnik, Croatia, August 30 — September 3, 1982.

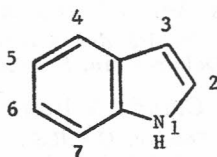
\*\* Authors to whom correspondence should be addressed.

\*\*\* Permanent address: Laboratoire de Chimie Organique A, Faculté des Sciences et Techniques de Saint-Jérôme, Université d'Aix-Marseille III, rue Henri Poincaré, F-13397 Marseille Cédex 13, France.

point, the only spectral parameter investigated so far has been the fluorescence quantum yield,  $\Phi$ , which was shown to decrease in the presence of substituents in the 3-position of the indole ring in the following order:<sup>11,32</sup>



Ricci and Nesta<sup>33</sup> explained this sequence as due to the intramolecular quenching of indole fluorescence by these carbonyl-group containing substituents, depending on their electrophilicity. Although some physical ground-state properties of indoles, such as the  $\text{pK}_a$  values and the infrared stretching frequencies have been correlated with the Hammett substituent constants,<sup>34-36</sup> no such correlations of the excited-state properties of indole derivatives have been reported so far.



Indole

The goal of the present work is to study the effect of substituents on the electronic absorption and fluorescence characteristics of a series of substituted indoles on quantitative basis, and to compare the results of the PPP (Pariser-Parr-Pople) calculations of these indole systems with the experimental spectral data.

#### EXPERIMENTAL

##### Compounds

Indole, 3-acetylintole, 5-bromoindole, 5-cyanoindole, 3-formylindole, 2-indolecarboxylic acid, 3-methylindole, and 5-nitroindole were purchased from Aldrich-Europe (Beerse, Belgium). 5-Methoxy-2-indolecarboxylic acid was obtained from the K&K Laboratories (Plainview, N. Y., U.S.A.). All these compounds were used without further purification. Their purity was checked by determining their melting points which were in good agreement with the values reported in the literature.

The solvents employed in this study were absolute ethanol («for analysis» grade, Merck, Darmstadt, Federal Republic of Germany), methanol (spectrophotometric grade, Gold Label, Aldrich Chemical Co., Milwaukee, Wisc., U.S.A.), cyclohexane (fluorescence grade, Merck, Darmstadt, Federal Republic of Germany), and deionized, degassed water.

##### Instruments

The electronic absorption spectra were recorded at room temperature (298 °K) on a Beckman model 3600 UV-VIS spectrophotometer. All excitation and emission fluorescence spectra were obtained at room temperature on a Perkin-Elmer model MPF-44B spectrofluorometer.

##### PPP (LCI-SCF-MO) Treatment

The usual version of the PPP (Pariser-Parr-Pople) method was used.<sup>37,58</sup> Interactions between monoexcited configurations, formed by promotion of one electron from one of the four highest occupied  $\pi$ -molecular orbitals to one of the four lowest unoccupied  $\pi$ -molecular orbitals, were considered. The systems studied were assumed to be planar and the rings were taken as regular pentagons and regular hexagons. All bond lengths were taken as 1.40 Å, except the C=O bond (keto,

1.23 Å) and the C—Br bond (1.86 Å). SCF molecular orbitals served as the basis for the CI calculations. Only resonance integrals between nearest neighbors were considered. The parameters used in the calculations are summarized in Table I. These parameters were tested and proven to be acceptable for the various types of atoms and bonds in previous publications.<sup>39-43</sup>

TABLE I  
Parameters Used in the PPP Calculations<sup>a</sup>

Atom, $\mu$	$I_{\mu}$	$A_{\mu}$	$\gamma_{\mu\mu}$	$Z_{\mu}$	$\beta_{C-\mu}$
C	11.22	0.69	10.53	1	-2.318
N	14.10	1.80	12.30	1	-2.318
O (OH)	32.90	10.00	22.90	2	-2.318
O (OCH <sub>3</sub> )	33.80	10.80	23.00	2	-2.040
O (C=O)	16.10	2.10	14.00	1	-2.225
CH <sub>3</sub> <sup>b</sup>	24.79	13.12	11.67	2	-1.377
Br	22.07	14.50	7.57	2	-0.695

<sup>a</sup> Values in eV.  $I_{\mu}$  and  $A_{\mu}$  are the ionization potential and the electron affinity of the atom  $\mu$  in the atomic valence state, respectively. The monocentric electronic repulsion integrals and core integrals between nearest neighbors are represented by  $\gamma_{\mu\mu}$  and  $\beta_{C-\mu}$ , respectively.

