

# PHOSPHORESCENCE AND POLARIZATION OF PHOSPHORESCENCE OF LINEAR POLYNUCLEAR *p*-QUINONES\*

M. NEPRAŠ and A. NOVÁK

*Research Institute of Organic Syntheses, 532 18 Pardubice - Rybitví*

Received December 7th, 1976

From shape of phosphorescence spectrum, its polarization and lifetime of phosphorescence, the types and energies of the lowest triplet states have been determined for a series of linear polynuclear *p*-quinones. On the basis of the obtained experimental results and the symmetry selection rules the mechanism of phosphorescence permission in the investigated systems has been discussed.

Studies of spectral and photochemical properties of polynuclear quinones pay attention mainly to determination of character of the lowest excited state from the luminescence properties of the respective compounds. Shcheglova and Shigorin studied<sup>1</sup> the luminescence spectrum of 1,4-naphthoquinone by the method of Shpolskij. On the basis of vibrational analysis (the distinct bands corresponding to the valence vibration frequency of C=O group) and short lifetime ( $5 \cdot 10^{-4}$  to  $6 \cdot 10^{-4}$  s), they classify luminescence as a sort of phosphorescence from the lowest triplet  $\pi\pi^*$ . The same conclusion was drawn also by Kuboyama and Yabe<sup>2</sup>, Sebtí<sup>3</sup>, and Kuboyama and Matsuzaki<sup>4</sup>. Much attention was paid to the luminescence of 9,10-anthraquinone. On the basis of detailed vibrational analysis of luminescence, Strokač and coworkers<sup>5,6</sup> came to the conclusion that the lowest excited state of this molecule is  $T_{\pi\pi^*}(B_{1g})$ . The same result was obtained by Drabe and coworkers<sup>7</sup> from a study of absorption and phosphorescence spectra of single crystal of 9,10-anthraquinone, by Kuboyama and Yabe<sup>2</sup>, Khalil and Goodman<sup>8</sup>, Narisawa and coworkers<sup>9</sup>. The lowest excited state of this molecule was identified as  $T_{\pi\pi^*}(A_u)$  by Sano and coworkers<sup>10</sup>, Dearman and coworkers<sup>11</sup>, Sebtí<sup>3</sup>, Scott and Watson<sup>12</sup>, Shcheglova and Gorelik<sup>13</sup> and Sebtí<sup>3</sup> ascribed the  $T_{\pi\pi^*}$  character to the lowest excited state of 1,4-anthraquinone on the basis of vibrational analysis. Whereas Shcheglova and Gorelik give the lifetime of 2 to 3 s, the phosphorescence lifetime found by Sebtí is of the order of  $10^{-3}$  s; the author explains this fact by a strong mixing of the triplet  $\pi\pi^*$  with the triplet  $\pi\pi^*$ . The luminescence of 5,12-tetracenequinone and 6,13-pentacenequinone was described by Zander<sup>14</sup>. The author is obviously wrong in taking the luminescence of the both compounds as phosphorescence from the triplet  $\pi\pi^*$ . Shcheglova and Lesenko<sup>15</sup> criticized the work of Zander, and they stated, on the basis of vibrational analysis of phosphorescence and solvent effect, that  $T_{\pi\pi^*}$  is the lowest excited state of 6,13-pentacenequinone.

In the context of complex studies of electronic structure of polynuclear quinones we have investigated also their luminescence spectra. The present paper gives the results of measurements of luminescence spectra at 77 K in various solvents, of the

\* Part VII in the series Electronic Structure and Properties of Polynuclear Aromatic Ketones and Quinones; Part VI: This Journal 41, 2669 (1976).

luminescence polarization and the respective lifetime. The main aim of this work is to obtain further evidence from the luminescence polarization study, which would enable a decision about the character of the lowest triplet of the abovementioned compounds.

