12. E. L. Eliel, Stereochemistry of Carbon Compounds, McGraw-Hill, New York (1962).
13. A. B. Grigor'ev, M. K. Polievktov, Yu. V. Tsukanov, V. G. Smirnova, V. G. Granik, and R. G. Glushkov, Zh. Org. Khim., 10, 855 (1974).
14. L. Hammett, Physical Organic Chemistry; Reaction Rates, Equilibria, and Mechanisms, McGraw-Hill, New York (1970).

LUMINESCENCE AND MASS-SPECTROMETRIC INVESTIGATION OF INDOLYLQUINOLINES AND INDOLYLACRIDINES

P. B. Kurapov and N. A. Klyuev

UDC 535.37;543.51:547.759.3'831'835

The quantum-chemical calculations in [1] show that the nitrogen atom in the pyridine ring is simultaneously a σ and a π acceptor of electrons, while the pyrrole nitrogen atom is a π donor and a σ acceptor, its strong π-donor properties more than compensating the σ-acceptor effect. The presence in one system of interacting π-electron-donor and π-electron-acceptor nuclei should result in significant intramolecular interactions, which increase the electron density in the region of the internuclear bond. The order of this bond, which is equal to ~0.4, indicates that it has a significant double-bond character [2].

With the aid of mass spectrometry it has previously been established that the molecular ion (M^+) in indolylquinolines [2] has conjugation between hetaryl nuclei. Criteria which make it possible to evaluate the conjugation in M^+ are enumerated in [3-5]. This fact has also been noted in the ground state for other bisheterocycles [6, 7].

The conjugation in compounds with such a structure is due to the nearly coplanar orientation of the rings, since the magnitude of the mesomeric effect (±M) is significantly dependent on the rotation angle of the conjugated groups relative to one another [8].

The energies of the barrier to internal rotation in bisheterocycles, which have been calculated or determined experimentally, are 3 to 12 kcal/mole [9, 10]. Such energy values suggest the real existence of stable conformers; however, their isolation is possible only at low temperatures.

The purpose of the present investigation was to determine the energy of the singlet transition (E_S) and the fluorescence quantum yield (φ_f) of a number of indolylquinolines and indolylacridines. In these compounds the π-donor and π-acceptor heterocyclic rings are joined to one another by a simple C-C bond. A relationship between the value of E_S and the planarity (or conjugation) of the molecule is known [11]: The smaller is the angle of rotation between the planes of the rings comprising the original molecule, the lower is the value of E_S. An increase in the conjugation in the compounds investigated should cause an increase in the fluorescence quantum yield, since the probability of intersystem crossing decreases [12]. In this case, a comparison of the values of E_S and φ_f obtained independently by investigating the luminescence spectra and the mass spectrometric data characterizing the conjugation in the systems under investigation is of definite interest.

We studied the following compounds:* 2-(indol-3-yl)quinoline (I), 4-(indol-3-yl)quinoline (II), 4-(1-methylindol-3-yl)quinoline (III), 2-(1-methylindol-3-yl)quinoline (IV), 2-(2-methylindol-3-yl)quinoline (V), 2-(indol-3-yl)-7-methylquinoline (VI), 2-(indol-3-yl)-8-methylquinoline (VII), 1-benzoyl-1,2-dihydro-2-(indol-3-yl)quinoline (VIII), 9-(indol-3-yl)-acridine (IX), 9-(1-methylindol-3-yl)acridine (X), and 9-(2-methylindol-3-yl)-acridine (XI). The values of E_S and φ_f and some mass-spectrometric characteristics for the compounds just listed are presented in Table 1.

According to this table, compounds I-IV, VI, and VII, in which π-electron conjugation between the rings is possible, fluoresce well in polar solvents under conditions for the existence of these molecules in a nearly

---

*We thank Prof. A. K. Sheinkman for supplying the compounds for the experiment.