<sup>b</sup> Heteroatom model of the methyl group.

The bicentric electronic repulsion integrals were calculated using the Mataga-Nishimoto formula:<sup>44</sup>

$$\gamma_{\mu\nu} = \frac{14.399}{l_{\mu\nu} + 1.328} \text{ eV}$$

where  $l_{\mu\nu}$  (in Å) is the distance between the atoms  $\mu$  and  $\nu$ . The calculations were carried out on an IBM 4331 computer.

## RESULTS AND DISCUSSION

### *Electronic Absorption and Fluorescence Spectra*

The electronic absorption spectral characteristics for the indole derivatives in cyclohexane, methanol, ethanol, ethanol-water (1:9, vol.), and in 0.1 M NaOH ethanolic solution are given in Table II. The two maxima and/or shoulders of the long-wavelength absorption band which are observed for indole, 5-bromoindole (Figure 1), 5-methoxy-2-indolecarboxylic acid, and 3-methylindole, can be attributed to the electronic transitions of the  ${}^1L_a$  and  ${}^1L_b$  states, as it was shown previously for some indoles.<sup>1,8,45</sup> The loss of this fine structure in the case of 3-acetylindole (Figure 2), 5-cyanoindole, 5-formylindole, 2-indolecarboxylic acid, and 5-nitroindole can be explained as due to the fact that the  ${}^1L_b$  band is completely hidden under the main  ${}^1L_a$  envelope. It is also worthwhile to note that the increase of the polarity of the solvent from cyclohexane to methanol produces a bathochromic shift of the long-wavelength absorption maximum, except in the case of 2-indolecarboxylic acid and 5-methoxy-2-indolecarboxylic acid.

Table III lists the excitation and emission fluorescence maxima of indole derivatives in cyclohexane and ethanol. The fluorescence emission maximum of indoles gives a bathochromic shift when a more polar solvent is used (Figure 3), except for the 2-carboxy and 5-methoxy-2-carboxy derivatives. A vibrational fine structure of the fluorescence emission band is observed in cyclohexane for most of the indoles, while it is absent in ethanol.

TABLE II

*Electronic Absorption Bands of Substituted Indoles in Different Solvents at 298° K<sup>a</sup>*

Solvent Compound	Cyclohexane	Methanol	Ethanol	0.1 M NaOH in ethanol	Ethanol- -water (1:9, vol.)
	<u>λ, nm</u>	<u>λ, nm</u>	<u>λ, nm</u>	<u>λ, nm</u>	<u>λ, nm</u>
Indole	<u>217</u>	<u>224</u>	<u>225</u>	<u>226</u>	<u>216</u>
	<u>268</u>	<u>273</u>	<u>272</u>	<u>273</u>	<u>273</u>
	<u>289</u>	<u>288</u>	<u>288</u>	<u>289</u>	<u>288</u>
3-Acetylindole	<u>212</u>	<u>219</u>	<u>217</u>	<u>226</u>	<u>209</u>
	<u>234</u>	<u>240</u>	<u>240</u>	<u>266</u>	<u>240</u>
	<u>282</u>	(252)	(252)	<u>332</u>	<u>260</u>
		<u>297</u>	<u>297</u>		<u>299</u>
5-Bromoindole	<u>224</u>	<u>224</u>	<u>226</u>	<u>228</u>	<u>220</u>
	<u>267</u>	<u>277</u>	<u>281</u>	<u>282</u>	<u>278</u>
	<u>273</u>	<u>287</u>	<u>290</u>	<u>284</u>	<u>286</u>
	<u>286</u>				
5-Cyanoindole	<u>228</u>	<u>237</u>	<u>236</u>	<u>237</u>	<u>237</u>
	<u>232</u>			<u>260</u>	
	<u>268</u>	<u>278</u>	<u>280</u>	<u>280</u>	<u>278</u>
3-Formylindole	<u>212</u>	<u>221</u>	<u>219</u>	<u>224</u>	<u>206</u>
	<u>236</u>	<u>242</u>	<u>245</u>		<u>244</u>
		<u>262</u>	<u>260</u>	<u>267</u>	<u>262</u>
	<u>282</u>	<u>298</u>	<u>298</u>	<u>328</u>	<u>300</u>
2-Indolecarboxylic acid	<u>219</u>	<u>226</u>	<u>226</u>	<u>231</u>	<u>216</u>
	<u>294</u>	<u>290</u>	<u>294</u>	<u>293</u>	<u>293</u>
5-Methoxy-2-indolecarboxylic acid	<u>220</u>	<u>225</u>	<u>223</u>	<u>230</u>	<u>216</u>
	<u>297</u>	<u>292</u>	<u>296</u>	<u>292</u>	<u>292</u>
	(331)	(325)	(325)		
3-Methylindole	<u>222</u>	<u>223</u>	<u>225</u>	<u>230</u>	<u>222</u>
	(272)	(278)	(275)	(276)	(274)
	<u>280</u>	<u>283</u>	<u>282</u>	<u>282</u>	<u>282</u>
	<u>292</u>	(291)	(290)	(292)	(288)
5-Nitroindole	<u>254</u>	<u>265</u>	<u>265</u>	<u>265</u>	<u>265</u>
	<u>263</u>				
	<u>305</u>	<u>325</u>	<u>322</u>	<u>321</u>	<u>337</u>

