Photophysical and Photochemical Properties of 2,3-Dihydro-4(1 H)-quinolinones. Part I. Fluorescence Properties

Sn. Bakalova*, L. Biczók**, I. Kavrakova*, and T. Bérces**

* Institute of Organic Chemistry with Centre of Photochemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria

** Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1025 Budapest, Pusztaszeri 59/67, Hungary

Z. Naturforsch. **45c**, 980–986 (1990); received March 16/July 2, 1990

Dihydroquinolinones, Fluorescence Properties, Excited Singlet States

Absorption spectra and fluorescence properties of 2,3-dihydro-4(1 H)-quinolinone derivatives were studied at room temperature in different solvents. It has been found that the fluorescence quantum yields and fluorescence decay times strongly depend on the molecular structure and solvent polarity. The character and the energy of excited states were determined by PPP and CNDO/S quantum-chemical calculations.

Introduction

While the photophysical and photochemical properties of benzodihydropyranones have been extensively studied [1–3], there are no data in the literature on the luminescence properties of their heteroanalogues, the dihydroquinolinones. Some derivatives of 2,3-dihydro-4(1 H)-quinolinone are known to possess analgesic effect [4], and the Mannich bases derived from these structures have been described as central nervous system depressants and compounds with antipyretic and antiflammatory activity [5].

In this paper we present results on the absorption and fluorescence properties of the 2,3-dihydro-4-(1 H)-quinolinones shown in Fig. 1. On the basis of the experimental data and the results of PPP and CNDO/S quantum-chemical calculations, assignments of the excited singlet states of these compounds are given.

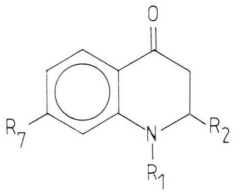

Fig. 1. Structure of the 2,3-dihydro-4(1 H)-quinolinones investigated:

Comp. No.	R_1	R_2	R_7
1	H	H	H
2	H	CH_3	H
3	H	H	CH_3O
4	H	H	OH
5	CH_3	H	H
6	$COCH_3$	H	H
7	$SO_2C_6H_4CH_3$	H	H

Reprint requests to Dr. Tibor Bérces.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0341–0382/90/0900–0980 $ 01.30/0

Results

Spectral characteristics

The UV-VIS absorption spectrum of 2,3-dihydro-4(1 H)-quinolinone (compound **1**) in cyclohexane and acetonitrile is shown in Fig. 2. The ab-

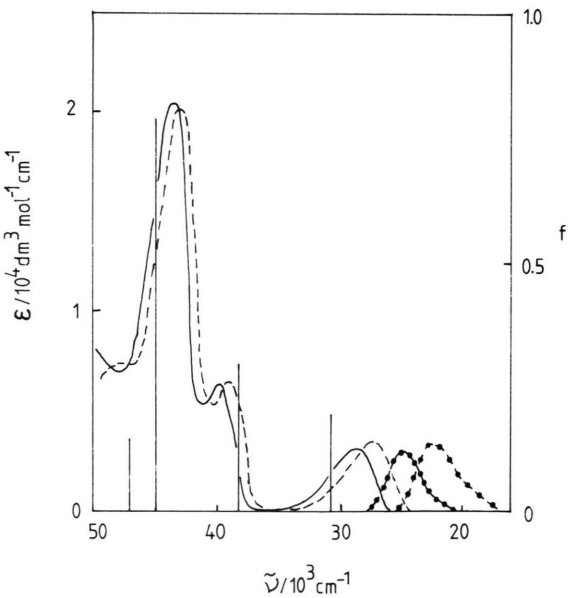

Fig. 2. Absorption and fluorescence spectra of **1** in cyclohexane (full line) and acetonitrile (broken line); fluorescence spectra (indicated by —●—● and —●— —●—) are given in arbitrary units; oscillator strengths, calculated by the PPP method, are represented by bars.