### EXPERIMENTAL

Preparation and purification of the investigated quinones and purification of the solvents were the same as in ref.<sup>16</sup>. The phosphorescence spectra, phosphorescence lifetime, and polarization spectra were measured with the use of an adapter for measurements at 77 K with a fluorescence spectrophotometer Hitachi Perkin-Elmer MPF-2A with a digital unit enabling collection of data on a punched tape. Results of the measurements were evaluated by a computer. The phosphorescence spectra were corrected with respect to the spectral dependence of sensitivity of emission part of the spectrophotometer; the polarization spectra of phosphorescence (PP) were corrected with respect to the polarization effects of the optical part of the apparatus and cell. The phosphorescence lifetime was evaluated from photographs of the phosphorescence decay curves recorded with a low-speed oscilloscope Tesla OPD 280. The excitation monochromator for the phosphorescence measurement of the individual quinones was adjusted in the following way (wavelength, nm/slitwidth, nm): 1,4-naphthoquinone 350/20; 9,10-anthraquinone 328/25; 1,4-anthraquinone 400/40; 5,12-tetracenequinone 385/40; 6,13-pentacenequinone 400/40.

### RESULTS AND DISCUSSION

Phosphorescence spectrum of 1,4-naphthoquinone in 3-methylpentane (Fig. 1) contains prominent intensive vibronic bands differing by integer multiples of the carbonyl valence vibration frequency. The phosphorescence lifetime in n-hydrocarbons is about  $5 \cdot 10^{-4}$  s (ref.<sup>1</sup>). These results allow to assign the  $n\pi^*$  character to the lowest triplet state, which stands in accord with literature data. This inter-

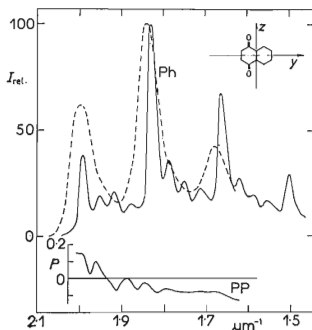


FIG. 1  
Phosphorescence (Ph) and Polarization (PP) Spectrum of 1,4-Naphthoquinone in 3-Methylpentane (—) and in Mixture Ethanol–Methanol 4 : 1 (.....) at 77 K

pretation is supported also by the sensitivity of the shape of spectrum to the solvent change. The phosphorescence spectrum of 1,4-naphthoquinone in mixed solvent ethanol-methanol 4 : 1 has a merged structure, being formed by only three broad bands. Broadening of vibronic bands in spectrum is obviously connected with the existence of a wide scale of energetic states which can be assumed by  $n$ -electrons of carbonyl on interaction with alcohol.

Irrespective of the lowest  $n\pi^*$  triplet having  $A_2$  or  $B_1$  symmetry, for symmetry reasons the phosphorescence spectrum can be polarized in the direction of axes  $y$  and  $z$  (in all the studied systems the  $x$  axis is perpendicular to the plane of the molecule, the  $z$  axis being parallel with  $C=O$  bonds). The above presumption is confirmed by the course of the PP spectrum measured for excitation predominantly in the region of the first absorption  $\pi - \pi^*$  band ( $A_1(y)$ )<sup>17</sup>; hence the phosphorescence spectrum of 1,4-naphthoquinone is a superposition of two components having different intensity distribution. In the region of  $O-O$  transition (the phosphorescence band at  $1.99 \mu\text{m}^{-1}$ ) the component polarized along  $y$  axis predominates. As the APP spectrum of 1,4-naphthoquinone measured with the emission monochromator adjusted at 543 nm ( $1.84 \mu\text{m}^{-1}$ ), *i.e.* in the region of negative values of PP spectrum, assumes also positive values<sup>17</sup>, the component predominating in the region of longer wavelengths has its polarization in the direction of  $z$  axis (the absorption spectrum refers to  $\pi - \pi^*$  transitions, *i.e.* transitions in the plane of the molecule; then the band polarized perpendicularly to  $y$  axis can be polarized only in the direction of  $z$  axis). With respect to the non-zero intensity of the  $O-O$  transition of phos-