<sup>a</sup> All concentrations were approximately  $1 \times 10^{-4}$  M. The wavelengths of the main absorption bands are underlined; the wavelengths of shoulders are given in parentheses.

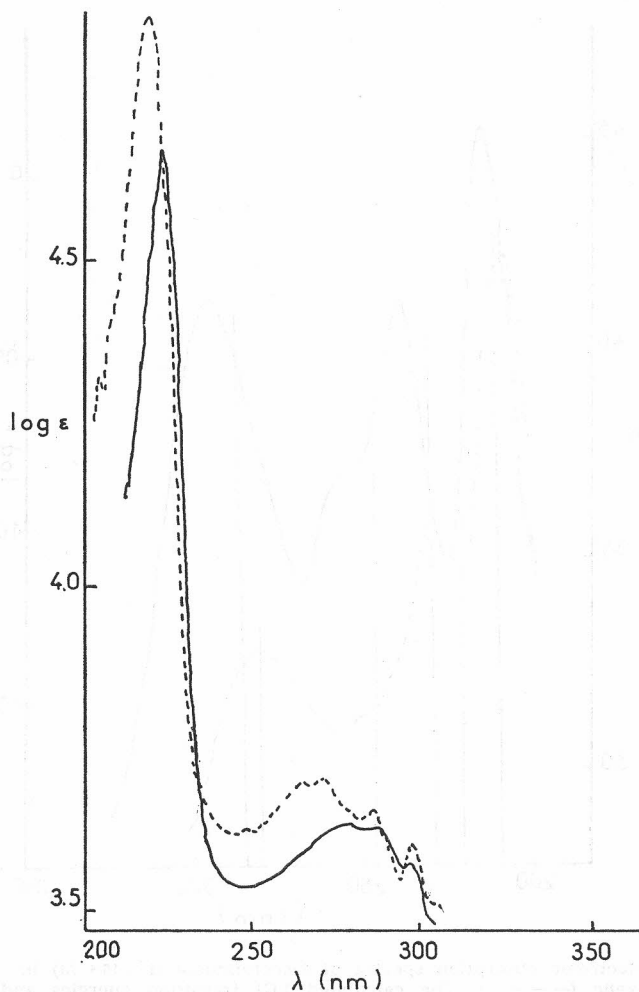


Figure 1. The electronic absorption spectra of 5-bromoindole ( $5 \times 10^{-4}$  M) in ethanol (—) and in cyclohexane (---).

### Effect of Substituents

It can be seen from Tables II and III that electron-withdrawing substituents exert a strong bathochromic shift of the  ${}^1L_a$  and  ${}^1L_b$  absorption bands and the fluorescence maxima; electron-donating substituents display a bathochromic shift of the absorption bands and of the fluorescence maxima as well.