sorption spectrum consists of three bands in the 200–420 nm region. The absorption coefficient in acetonitrile has been measured to be 4000 dm^3 mol^{-1} cm^{-1} at the maximum of the longest wavelength absorption band. The peaks are shifted towards longer wavelengths with increasing solvent polarity. The longest wavelength absorption maximum is displaced by about 1200 cm^{-1} when cyclohexane solvent is replaced by acetonitrile. In Table I are given the spectral characteristics of the investigated compounds in cyclohexane, diethyl ether and acetonitrile. The absorption spectra of compounds **2–5** are similar in shape and in the location of the maximum to that of compound **1.**

In non-polar solvents (heptane, cyclohexane), weak but distinct shoulders are observed around 27,100 cm^{-1} in the absorption spectra of **6** and **7.** In polar solvents these are completely overlapped by the red-shifted intense band. Considering the observed solvent shifts and the small extinction coefficients, the weak shoulders can be assigned to the $n\pi^*$ singlet transition. Thus, one estimates the energy for the $^1(n,\pi^*)$ state of 27,000–28,000 cm^{-1} which is close to that of the $^1(n,\pi^*)$ state of many aromatic aldehydes and ketones (*i.e.* 27,000 cm^{-1} [6]) and to the benzodihydropyranones (*i.e.* 27,700 cm^{-1} [3]) which are the heteroanalogues of the dihydroquinolinones.

Table I. Spectral characteristics in non-deaerated solution, λ_A and λ_F are the maxima of the lowest energy absorption band and the fluorescence band resp., Q_F is the fluorescence quantum yield.

Comp. No.	Cyclohexane λ_A/nm	λ_F/nm	Q_F	Acetonitrile λ_A/nm	λ_F/nm	Q_F
1	351	400	0.002	366	450	0.27
2	350	400	0.002	366	448	0.28
3	335	392	0.001	350	428	0.24
4	NM[a]	NM[a]	NM[a]	348	429	0.20
5	362	407	0.026	379	464	0.28
6	318	NM[b]	NM[b]	325	NM[b]	NM[b]
7	315	NM[b]	NM[b]	322	NM[b]	NM[b]

NM, means no measurement; [a] poor solubility; [b] photochemical instability.

In polar non-deaerated solvents the studied compounds exhibit relatively intense fluorescence with a quantum yield of Q_F = 0.22–0.38 (see Table I). The fluorescence bands are broad and structureless. Upon decrease of the solvent polarity the fluorescence maxima move to the blue and a large decrease of the fluorescence quantum yield occurs. (For most of the studied compounds, $Q_F \sim 0.001$ in hydrocarbon solvents.)

Substituent R_1 has a substantial influence on the fluorescence properties. The replacement of the hydrogen atom in **1** with a methyl group (compound **5**) which is a weak electron donor leads to a slight red shift of the spectra and a significant increase of the fluorescence intensity in non-polar solvents. An electron withdrawing R_1 substituent, as for instance an acetyl or tosyl group leads to a blue displacement of the spectra and compounds **6** and **7** are hardly fluorescent in any solvent.

An electron donor substitution in position 7 (compounds **3** and **4**) leads to a blue shift of the electronic spectra accompanied by a decrease of the fluorescence quantum yield.

Substitution in position 2 by an electron donating methyl group (compound **2**) had no significant effect neither on the spectra nor on the fluorescence yields.

Table II shows the fluorescence lifetimes τ_F of the studied compounds and the calculated rate constants for radiative and non-radiative decay of

Table II. Singlet lifetimes (τ_F) and rate constants for radiative (k_F) and non-radiative (k_{NR}) deactivation of the singlet excited state in non-deaerated acetonitrile solution, χ^2 is the reduced chi-square and DW denotes the Durbin-Watson parameter.