K. A. Timiryazeva Moscow Agricultural Academy, Moscow 127550; All-Union Scientific-Research Institute of Antibiotics, Moscow 113105. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1237-1242, September, 1979. Original article submitted November 12, 1978.

0009-3122/79/1509-1002$07.50

TABLE 1. Luminescence Characteristics and Some Mass-Spectrometric Data for Indolylquinolines I-VIII and Indolylacridines IX-XI

Compound	E_s, kcal/mole	φ_f	Temperature, °K	W_M	$I_{M^+}/I_{[M-H]^+}$ (A)	$I_{M^+}/I_{[M-2H]^+}$ (B)	Literature cited for mass spectrum
Indole	$98{,}6^{18}$	0,196	293	39,3	—	—	15
Quinoline	$92{,}2^{19}$	$0{,}053^{19}$	293	34,5	5,7	66,6	15
Acridine	$72{,}9^{19}$	0,029	293	35,2	7,0	14,0	15
I	76,0	0,540	293	19,3	1,6	3,6	2
	77,0	0,60	77				
II	69,5	0,296	293	22,6	2,0	3,6	2
	70,0	0,22	77				
III	73,0	0,350	293	21,7	3,3	10,8	16
	73,0	0,24	77				
IV	74,5	0,412	293	21,9	2,9	12,8	16
	74,3	0,25	77				
V	—	$\ll 0{,}1$	293	7,0	1,9	7,0	
	—	$\ll 0{,}1$	77				
VI	78,0	0,170	293	20,6	2,9	9,0	16
	77,5	0,37	77				
VII	72,8	0,251	293	27,9	4,9	16,6	
	73,0	0,25	77				
VIII	—	$\ll 0{,}1$	293	1,1	—	—	17
	82,0	0,09	77				
IX	62,0	0,05	293	22,4	1,9	3,5	
	58,5	0,21	77				
X	—	$\ll 0{,}1$	293	18,1	2,6	10,0	
	58,5	0,23	77				
XI	—	$\ll 0{,}1$	293	7,1	1,3	2,2	
	58,5	0,11	77				

planar conformation. The values of φ_f are 1.5 to 2 times higher than for indole and 4 to 10 times higher than for quinoline. Accordingly, the values of E_S are 20-25 kcal/mole lower than in the case of indole and ~20 kcal/mole lower than in the case of quinoline.

The weak dependence of the spectral characteristics on the temperature suggests that the existing conformers of I-IV, VI, and VII in polar solvents are relatively stable.

Thus, the experimental data presented in Table 1 provide evidence of the significant conjugation between hetaryl nuclei. The introduction of a methyl group into the α position of the indole ring (V) destroys the coplanarity of the sytem due to the steric interaction and results in quenching of the fluorescence. A similar effect is observed for compound VIII, in which the internuclear bond is a simple σ bond and there is no conjugation.

The same rule also follows from the mass-spectrometric data. All the compounds I-IV, VI, and VII have a high resistance (W_M) to electron impact (~20% of the total ion current), providing indirect evidence of the π character of the internuclear bond. The peaks of the $[M-H]^+$ and $[M-2H]^+$ ions have appreciable intensities. While in indole, quinoline, and acridine the processes resulting in the elimination of hydrogen atoms from M^+ are governed by randomization factors, the formation of the same ions during the fragmentation of I-IV, VI, and VII is due to dehydrogenation ring condensation processes (according to the pattern for the formation of diphenylene) [2, 3, 5, 18]. This process is naturally energetically more favorable when M^+ has a coplanar conformation. The values of W_M and the indicated ratios of the intensities (I) of the peaks of the ions $I_{M^+}/I_{[M-H]^+}$ (A) and $I_{M^+}/I_{[M-2H]^+}$ (B) can serve to some extent as criteria in the evaluation of the planarity of the molecule as a whole.

The values of W_M for compounds V and VIII are sharply reduced by factors of ~3 and ~20, respectively. The similar values of A and B for V and for I-IV, VI, and VII are due to the ordinary β elimination of a hydrogen atom from the methyl group followed by the expansion to the indole ring to form a quinoline cation [3].