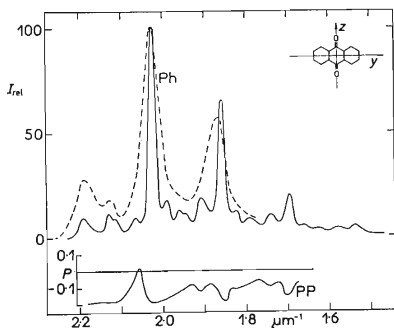
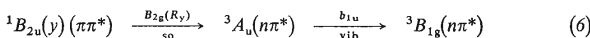
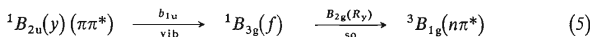
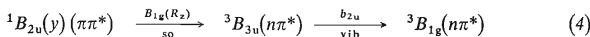
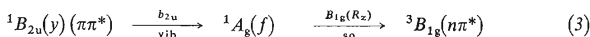
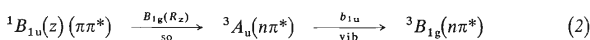
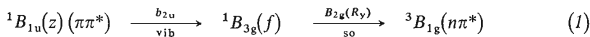
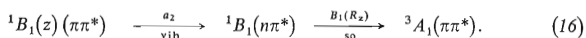
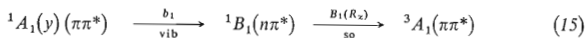
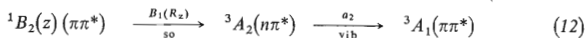
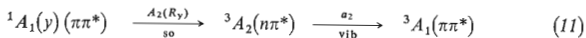
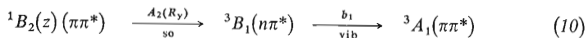
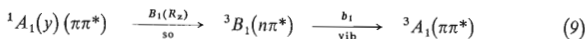
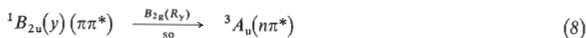
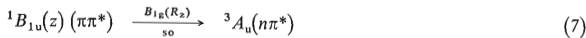


FIG. 2  
9,10-Anthraquinone (for caption see Fig. 1)

phorescence it seems likely that the component polarized along  $y$  axis is allowed by spin-orbital interaction with  $\pi - \pi^*$  transition  $^1A_1$ ; in the case of the component polarized along  $z$  axis experiment cannot decide unambiguously whether it is allowed also by mere spin-orbital interaction with  $\pi - \pi^*$  transition  $^1B_2$  (this mechanism could be supported by a small energetical difference between the excited  $\pi - \pi^*$  states  $^1A_1$  and  $^1B_2$ ) or by some of possible spin-orbital vibronic mechanisms; the latter explanation is supported by small intensity of the  $z$  component in the region of O—O transition.

Phosphorescence spectrum of 9,10-anthraquinone in 3-methylpentane (Fig. 2) is formed from a series of bands of vibronic structure showing a marked repetition, the difference between the corresponding vibronic bands being related to the carbonyl valence vibration. As it was the case with 1,4-naphthoquinone, here also the vibration structure of spectrum is lost on changing the solvent (alkane to alcohol) due to substantial broadening of vibronic bands. The phosphorescence lifetime of 9,10-anthraquinone in 3-methylpentane was found to be  $4 \cdot 10^{-3}$  s (the same value is given for EPA solvent<sup>18</sup>). On the basis of the results given it is possible to assign  $n\pi^*$  character to the lowest triplet. From comparison of APP spectrum<sup>17,19</sup> and the PP spectrum measured for excitation in the first absorption band ( $B_{2u}$ ) it follows that the phosphorescence is polarized predominantly in the direction parallel with C=O bands; at the same time, however, the PP curve shows deviations to positive values of polarization degree, too (the polarization parallel with  $y$  axis). Thus from the polarization measurements it follows that, besides the mechanisms (1) and (2) (ref.<sup>5,8</sup>) by which the  $z$ -polarized component becomes involved in the phosphorescence from  $^3B_{1g}$  triplet, it is necessary to consider also further mechanisms (3) to (6) by which the  $y$ -polarized component can be involved in phosphorescence, too.