Comp. No.	λ_{exc}/nm	τ_F/ns	$10^{-7} \times k_F/s^{-1}$	$10^{-7} \times k_{NR}/s^{-1}$	χ^2	DW
1	370	9.4	2.9	7.7	1.31	1.58
2	370	10.2	2.7	7.1	1.33	1.76
3	355	7.8	3.1	9.7	1.13	1.82
4	360	6.9	2.9	11.6	1.38	1.72
5	375	10.4	2.7	6.9	1.32	1.83

the excited singlet state in acetonitrile. In all cases the fluorescence decay curves could be fitted with good precision by a single exponential function. In polar non-deaerated solvents the τ_F values are in the range of 6–11 ns; the fluorescence rate constants k_F and the k_{NR} rate constants for the non-radiative deactivation processes are both of the order of 10^7-10^8 s^{-1}. (It is to be noted, however that 30–40% fluorescence quenching occurs in the presence of air, as shown by comparison with the results obtained with oxygen-free systems.)

In hydrocarbon solvents at room temperature, the fluorescence lifetimes are less than 1 ns, *i.e.* too short to be determined on our instrument with the required accuracy. At lower temperatures the lifetimes become longer (τ_F = 1.27 ns for compound **2** in methylcyclohexane at 220 K). The radiative rate constant of **2** in methylcyclohexane determined in the temperature range 200–230 K is 1.8×10^7 s^{-1}. As a first approximation we assume that k_F is temperature-independent and the value is the same at room temperature.

Upon freezing the 2-methyl-tetrahydrofuran (2-MTHF) solutions of compounds **1–5,** the fluorescence maximum shifts to shorter wavelength, the fluorescence intensity is enhanced and a weak phosphorescence emission with a lifetime around 1 s is observed. Fig. 3 shows the corrected emission spectra of compound **2** in 2-MTHF at 297 and 77 K.

Quantum-chemical investigations

To clarify the character of the excited states we have performed quantum-chemical calculations

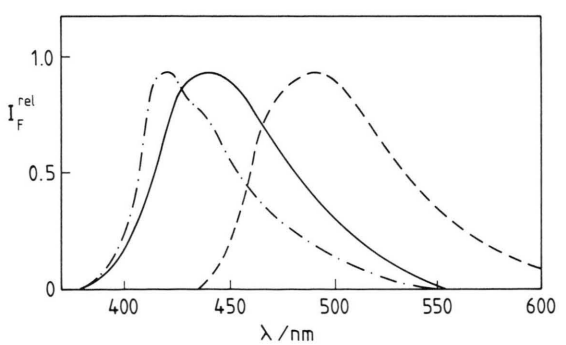

Fig. 3. Corrected emission spectra of **2** in 2-MTHF: Fluorescence at 297 K (——); fluorescence at 77 K (–·–·–); phosphorescence at 77 K (– – – –).

for **1** by the Pariser-Parr-Pople (PPP) method (SCF-CI) taking into account all singly excited configurations with a standard parametrization [7]. Fig. 2 allows a comparison of the measured absorption spectrum of **1** in cyclohexane and the calculated energies of the ππ* transitions. (The length of the line is proportional to the calculated oscillator strength *f*.) It can be seen that the experimental absorption spectrum agrees well with the quantum-chemical calculations; the difference between the calculated and the experimental Franck-Condon transition energies is within the accuracy of the PPP method.

CNDO/S calculations using a standard parametrization [8] have been performed for **1** and **2.** All singly excited configurations have been included in the configuration interaction. The geometries of the molecules have been optimized by the MNDO method [9]; all internal coordinates (bond lengths, dihedral and valence angles) have been varied in the optimization procedure. The results of calculations together with the transition energies derived from the absorption spectrum in cyclohexane are given in Table III. The agreement between calculated and experimental energies is reasonable. Some deviation is expected since the CNDO/S method is known to overstabilize molecules with carboxylic type lone-pair electrons [10].