As shown in Table IV, satisfactory linear correlations are obtained between the wavenumbers of the long-wavelength absorption maxima,  $\tilde{\nu}_{AB}$ , and the ground-state  $\sigma$  Hammett substituent constants<sup>35,36,46</sup> for most indole derivatives in several solvents. It is also interesting to note that two separate correlations are obtained for electron-withdrawing substituents ( $\sigma > 0$ ), with negative  $\rho$  values, and for electron-donating substituents ( $\sigma < 0$ ), with positive  $\rho$  values

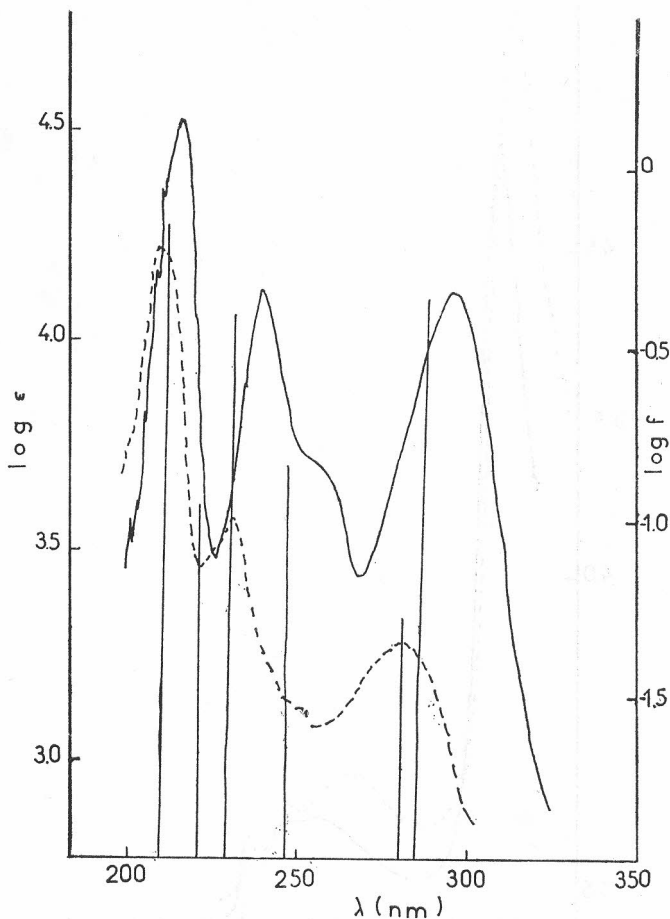


Figure 2. The electronic absorption spectra of 3-acetylindole ( $1 \times 10^{-4}$  M) in ethanol (—) and in cyclohexane (---). The calculated LCI transition energies and intensities are shown as full straight lines. The scale for the calculated oscillator strength is indicated on the right-hand side.

(cf. also Figure 4). A similar behavior was recently observed for the Hammett correlations of electronic absorption maxima of phenylpyrazolone dyes<sup>47</sup> and monosubstituted benzenes.<sup>48</sup>

Good linear correlations were also obtained between the wavenumbers of the fluorescence maxima,  $\tilde{\nu}_{\text{Fl}}$ , of indoles and the Hammett substituent constants (Table IV), with negative  $\rho$  values for the electron-withdrawing substituents and positive  $\rho$  values for the electron-donating substituents (Figure 5).

Larger positive than negative  $\rho$ 's (absolute values) indicate that the electronic  $S_0 \rightarrow S_1$  transition energy gap is more lowered by electron-donating substituents than by electron-withdrawing substituents.

TABLE III

*Fluorescence Excitation and Emission Spectra of Substituted Indoles at 298 °K<sup>a</sup>*

Solvent Compound	Cyclohexane		Ethanol	
	$\lambda$ , nm		$\lambda$ , nm	
	Excitation	Emission	Excitation	Emission
Indole	<u>289</u>	<u>303</u> (308)	<u>288</u>	<u>332</u>
3-Acetylindole	<u>232</u> (269) 284	<u>(312)</u> 330	<u>289</u>	<u>368</u>
5-Bromoindole	<u>248</u> 286	<u>313</u>	<u>286</u>	<u>328</u>
5-Cyanoindole	<u>(262)</u> 294 302	<u>322</u> (332)	<u>292</u>	<u>357</u>
3-Formylindole	<u>248</u> 284 302	<u>331</u>	<u>282</u>	<u>372</u>
2-Indolecarboxylic acid	<u>234</u> 292	<u>(345)</u> 353	<u>238</u> 294	<u>350</u>
5-Methoxy-2-indolecarboxylic acid	<u>294</u> 335	<u>373</u>	<u>296</u>	<u>372</u>
5-Methylindole	<u>(286)</u> 291	<u>308</u> (319)	<u>294</u>	<u>370</u>
5-Nitroindole	<u>230</u> 283	<u>330</u>	<u>235</u> 290	<u>360</u>

<sup>a</sup> All concentrations were approximately  $1 \times 10^{-5}$  M. The wavelengths of the main fluorescence bands are underlined; the wavelengths of shoulders are given in parentheses.