On the contrary, if the lowest triplet  $n\pi^*$  is considered to have  ${}^3A_u$  symmetry (refs<sup>3,10-12</sup>), the both components can be involved in the phosphorescence by more spin-orbital interaction (7), (8). From available experimental data it cannot be decided unambiguously whether the lowest triplet  $n\pi^*$  has  $B_{1g}$  or  $A_u$  symmetry. Differentiation between a vibronic transition and O—O transition whose intensity and polarization are characteristic for the participating electronic states represents a fundamental problem; unfortunately there is no unambiguous rule for their differentiation. From the overall character of the PP curve it is obvious that the positively polarized component of phosphorescence (polarization along *y* axis) has a substantially lower intensity than the *z*-polarized component. According to the perturbation theory of spin-orbital and spin-orbital-vibronic interaction a more significant mixing of  $n\pi^*$  triplet with the first allowed  $\pi\pi^*$  transition ( ${}^1B_{2u}(y)$ )<sup>17</sup> of 9,10-anthraquinone could be expected from the energetical point of view. Pure energetic difference between two interacting states is, in this case, obviously not the single decisive measure for the extent of interaction. These circumstances were not discussed in the cited papers, and they could contribute to a more rigorous vibrational analysis and safer characterization of the lowest  $n\pi^*$  triplet of 9,10-anthraquinone.

The phosphorescence spectrum of 1,4-anthraquinone in 3-methylpentane (Fig. 3) shows a substantially worse resolved vibration structure than those of 1,4-naphthoquinone and 9,10-anthraquinone. Change of solvent from 3-methylpentane to alcohol mixture has a much smaller effect on the vibration structure than in the case of the abovementioned quinones. At the same time in alcoholic solvent the maxima are closer. The phosphorescence lifetime  $9 \cdot 10^{-2}$  s found in both 3-methylpentane and alcoholic mixture differs considerably from those published for n-heptane<sup>3</sup> ( $10^{-3}$  s) and mixture chlorobenzene-hexane<sup>13</sup> (2 to 3 s). In the phosphorescence spectrum the carbonyl valence vibrations cannot be identified quite unambiguously. These experimental results are between the limit values characteristic for  $n\pi^*$  and  $\pi\pi^*$  phosphorescence, and they indicate intensive mixing of  $T_{n\pi^*}$  and  $T_{\pi\pi^*}$  in 3-methylpentane. As the difference between the transition probabilities  $S_0 - T_{n\pi^*}$  and  $S_0 - T_{\pi\pi^*}$  is in order of magnitude, predominant  $\pi\pi^*$  character can be assigned to the lowest triplet. In the opposite case the spectral characteristics typical for  $n\pi^*$  phosphorescence<sup>20</sup> would have to predominate entirely. From the analysis of APP<sup>17</sup> and PP spectra it follows that two mutually perpendicularly polarized components contribute to the phosphorescence of 1,4-anthraquinone. In the region of oscillations of PP curve towards positive values of polarization degree the  $y$ -polarized component predominates (the excitation in the region of the first absorption transition  $A_1(y)$ )<sup>17</sup>. Towards longer wavelengths the component polarized perpendicularly to  $y$  axis predominates. As the APP curve<sup>17</sup> measured in the region of negative polarization of the phosphorescence spectrum shows also a positive polarization

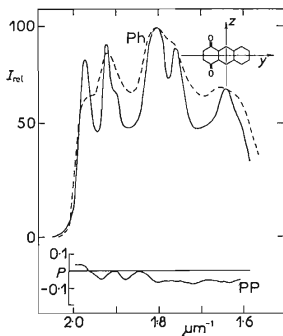


FIG. 3

1,4-Anthraquinone (for caption see Fig. 1)