It can be seen from Table III that all transitions are of mixed character. The nπ* transitions (both singlet and triplet) are determined predominantly by the $V_2^{i'}$ configurations (i = 1, 3). The longest wavelength ππ* transitions are composed mainly from the $V_1^{1'}$ configuration which corresponds to a HOMO-LUMO transition. Its contribution decreases in the ππ* transitions of lower energy.

The PPP and CNDO/S quantum-chemical calculations predict four singlet ππ* transitions below 6 eV. Fig. 4 and Fig. 5 show the electron density distribution in the ground and the first three excited singlet states. It can be seen that $S_2(\pi,\pi^*)$ is characterized by a partial intramolecular charge transfer (ICT) from the nitrogen atom to the carbonyl group, while $S_3(\pi,\pi^*)$ has mainly the local excitation (LE) character of aniline. A comparison with the aminoacetophenones [11] shows that the relative ordering of the low-lying ππ* states of **1** and **2** is the same as in *p*-amino- and *p*-dimethylaminoacetophenone.

Table III. Theoretical (CNDO/S) and experimental transition energies of **2** in eV and composition of the transitions (– designates less than 1%).

Trans.	Type	E_{calc}	Composition						E_{exp}
			$V_2^{1'}$	$V_2^{3'}$	$V_1^{1'}$	$V_1^{2'}$	$V_3^{1'}$	$V_3^{2'}$	
S_1	nπ*	3.180	43.9	45.1	–	–	–	–	
S_2	ππ*	4.062	–	–	62.9	11.4	4.7	14.2	3.533[b]
S_3	ππ*	4.227	–	–	13.6	49.9	25.8	2.8	4.878[b]
S_4	ππ*	5.489	–	–	–	30.4	59.2	1.0	5.393[b]
S_5	ππ*	5.693	–	–	16.0	–	1.3	68.3	
T_1	ππ*	2.719	–	–	71.8	12.9	5.5	2.6	2.712[c]
T_2	nπ*	2.963[a]	40.8	48.3	–	–	–	–	
T_3	ππ*	3.756	–	–	16.4	70.3	–	4.7	

[a] Modified energy (see text); [b] evaluated from the absorption spectrum in hexane; [c] determined from the average of the "half-height" energies of the phosphorescence and phosphorescence excitation spectrum in frozen solution.

Due to inherent assumptions in the CNDO method, the $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states are always degenerate. It is known from experimental observations that the average S–T split for substituted benzaldehydes is 1750 ± 30 cm^{-1} (0.217 eV) [12]. In order to correct for the S–T degeneracy in our calculations, we have made use of the above experimental data to modify the $^3(n,\pi^*)$ state energy (as done in [13]) by substracting 0.217 eV from the degenerate energy value calculated for $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states. This modified $^3(n,\pi^*)$ state energy is given in Table III.