### PPP Calculations

In order to interpret the electronic absorption and fluorescence spectra of substituted indoles and the substituent effects, the PPP (LCI-SCF-MO) treatment was carried out to determine the calculated electronic transitions. In Table V, the calculated LCI transition energies and intensities are compared with the experimental absorption data for selected indoles. It can be seen that there is generally an acceptable agreement between the calculated transitions and the experimental electronic absorption spectra of most of the indole derivatives as shown in Figure 2 for 3-acetylindole. In some cases, certain calculated transitions do not show as maxima on the absorption curves because they are hidden under the envelopes of other main bands.

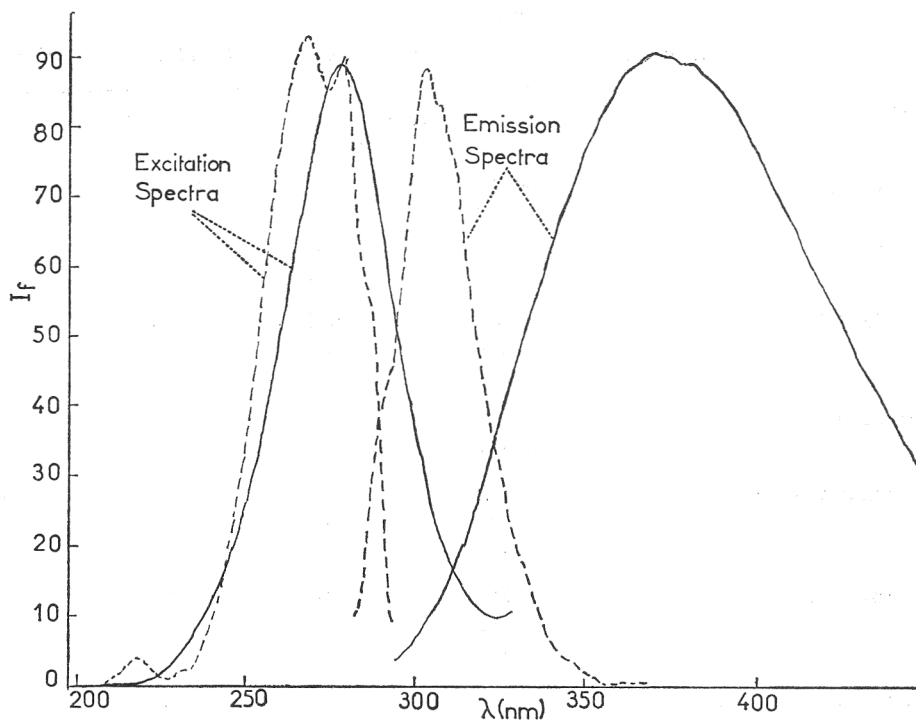


Figure 3. The fluorescence excitation and emission spectra of 3-acetylindole ( $1 \times 10^{-5}$  M) in ethanol (—) and in cyclohexane (---).  $I_f$  = relative fluorescence intensity.