The more rigorous proof of the existence of conjugation between the hetaryl rings is associated with the study of the fragmentation of M^+ in the cases of I-VIII. In the absence of conjugation the internuclear bond is a simple σ bond, and in the first fragmentation step it should break under the effect of electron impact. As a result of this act, the mass spectrum should show ions with mass numbers corresponding to the quinoline and indole fragments of the original molecule (with consideration of the localization of the positive charges in the ions on the heteroatoms [3, 19]). If the character of the internuclear bond is similar to an ordinary π bond (which is realized under the conditions of a nearly planar configuration of the molecule), its cleavage does not occur. Table 2 presents the results of an investigation of the mass spectra of metastable ions [20] of several specimens

TABLE 2. Mass Spectra of Metastable Ions Obtained by the DADI Technique for the Specimens Investigated of I, IV, IX, and XI (the accuracy is ±0.01 V)

Compound	Mass number of "mother" ion	Initial voltage, E_0, V	Deflecting voltage, E, V	Fragmentation process (mass number of "daughter" ion)
I	244 M^+	508,1	506,02	$M^+ \xrightarrow{-H} [M-H]^+$ (243)
		508,1	451,90	$M^+ \xrightarrow{-HCN} [M-HCN]^+$ (217)
	243 $[M-H]^+$	507,4	505,32	$[M-H]^+ \xrightarrow{-H} [M-2H]^+$ (242)
		507,4	450,98	$[M-H]^+ \xrightarrow{-HCN} [M-H_2CN]^+$ (216)
IV	258 M^+	506,3	504,32	$M^+ \xrightarrow{-H} [M-H]^+$ (257)
		506,3	425,85	$M^+ \xrightarrow{-CH_3CN} [M-CH_3CN]^+$ (217)
	257 $[M-H]^+$	507,1	505,12	$[M-H]^+ \xrightarrow{-H} [M-2H]^+$ (256)
		507,1	477,48	$[M-H]^+ \xrightarrow{-CH_3} [M-CH_4]^+$ (242)
V	258 M^+	506,3	504,32	$M^+ \xrightarrow{-H} [M-H]^+$ (257)
		506,3	476,68	$M^+ \xrightarrow{-CH_3} [M-CH_3]^+$ (243)
		506,3	425,85	$M^+ \xrightarrow{-CH_3CN} [M-CH_3CN]^+$ (217)
		506,3	255,12	$M^+ \xrightarrow{-C_9H_6N} [M-C_9H_6N]^+$ (130)
		506,3	251,18	$M^+ \xrightarrow{-C_9H_8N} [M-C_9H_8N]^+$ (128)
	257 $[M-H]^+$	508,5	506,52	$[M-H]^+ \xrightarrow{-H} [M-2H]^+$ (256)
		508,5	455,11	$[M-H]^+ \xrightarrow{-HCN} [M-H_2CN]^+$ (230)
IX	294 M^+	507,3	505,58	$M^+ \xrightarrow{-H} [M-H]^+$ (293)
		507,3	460,73	$M^+ \xrightarrow{-HCN} [M-HCN]^+$ (267)
	293 $[M-H]^+$	506,0	504,28	$[M-H]^+ \xrightarrow{-H} [M-2H]^+$ (292)
		506,0	459,35	$[M-H]^+ \xrightarrow{-HCN} [M-H_2CN]^+$ (266)
XI	308 M^+	506,1	503,43	$M^+ \xrightarrow{-H} [M-H]^+$ (307)
		506,1	481,45	$M^+ \xrightarrow{-CH_3} [M-CH_3]^+$ (293)
		506,1	292,48	$M^+ \xrightarrow{-C_9H_8N} [M-C_9H_8N]^+$ (178)
		506,1	213,62	$M^+ \xrightarrow{-C_{13}H_8N} [M-C_{13}H_8N]^+$ (130)
	307 $[M-H]^+$	509,1	507,42	$[M-H]^+ \xrightarrow{-H} [M-2H]^+$ (306)
		509,1	464,35	$[M-H]^+ \xrightarrow{-HCN} [M-H_2CN]^+$ (280)

of compounds I–XI. The spectra themselves were partially published in [2, 16] and are presented in the experimental part of the present report.