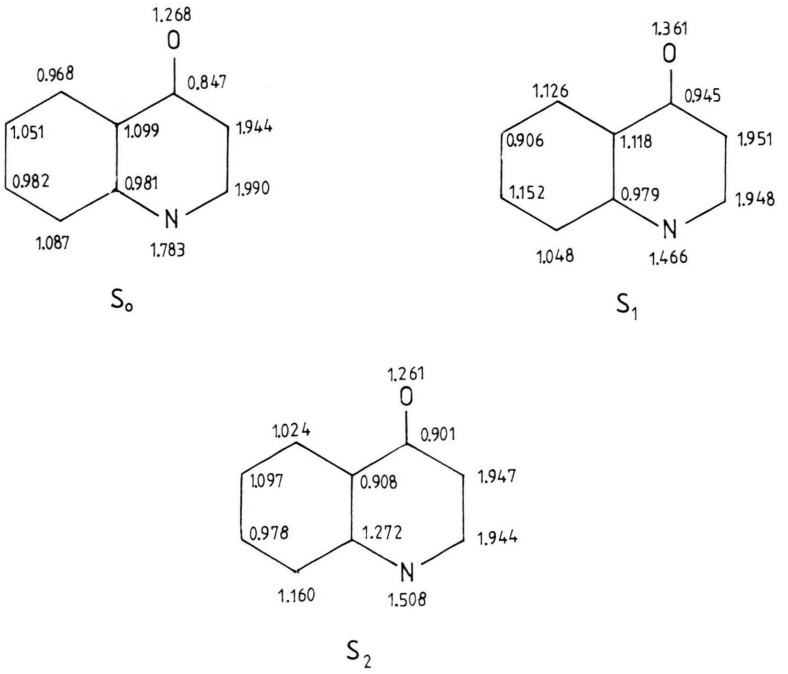

Fig. 4. Electron density distribution of the ground and excited singlet states of **1** calculated by the PPP method.

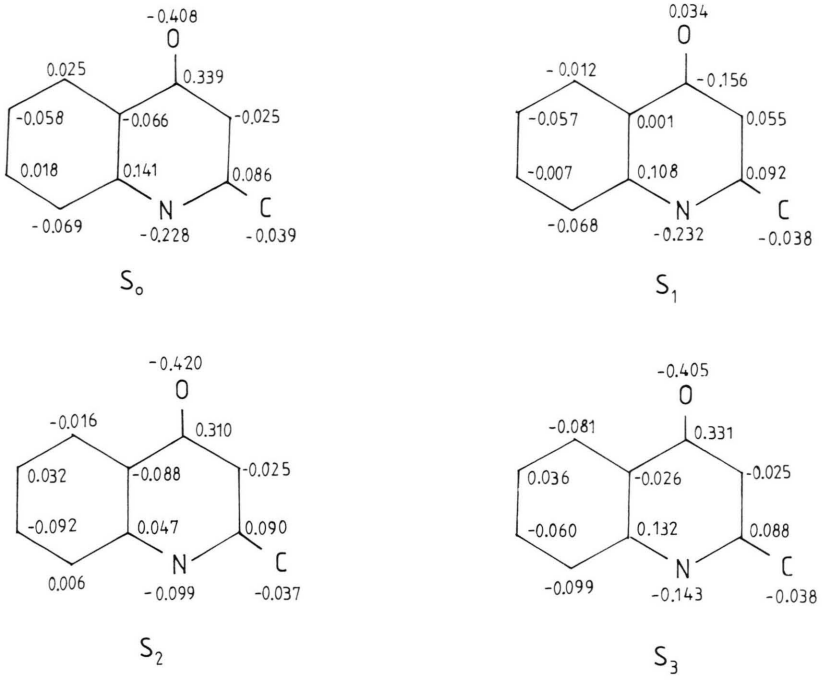

Fig. 5. Electron density distribution of the ground and excited singlet states of **1** calculated by the CNDO/S method.

Discussion

The observed effect of the substituents and of the solvent polarity on the electronic spectra as well as the results of the PPP and CNDO/S quantum-chemical calculations indicate that the lowest $^1(\pi,\pi^*)$ singlet state has an intramolecular charge transfer (ICT) character. The calculated electron density distributions (see Fig. 4 and 5) show that in this low-lying singlet state electron displacement from the nitrogen to the carbonyl group occurred. A similar nitrogen-carbonyl interaction has been found previously for substituted dihydroquinolinones [14].

The pronounced effect of R_1 substitution on the electronic spectra is a particularly convincing evidence for the proposed electron delocalization. The effect of R_1 may be explained by its influence on the electron density at the nitrogen atom and hereby on the charge transfer from the nitrogen atom to the carbonyl group. Thus, suppression of the nitrogen-carbonyl interaction for instance by acylation on the nitrogen (as in case of compound **6**) shifts the absorption spectrum to shorter wavelengths, while substitution at the nitrogen atom with an electron donating group (as in case of compound **5**) causes a red shift in the electronic spectra.