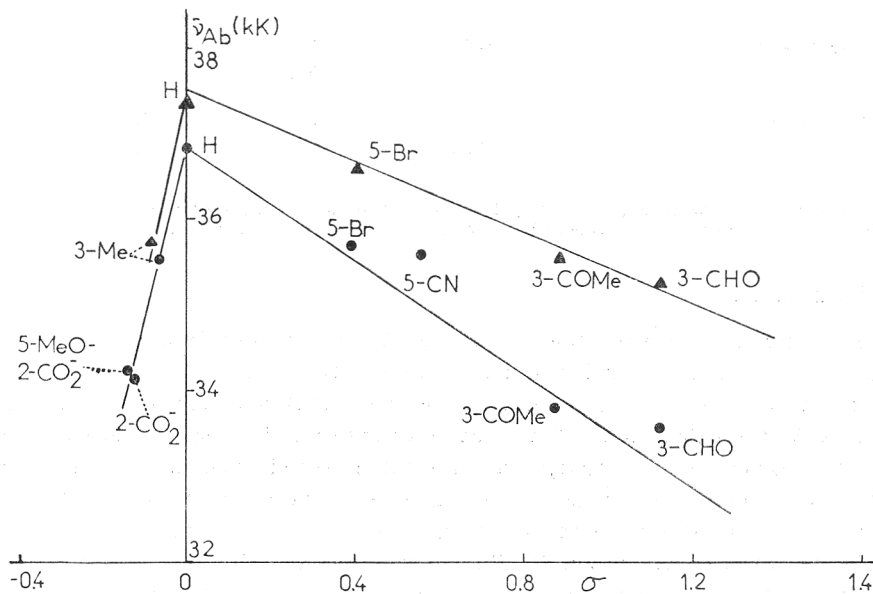


Figure 4. Correlations between the wavenumbers of the electronic absorption maxima of substituted indoles and the Hammett substituent constants; ● — in ethanol; ▲ — in cyclohexane.



TABLE IV

*Hammett Correlations of the Electronic Absorption and Fluorescence Wavenumbers of Substituted Indoles*

Spectral parameter <sup>a</sup>	Solvent	$\sigma$	$\rho$ (kK) <sup>b</sup>	$\tilde{\nu}_0$ (kK) <sup>c</sup>	$r^d$
$\tilde{\nu}_{Ab}$	Cyclohexane	$\sigma > 0$	-1.87	37.29	0.992
		$\sigma < 0$	+22.8	37.30	1.000
$\tilde{\nu}_{Ab}$	Methanol	$\sigma > 0$	-3.13	37.02	0.930
		$\sigma < 0$	+18.6	36.60	1.000
$\tilde{\nu}_{Ab}$	Ethanol	$\sigma > 0$	-3.17	36.94	0.965
		$\sigma < 0$	+19.9	36.81	0.989
$\tilde{\nu}_{Ab}$	Ethanol-water (1 : 9, vol.)	$\sigma > 0$	-3.43	37.09	0.938
		$\sigma < 0$	+12.7	36.53	0.986
$\tilde{\nu}_{Fl}$	Cyclohexane	$\sigma > 0$	-2.50	32.84	0.953
		$\sigma < 0$	+44.3	30.10	1.000
$\tilde{\nu}_{Fl}$	Ethanol	$\sigma > 0$	-3.16	29.85	0.950
		$\sigma < 0$	+7.14	33.00	1.000

<sup>a</sup>  $\tilde{\nu}_{Ab}$ -wavenumber of the longest wavelength absorption maximum;  $\tilde{\nu}_{Fl}$ -wavenumber of the fluorescence emission maximum. <sup>b</sup>  $\rho$ -reaction constant. <sup>c</sup>  $\tilde{\nu}_0$ -wavenumber at the intercept. <sup>d</sup>  $r$ -correlation coefficient.

TABLE V

Experimental and Calculated Electronic Spectral Transitions of Indole Derivatives  
(in Ethanol)

Compound	Experimental		Calculated	
	$\nu_{\max}^a$ (kK)	$\log \epsilon^b$	$\tilde{\nu}_{\max}^a$ (kK)	$\log f^c$
Indole	34.72	3.65	36.00	-1.680
	36.76	3.78	38.04	-0.612
	44.44	4.53	47.03	0.118
3-Acetylandole	33.67	4.11	35.21	-0.351
			35.67	-1.303
	39.68	4.13	40.52	-0.827
	41.67	—	43.79	-0.395
	46.08	4.53	45.34	-0.967
		47.89	-0.172	
		50.91	-0.747	
5-Bromoindole	34.48	3.59	35.94	-1.617
	35.59	3.77	38.06	-0.620
	44.25	4.67	46.98	-0.121
3-Formylindole	33.56	4.10	34.75	-0.434
	38.46	4.04	35.96	-0.954
	40.81	4.12	40.71	-0.582
			44.21	-0.293
	45.66	4.46	46.72	-0.314
		47.89	-0.472	
2-Indolecarboxylic acid	34.01	4.23	34.01	-0.478
			35.13	-0.486
			41.97	-0.238
	44.25	4.49	44.38	-0.833
			46.24	-0.773
			48.46	-0.872
		50.21	-0.455	
5-Methoxy-2-indolecarboxylic acid	30.77	3.60	31.69	-0.920
	33.78	4.17	34.66	-0.226
			41.33	-0.286
	44.84	4.39	43.03	-0.718
			45.10	-1.595
			47.31	-0.318
		49.42	-0.355	
		49.71	-0.488	
3-Methylindole	34.48	3.76		
	35.46	3.83	35.74	-1.316
	36.36	3.81	37.12	-0.708
	44.44	4.59	46.27	0.087
			49.60	-1.490

<sup>a</sup>  $\tilde{\nu}_{\max}$ -wavenumber of the electronic transition (absorption). <sup>b</sup>  $\epsilon$  is expressed in mole<sup>-1</sup> cm<sup>-1</sup>.  
<sup>c</sup>  $f$ -oscillator strength;  $\log f + 4 \doteq \log \epsilon$ .