From the data in Table 2 it follows that cleavage of the internuclear bond in M^+ of compounds I, IV, and IX does not occur, confirming our ideas. On the other hand, in compounds V and XI, in which the methyl group destroys the coplanarity of M^+, cleavage of the internuclear bond is observed (ions with m/e 128, 130, and 178 form).

Thus, the symbatic nature of E_S, φ_f, and the mass-spectrometric data (W_M, A, and B in the spectra of the metastable ions) is clearly traced in the series of indolylquinolines consisting of I–VII. The results of independently carried out experiments support the maximum conjugation between the hetaryl nuclei of the system.

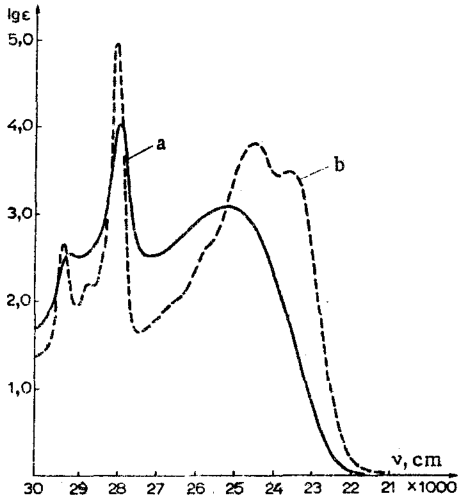

Fig. 1. Ultraviolet spectrum of IX (the solvent was a 2:1 ethanol–diethyl ether mixture): a) at 293°K; b) at 77°K.

TABLE 3. Mass Spectra of Compounds V, VII, and IX–XI

Compound	Values of m/e (intensities of ion peaks as percentages of the maximum)
V	63 (3,0), 77 (3,5), 89 (4,0), 102 (3,5), 108,5 (3,0), 114 (3,6), 115 (4,5), 116 (4,0), 121,5 (3,3), 127 (3,8), 128 (10,1), 129 (4,1), 130 (100,0), 131 (10,2), 216 (4,3), 217 (5,1), 230 (6,4), 243 (4,8), 256 (5,3), 257 (19,5), 258 (37,2), 259 (6,0)
VII	63 (3,0), 77 (3,2), 89 (3,1), 102 (3,5), 115 (3,0), 121,5 (3,0), 122 (3,0), 128 (3,0), 128,5 (4,6), 129 (11,0), 216 (3,0), 228 (4.6), 229 (3,5), 230 (3,9), 242 (6,3), 243 (8,2), 244 (5,3), 256 (6.0), 257 (20.4), 258 (100,0), 259 (22,0)
IX	51 (3,4), 63 (3,4), 77 (4,1), 119 (3,5), 132 (4,0), 132,5 (10,1), 133 (8,2), 133,5 (3,0), 146 (9,6), 146,5 (26,0), 147 (18,5), 147,5 (4,1), 238 (3,8), 264 (7,8), 265 (8,1), 266 (10,2), 267 (5,0), 292 (28,6), 293 (52,6), 294 (100,0), 295 (23,5)
X	51 (3,5), 63 (3,0), 76 (3,8), 133 (3,9), 133.5 (10,3), 146,5 (3,2), 147 (6,1), 147,5 (4,6), 153,5 (4,7), 154 (10,7), 154,5 (11,4), 238 (3,5), 264 (8,8), 265 (8,3), 266 (7,5), 267 (3,3), 291 (11,3), 292 (20.0), 293 (13,9), 294 (5,0), 305 (4,3), 306 (10,0), 307 (38,0), 308 (100,0), 309 (26.1)
XI	51 (3,6), 76 (3,2), 77 (6,0), 103 (6,3), 129 (5,6), 130 (16,5), 132 (4,0), 132,5 (8,6), 139,5 (3,5), 140 (4,1), 145,5 (24,4), 146 (6,3), 146,5 (4,0), 151 (10,0), 152,5 (4,8), 153 (8,0), 153,5 (4,2), 154 (3.0), 178 (11,6), 264 (6,3), 265 (7,0), 280 (7,0), 291 (11,4), 292 (9,8), 293 (10,4), 304 (4,4), 305 (13,7), 306 (45,4), 307 (76,9), 308 (100,0), 309 (24,4)