It has been found that an increase in the solvent polarity caused a shift of the electronic spectra to longer wavelengths. This solvent polarity effect together with the 10^7 s^{-1} magnitude obtained for k_F in acetonitrile (see Table II) suggest that the lowest singlet state in polar solvents is of $\pi\pi^*$ character. Although no unambiguous conclusion can be made regarding the non-polar solvents, however, the similar magnitude of the fluorescence rate coefficient found in methylcyclohexane and in acetonitrile for compound **2** strongly suggests that the lowest singlet state in non-polar solvents is also of $\pi\pi^*$ character.

Transition to the $^1(n,\pi^*)$ state has been brought into connection with the shoulder observed at 27,100 cm^{-1} in the absorption spectra of compounds **6** and **7** in cyclohexane. No such indication of the $n\pi^*$ transitions were found in case of compounds **1–5** where it may be covered by the intense $\pi\pi^*$ transition. Since the energies of the $n\pi^*$ states may not be expected to change too much [15], we can assume the same value of 27,100 cm^{-1}

also for the energy of the nπ* transition of compounds **1–5.**

The energy of the Franck-Condon ππ* transition, determined from the absorption spectrum of compounds **1** and **2** in cyclohexane, is 28,500 cm^{-1}. This is much higher than the energy of the nπ* transition. The large difference is in qualitative agreement with the results of the CNDO/S quantum-chemical calculations.

The energy of the nπ* O–O transition is expected to be close to the nπ* Franck-Condon transition since nπ* excitation affects mainly the geometry of the carbonyl group (localized transition). The energy of the lowest singlet ππ* O–O transition, estimated from the location of the intersection of the normalized absorption and fluorescence spectra, is 26,600 cm^{-1} for **1** in cyclohexane. This means that there is only a small difference (of about 500 cm^{-1}) between the zero vibrational levels of the lowest $^1(n,\pi^*)$ and $^1(\pi,\pi^*)$ states of **1** in non-polar solvent. On the basis of the experience obtained with various heterocycles and aromatic carbonyl compounds, the close proximity of states may result in very efficient non-radiative decay from the lower of the two close lying excited states [16, 17]. We consider efficient non-radiative decay to be the reason for the short lifetime of less than 1 ns and very weak fluorescence found in case of compound **1** in non-polar solvent.

In Fig. 6, the effect of R_1 substitution and the solvent effect on the location of the two lower singlet excited states is shown. The energy levels for compound **2** in the non-polar cyclohexane are given first. Due to the proximity effect, short singlet lifetime and weak fluorescence is observed [16, 17]. Substitution on the nitrogen atom by an electron donating methyl group stabilizes the $^1(\pi,\pi^*)$ state and increases the energy gap between $^1(n,\pi^*)$ and $^1(\pi,\pi^*)$ states. This increases the singlet lifetime and the fluorescence intensity (Q_F = 0.043). The last part of the Fig. shows the solvent effect. The considerable stabilization of $^1(\pi,\pi^*)$ state in polar acetonitrile results in a large gap between the two lower states. Thus, compound **2** in acetonitrile has a singlet lifetime of about 10 ns and is characterized by a fluorescence quantum yield of 0.37.

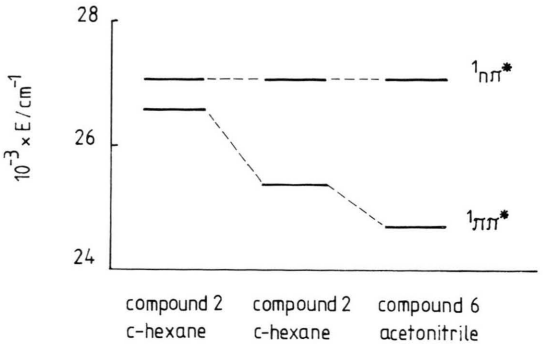

Fig. 6. Singlet energy levels of **2** in cyclohexane and acetonitrile and of **5** in cyclohexane.