The results of the PPP calculations also provide information about the distribution of  $\pi$ -electrons in the ground and the first excited singlet state of the systems under study. The  $\pi$ -electron densities can be used to predict the reactivity of indole and its derivatives toward various reagents and to

assess the differences in their ground- and excited-state reactivities.<sup>49</sup> It is worth noting that the  $\pi$ -electron density on the nitrogen atom of the indole ring shows a slight decrease when going from the ground state to the first excited singlet state ( $q_N$ , 1.629 and 1.610 for  $S_0$  and  $S_1$ , respectively) thus indicating a decrease of the basicity of the indole system in the first excited singlet state. In substituted indoles, this decrease is observed regardless of the nature of the substituent (electron-donating or electron-withdrawing) and its position.

*Acknowledgement.* — Financial support of this work by the Robert A. Welch Foundation, Houston, Texas (Grant No. AH-461) is gratefully acknowledged.

## REFERENCES

1. S. V. Konev, *Fluorescence and Phosphorescence of Proteins and Nucleic Acids*, Plenum Press, New York, N. Y., 1967.
2. R. Lumry and M. Hershberger, *Photochem. Photobiol.* **27** (1978) 819.
3. S. V. Konev and E. A. Chernitskii, *Biofizika* **9** (1964) 520.
4. G. S. Kembrovskii, V. P. Bobrovich, and S. V. Konev, *Zh. Prikl. Spektrosk.* **5** (1966) 695.
5. M. G. M. Balemans and F. C. G. van de Veerdonk, *Experientia* **23** (1967) 906.
6. R. F. Chen, G. G. Vurek, and N. Alexander, *Science* **156** (1967) 949.
7. I. D. Volotovskii, S. V. Konev, and E. A. Chernitskii, *Biofizika* **12** (1967) 421.
8. P. S. Song and W. E. Kurtin, *J. Amer. Chem. Soc.* **91** (1969) 4892.
9. E. Vander Donckt, *Bull. Soc. Chim. Belg.* **78** (1969) 69.
10. E. P. Kirby and R. F. Steiner, *J. Phys. Chem.* **74** (1970) 4480.
11. J. Feitelson, *Israel J. Chem.* **8** (1970) 241.
12. E. P. Busel and E. A. Burshtein, *Biofizika* **15** (1970) 993; *Biophysics* (Engl. Transl.) **15** (1970) 1027.
13. R. Santus, M. Aubailly, and C. Hélène, *C. R. Acad. Sci., Sér. C*, **272** (1971) 2008.
14. R. Santus, T. Montenay-Garestier, C. Hélène, and M. Aubailly, *J. Phys. Chem.* **75** (1971) 3061.
15. Y. Yamamoto and J. Tanaka, *Bull. Chem. Soc. Jpn.* **45** (1972) 1362.
16. E. H. Strickland and C. Billups, *Biopolymers* **12** (1973) 1989.
17. P. M. Froehlich and M. Yeats, *Anal. Chim. Acta* **87** (1976) 185.
18. P. M. Froehlich, D. Gantt, and V. Paramasigamani, *Photochem. Photobiol.* **26** (1977) 639.
19. G. Laustriat, D. Gerard, and C. Hasselmann, *Jerusalem Symp. Quantum Chem. Biochem.* **10** (1977) 151.
20. M. Sun and P. S. Song, *Photochem. Photobiol.* **25** (1977) 3.
21. I. Gryczynski and A. Kawski, *Z. Naturforsch.* **30a** (1975) 287.
22. L. J. Andrews and L. S. Forster, *Photochem. Photobiol.* **19** (1974) 353.
23. B. Valeur and G. Weber, *Photochem. Photobiol.* **25** (1977) 441.
24. N. Lasser, J. Feitelson, and R. Lumry, *Israel J. Chem.* **16** (1977) 330.
25. I. Tatischeff, R. Klein, T. Zemb, and M. Duquesne, *Chem. Phys. Lett.* **54** (1978) 394.
26. L. Kevan and H. B. Steen, *Chem. Phys. Lett.* **34** (1975) 184.
27. R. Klein and I. Tatischeff, *Chem. Phys. Lett.* **51** (1977) 333.
28. F. Wilkinson and A. Garner, *Photochem. Photobiol.* **27** (1978) 659.
29. F. D. Bryant, R. Santus, and L. I. Grossweiner, *J. Phys. Chem.* **79** (1975) 2711.
30. D. V. Bent and E. Hayon, *J. Amer. Chem. Soc.* **97** (1975) 2612.
31. A. G. Szabo and D. M. Rayner, *J. Amer. Chem. Soc.* **102** (1980) 554.
32. R. W. Cowgill, *Arch. Biochem. Biophys.* **100** (1963) 36.
33. R. W. Ricci and J. M. Nesta, *J. Phys. Chem.* **80** (1976) 974.
34. P. Tomasik and C. D. Johnson, *Advan. Heterocycl. Chem.* **20** (1976) 1.
35. G. Yagil, *Tetrahedron* **23** (1967) 2855.