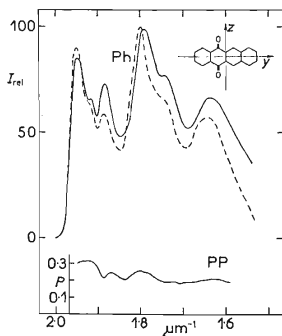


FIG. 4

5,12-Tetracenequinone (for caption see Fig. 1)

degré, the second component must be polarized in the plane of the molecule, too, *i.e.* along *z* axis. Thus the both components steal their intensity from the symmetrically allowed singlet  $\pi\pi^*$  transitions and obviously are considerably overlapped (low values of the polarization degree). From theoretical calculation and analysis of the APP curve we assigned  $\pi\pi^*(A_1)$  character to the lowest singlet. If we justifiably presume this character also for the lowest triplet, then it is impossible for the both components of phosphorescence polarized in the plain of the molecule to be allowed by pure spin-orbital interaction. The mentioned spin-orbital vibronic interactions (9) to (16) are possible for the both components to be involved in the phosphorescence of 1,4-anthraquinone. The intermediate states  $B_1$  and  $A_2$  can be singlets or triplets of the type  $n\pi^*$  or  $\sigma\pi^*(\pi\sigma^*)$ . With respect to the product of energy differences  $(S_{\pi\pi^*}^2 - T_{\pi\pi^*})(T_{\pi\pi^*} - T_{n\pi^*})$  being smaller than  $(S_{\pi\pi^*}^2 - S_{n\pi^*})(S_{n\pi^*} - T_{n\pi^*})$ , ( $S_{\pi\pi^*}^2 \approx \approx 3.00 \mu\text{m}^{-1}$ ), and with respect to that in the *z*-polarized component it is possible to find bands with the frequency difference corresponding to vibration of carbonyl, it is quite likely that this component becomes involved in the phosphorescence of 1,4-anthraquinone by the mechanism (10) or (12), *i.e.* by spin-orbital vibronic interaction in the triplet manifold through the intermediate state  $T_{n\pi^*}$ . On the contrary, the bands with the frequency of carbonyl vibration cannot be identified in the *y*-polarized component. It is likely that this component becomes involved in the phosphorescence by some of the mechanisms (9), (11), (13), (15), the intermediate states with  $A_2$  or  $B_1$  symmetry being  $\sigma\pi^*(\pi\sigma^*)$  states. Due to rather flat vibration structure of phosphorescence in the frozen organic glass it is impossible to carry out any detailed analysis of the spectrum. No existence of dual phosphorescence was found<sup>21</sup>.

The maxima of the phosphorescence spectrum of 5,12-tetracenequinone (Fig. 4) and especially of 6,13-pentacenequinone (Fig. 5) are closer than it would correspond

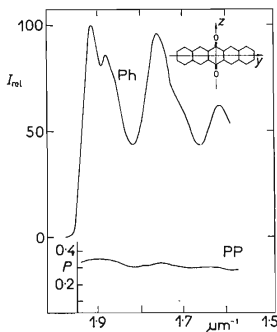


FIG. 5  
6,13-Pentacenequinone (for caption see Fig. 1)

to the carbonyl valence vibration, the shape of the spectra and distances of maxima being similar to those in the phosphorescence spectrum of naphthalene. Change of solvent (hydrocarbon to alcohol) has only slight effect on the band width of phosphorescence spectrum of the both quinones. The same lifetime 0.3 s was measured for the phosphorescence of the both substances (Zander gives<sup>14</sup> the time shorter than 0.5 s). In the whole spectral region of the both quinones the phosphorescence polarization is predominantly in direction of  $y$  axis (positive value of polarization degree). Hence in the both cases only one component contributes predominantly to the phosphorescence, the component being allowed by some spin-orbital vibronic mechanism (mechanisms (9), (11), (13), (15) in the case of tetracenequinone and mechanisms (3) to (6) for pentacenequinone).

From the found facts it is possible to give the energy scheme (Fig. 6) for the studied systems. Wavy line denotes the states the energy of which was determined with little accuracy; dashed line denotes the states for which there are no experimental data and their energy was estimated on the basis of presumption of equal magnitude of singlet-triplet splitting of structurally similar quinones for which the magnitude of this splitting could be experimentally determined. For the triplet states  $n\pi^*$  of 1,4-anthraquinone, 5,12-tetracenequinone and 6,13-pentacenequinone we used the value  $0.18 \mu\text{m}^{-1}$  of singlet-triplet splitting found for 9,10-anthraquinone. For the triplet state  $\pi\pi^*$  of 1,4-naphthoquinone we used the value  $0.53 \mu\text{m}^{-1}$  found for 1,4-anthraquinone, and for 9,10-anthraquinone the value  $0.65 \mu\text{m}^{-1}$  was used which was found for 6,13-pentacenequinone. From Fig. 6 there follows a rule for the lowest  $n\pi^*$  and  $\pi\pi^*$  states, that linear annellation leading to decrease of difference in the numbers of benzene rings at the both sides of the quinoid ring causes a weak hypsochromic shift of  $n\pi^*$  states, the energy of the lowest  $\pi\pi^*$  states being maintained; the linear