Experimental

The investigated compounds have been synthesized as described in [18–22] and purified by recrystallization or by preparative thin-layer chromatography. The UV-VIS absorption spectra were taken on a spectrophotometer Specord M-40 (Carl Zeiss, Jena, G.D.R.). The fluorescence spectra were recorded on a Perkin-Elmer MPF-44 spectrofluorometer. The fluorescence quantum yields Q_F are determined relative to quinine bisulfate in 1 N H_2SO_4 media (Q_F = 0.546 [23]). Singlet fluorescence lifetimes are measured with the time-correlated single-photon counting technique using a commercial Applied Photophysics SP-3 instrument. The nanosecond flash lamp was filled with hydrogen and operated at a frequency of 40 kHz. A high intensity greating monochromator was used to select the excitation wavelength; a GG 455 cut-off filter is placed in front of the "stop" photomultiplier (Mullard XP 2020 Q). Fluorescence decay curves were analyzed by a non-linear least-square reconvolution technique [24]. All solvents used were of spectroscopic grade.

[1] R. Matsushima, T. Kishimoto, M. Suzuki, M. Morioka, and H. Mizuno, Bull. Chem. Soc. Japan **54,** 2938 (1980).
[2] R. Matsushima and K. Sakai, J. Chem. Soc., Perkin Trans. **2,** 1217 (1986).
[3] R. Matsushima, Y. Hiramatsu, and T. Kitanishi, J. Chem. Soc., Perkin Trans. **2,** 847 (1988).
[4] M. S. Atwal, L. Bauer, S. N. Dixit, J. E. Gearien, and R. W. Morris, J. Med. Chem. **8,** 566 (1965).
[5] J. W. Bolger, U.S. Pat. **3,** 287450 (1966).
[6] Ch. Rau, Electron Spectra in Chemistry (Russ.), Mir, Moscow 1964.
[7] J. Griffiths, Dyes and Pigments **3,** 211 (1982).
[8] J. Del Bene and H. H. Jaffe, J. Chem. Phys. **48,** 1807, 4050 (1968).
[9] M. S. Dewar and W. Thiel, J. Am. Chem. Soc. **99,** 4899 (1977).
[10] W. H. Orrtung, G. W. Scott, and D. Vosooghi, J. Mol. Struct. (Theochem.) **109,** 161 (1984).
[11] R. Nakagaki, S. Nagakura, T. Kobayashi, and S. Iwata, Bull. Chem. Soc. Japan **51,** 2867 (1978).
[12] E. Van der Donckt and C. Vogels. Spectrochim. Acta, Part A **28,** 969 (1972).
[13] D. V. S. Jain and V. K. Gombar, Indian J. Chem. **18A,** 375 (1979).
[14] T. Braunholtz and F. G. Mann, J. Chem. Soc. **1957,** 4166.
[15] J. Fabian and H. Hartmann, Light Absorption of Organic Colorants: Theoretical Treatment and Empirical Rules, Springer Verlag, Berlin 1980.
[16] W. A. Wassam, Jr. and E. C. Lim, J. Chem. Phys. **68,** 433 (1978).
[17] T. Lai, B. Lim, and E. C. Lim, J. Am. Chem. Soc. **104,** 7631 (1982).
[18] R. F. Collins, J. Chem. Soc. **1960,** 2053.
[19] D. Sokolov and B. Sidikov, Izv. Akad. Nauk Kaz. S.S.S.R., Ser. Khim. **20,** 44 (1970).
[20] S. Kessa, A. Lumb, and R. Mayor, Indian J. Chem. **5,** 18 (1970).
[21] J. Merchant and V. Shankaranarayer, Chem. Ind. **1979,** 320.
[22] S. Kano, T. Ebata, and S. Shiboya, J. Chem. Soc., Perkin Trans. 1 **1980,** 2105.
[23] W. H. Melhuish, J. Am. Chem. Soc. **65,** 229 (1961).
[24] D. V. O'Connor and D. Phillips, Time-Correlated Single Photon Counting, Academic Press, London 1984.