36. M. Charton, in: *Correlation Analysis in Chemistry, Recent Adv.* (N. B. Chapman and J. Shorter, Eds.), Plenum Press, New York, N. Y., 1978, p. 175.
37. R. Pariser and R. G. Parr, *J. Chem. Phys.* **21** (1953) 466, 767.
38. J. A. Pople, *Trans. Faraday Soc.* **49** (1953) 1375.
39. C. Párkányi, E. J. Baum, J. Wyatt, and J. N. Pitts, Jr., *J. Phys. Chem.* **73** (1969) 1132.
40. A. T. Jeffries, III, and C. Párkányi, *J. Phys. Chem.* **80** (1976) 287.
41. C. Párkányi, G. M. Sanders, and M. van Dijk, *Recl. Trav. Chim. Pays-Bas* **100** (1981) 161.
42. C. Párkányi, G. Vernin, M. Julliard, and J. Metzger, *Helv. Chim. Acta* **64** (1981) 171.
43. Details concerning the parameterization and additional references are available upon request from the authors.
44. N. Mataga and K. Nishimoto, *Z. Physik. Chem. (Frankfurt am Main)* **13** (1957) 140.
45. J. J. Aaron, A. Tine, M. E. Wojciechowska, and C. Párkányi, to be published in *J. Luminescence*.
46. The  $\sigma_p^-$ ,  $\sigma_m$ ,  $\sigma_I$ , or  $\sigma_0$  Hammett constants were used depending on the position and the type of the respective substituents.
47. P. Nikolov, F. Fratev, S. Stoyanov, and O. E. Polansky, *Z. Naturforsch.* **36a** (1981) 191.
48. O. E. Polansky, F. Fratev, and P. Nikolov, *Z. Naturforsch.* **36a** (1981) 197.
49. The ground- and excited-state  $\pi$ -electron densities for the indoles under study are available upon request from the authors.

#### SAŽETAK

#### Elektronski apsorpcijski i fluorescencijski spektri indolnih derivata. Kvantitativna obradba utjecaja supstituenata i teorijsko razmatranje

J. J. Aaron, A. Tine, C. Villiers, C. Párkányi i D. Bouin

Apsorpcijski spektri devet supstituiranih indola s acetil-, bromo-, karboksi-, cijano-, formil-, metoksi-, metil- i nitro-supstituentima izmjereni su pri sobnoj temperaturi u cikloheksanu, metanolu, etanolu, smjesi etanol-voda (vol. omjer 1:9) i u etanolnoj otopini 0.1 mol/L NaOH. Pobudni i emisijski spektri fluorescencije tih spojeva dobiveni su pri sobnoj temperaturi u cikloheksanu i etanolu. Ustanovljene su zadovoljavajuće linearne Hammettove korelacije za valne brojeve maksimuma elektronske apsorpcije i fluorescencije većine indola. PPP kvantno-kemijski proračuni pokazuju dobro slaganje eksperimentalnih i izračunanih elektronskih prijelaza i daju informaciju o distribuciji  $\pi$ -elektrona u osnovnim i najnižima pobuđenim satnjima indolnih derivata.