Such a clear correlation between the parameters presented in Table 1 is not observed in the series of indolylacridines consisting of IX–XI. For example, the values of E_S for compounds IX–XI are lower than that for acridine by only ~10 kcal/mole, and the value of φ_f in a polar solvent is at a minimum, suggesting that there is no significant conjugation between the hetaryl fragments. However, when the temperature is lowered, the value of φ_f increases significantly, and E_S decreases, suggesting the formation of a more planar conformation.

In addition, the presence of conjugation in this system can be verified with the aid of electronic absorption spectra recorded under low-temperature conditions. In fact, it was found that at 77°K there is a bathochromatic shift of the long-wave band in the UV spectrum of compound IX (Fig. 1), which is evidence of an increase in conjugation.

From the mass-spectrometric data it follows that M^+ of compounds IX and X has a nearly planar conformation: 1) the value of W_M is fairly high; 2) the dehydrogenation processes are intense and result in the cyclization of the hetaryl nuclei, as indicated by the values of A and B and the appearance in the mass spectra of intense peaks for the doubly charged ions $[M-H]^{2+}$ and $[M-2H]^{2+}$ [2, 3, 5]; 3) cleavage of the internuclear bond does not occur (Table 2). Conversely, M^+ for compound XI has a larger packing angle between the planes of acridine and indole fragments (owing to the introduction of a methyl group in the α position of indole). As a result, the value of W_M decreases appreciably, and cleavage of the internuclear bond is observed (Table 2). It is obvious that in this case, too, the values of A and B are influenced by the β elimination of a hydrogen atom from the methyl group (in analogy to compound V).

EXPERIMENTAL

The luminescence investigations at 293°K were carried out on an Hitachi model ESP-3T spectrophotometer equipped with a G-3 factory fluorescence attachment. The spectra at 77°K were obtained on an SP-700 spectrophotometer with a special attachment for recording the low-temperature spectra, which was similar to that described in [21]. The luminescence was excited with the aid of an Hg lamp at $\lambda = 365$ nm. At 293°K the relative fluorescence quantum yields (φ_f) were determined according to the method in [22]. A solution of 10^{-5} mole/liter quinine bisulfate in 0.1 N sulfuric acid ($\varphi_f = 0.55$) served as a reference [22]. At 77°K a solution of benzophenone in a 2:1 ethanol–diethyl ether system ($\varphi_p = 0.71$) [22] served as the reference for the determination of φ_f. The individuality of the compounds was monitored by thin-layer chromatography in a loose layer of Al_2O_3 (third activity grade). The eluent was a 1:6:1:30 methanol–benzene–hexane–chloroform mixture. Absolute ethanol served as the solvent at 293°K, and a 2:1 mixture of ethanol and diethyl ether served as the solvent at 77°K.

The low-resolution mass spectra of V, VII and IX-XI were obtained for the first time and are presented in Table 3.* The standard conditions for recording the mass spectra were as follows: accelerating voltage, 3 kV; cathode emission current, 300 μA; ionization energy, 70 eV; temperature of the ion source, 180°C.† A Varian model MAT-311 mass spectrometer was used.