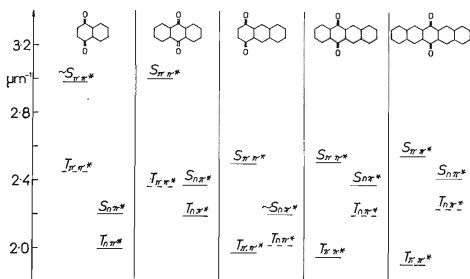


FIG. 6

Energy Scheme of the Lowest Excited States of Linear  $p$ -Quinones



annellation increasing this difference causes a marked bathochromic shift of  $\pi\pi^*$  states, the energy of  $n\pi^*$  states being maintained. Further linear annellation gives 6,15-hexacenequinone and 7,16-heptacenequinone which exhibit fluorescence<sup>14</sup>. This fact indicates that singlet and triplet  $n\pi^*$  lie above the lowest singlet and triplet  $\pi\pi^*$  for both these substances.

## REFERENCES

1. Shcheglova N. A., Shigorin D. N.: *Zh. Fiz. Khim.* **38**, 1261 (1964).
2. Kuboyama A., Yabe S.: *Bull. Chem. Soc. Jap.* **40**, 2475 (1967).
3. Sebtí M.: *Thesis*. University Bordeaux, 1972.
4. Kuboyama A., Matsuzaki S.: Reports of the Government Chemical Industrial Research Institute, Tokyo **64**, 105 (1969).
5. Strokach N. S., Gastilovich E. A., Shigorin D. N.: *Dokl. Akad. Nauk SSSR* **202**, 136 (1972).
6. Strokach N. S., Gastilovich E. A., Shigorin D. N.: *Opt. Spektrosk.* **35**, 238 (1973).
7. Drabe K. E., Veenliet H., Wiersma D. A.: *Chem. Phys. Lett.* **35**, 469 (1975).
8. Khalil O. S., Goodman L.: *J. Phys. Chem.* **80**, 2170 (1976).
9. Narisawa T., Sano M., I'Haya Y. J.: *Chem. Lett.* **1975**, 1289.
10. Sano M., Narisawa T., I'Haya Y. J.: Proceedings of the Seventh Molecular Crystals Symposium, Nikko, Japan 1975.
11. Dearman H. H., Sundarachari N., Ülkü D.: *J. Chem. Phys.* **45**, 4363 (1966).
12. Scott J. D., Watson W. H.: *J. Chem. Phys.* **49**, 4246 (1968).
13. Shcheglova N. A., Gorelik M. V.: *Zh. Fiz. Khim.* **44**, 2988 (1970).
14. Zander M.: *Ber. Bunsenges. Phys. Chem.* **71**, 424 (1967).
15. Shcheglova N. A., Lesnenko L. G.: *Opt. Spektrosk.* **31**, 360 (1971).
16. Nepraš M., Kratochvíl V., Titz M., Novák A., Slavík V.: *This Journal* **38**, 1003 (1973).
17. Novák A., Titz M., Nepraš M.: *This Journal* **39**, 1532 (1974).
18. Parker C. A., Hatchard C. G.: *Analyst (London)* **87**, 664 (1962).
19. Drott H. R., Dearman H. H.: *J. Chem. Phys.* **47**, 1896 (1967).
20. McGlynn S. P., Azumi T., Kinoshita M.: *Molecular Spectroscopy of the Triplet State*. Prentice-Hall, 1969.
21. Chu S. Y., Goodman L.: *Chem. Phys. Lett.* **34**, 232 (1975).

Translated by J. Panchartek.