LITERATURE CITED

1. M. Ciureanu, Rev. Roum. Chim., 21, 1007 (1976).
2. N. A. Klyuev, A. K. Sheinkman, R. A. Khmel'nitskii, G. A. Mal'tseva, and N. R. Kal'nitskii, Zh. Org. Khim., 13, 1079 (1977).
3. N. A. Klyuev, R. A. Khmel'nitskii, G. A. Mal'tseva, A. K. Sheinkman, V. A. Ivanov, and B. M. Zolotarev, Khim. Geterotsikl. Soedin., No. 7, 979 (1973).
4. N. A. Klyuev, A. K. Sheinkman, and A. N. Smirnov, Khim. Geterotsikl. Soedin., No. 6, 812 (1976).
5. N. A. Klyuev, R. A. Khmel'nitskii, O. N. Chupakhin, G. A. Mal'tseva, V. L. Rusinov, and I. Ya. Postovskii, Khim. Geterotsikl. Soedin., No. 7, 983 (1975).
6. I. I. Grandberg, Zh. Obshch. Khim., 33, 504 (1963).
7. I. I. Grandberg, S. B. Nikitina, A. N. Kost, and G. K. Faizova, Izv. TSKhA, No. 6, 219 (1968).
8. E. A. Braude, F. Soudheimer, and W. F. Forber, Nature, London, No. 173, 117 (1954).
9. I. B. Berlman, J. Phys. Chem., 74, 3085 (1970); I. B. Berlman, H. O. Wirth, and O. S. Steingraber, J. Phys. Chem., 75, 318 (1971).
10. H. J. Z. Hofmann, Z. Chem., 15, 76 (1975).
11. Yu. S. Mangutova, L. S. Mal'tseva, F. G. Kamenev, V. B. Leont'ev, S. Mukhamedkhanova, O. G. Otroshchenko, and A. S. Sadykov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1510 (1973).
12. N. S. Kozlov, L. F. Gladchenko, V. A. Serzhanina, G. V. Vorob'eva, O. D. Zhikhareva, G. S. Shmanai, and R. D. Sauts, Khim. Geterotsikl. Soedin., No. 9, 1237 (1977).
13. T. K. Efimova, L. G. Tret'yakova, N. N. Suvorov, L. B. Shagalov, A. V. Karyakin, L. I. Anikina, V. M. Pivovarov, and T. A. Tkachenko, Khim. Geterotsikl. Soedin., No. 7, 950 (1975).
14. R. W. Warner, P. Hochmann, and A. J. Bayoumi, Mol. Spectr., 54, 167 (1975).
15. American Petroleum Institute, Research Project 44, Mass Spectral Data, New York (1952), Nos. 623, 625, 639.
16. A. K. Sheinkman, V. A. Ivanov, N. A. Klyuev, and G. A. Mal'tseva, Zh. Org. Khim., 9, 2550 (1973).
17. N. A. Klyuev, A. K. Sheinkman, and V. G. Zhil'nikov, Dokl. Akad. Nauk SSSR, 232, 618 (1977).
18. P. B. Terent'ev, R. A. Khmel'nitskii, I. S. Khromov, A. N. Kost, I. P. Gloriozov, and M. Islam, Zh. Org. Khim., 6, 606 (1970).
19. N. A. Klyuev, G. A. Mal'tseva, R. A. Khmel'nitskii, A. K. Sheinkman, A. A. Deikalo, and T. V. Stupnikova, Izv. TSKhA, No. 3, 200 (1974).
20. V. Lohle and C. Offinger, Int. J. Mass Spectrom. Ion Phys., 5, 265 (1970).
21. V. S. Gurman and V. I. Pergushov, Zh. Fiz. Khim., 49, 1839 (1975).
22. C. Parker, Photoluminescence of Solutions, Elsevier, New York (1968).

---

*The ion peaks with an intensity greater than 3% of the maximum peak in the mass spectrum are indicated.

†The admission of the specimens into the ion source was monitored according to the total ionic current (ΣI = 480 to 520 μA).