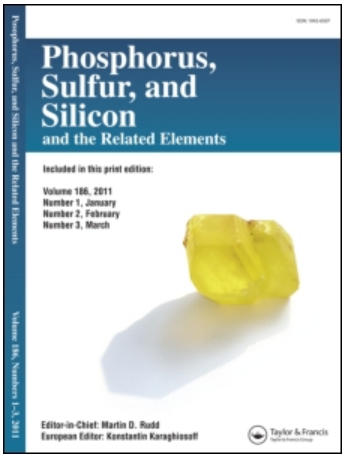


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ABSORPTION SPECTRA AND PPP-MO CALCULATIONS OF THIOPYRAN AND RELATED COMPOUNDS

H. Nakazumi[a]; T. Ueyama[a]; T. Kitaguchi[a]; T. Kitao[a]
[a] Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka, Japan

To cite this Article Nakazumi, H. , Ueyama, T. , Kitaguchi, T. and Kitao, T.(1983) 'ABSORPTION SPECTRA AND PPP-MO CALCULATIONS OF THIOPYRAN AND RELATED COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 16: 1, 59 — 66
To link to this Article: DOI: 10.1080/03086648308077752
URL: http://dx.doi.org/10.1080/03086648308077752

Phosphorus and Sulfur, 1983, Vol. 16, pp. 59–66
0308-664X/83/1601-0059/$18.50/0

ABSORPTION SPECTRA AND PPP-MO CALCULATIONS OF THIOPYRAN AND RELATED COMPOUNDS

H. NAKAZUMI, T. UEYAMA, T. KITAGUCHI and T. KITAO

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

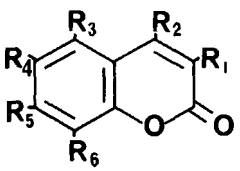
(*Received December 14, 1982; in final form February 23, 1983*)

The absorption bands of the coumarin, the thiocoumarin and thiochromone have been examined by the PPP calculation with variable β approximation, changing with increasing ring size. The calculated longest-wavelengths (λ_1) of these series were in good agreement with the experimental values measured in ethanol. A bathochromic displacement of λ_1 produced by annelation of a benzene ring to a 2H-pyran-2-one, a coumarin and its thio analogues might be mainly due to a reduction of LUMO energy levels and/or increase of HOMO energy levels. The substituent effect on absorption spectra in the coumarin, the thiocoumarin and thiochromone series has also been examined, and discussed in terms of PPP calculations.

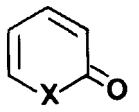
The relationship between color and constitution of organic compounds, largely important synthetic dyes, has been interpreted with the aid of PPP-type calculations in excellent textbooks about color chemistry.[2,3] Griffiths *et al.*[4,5] recently reported the absorption spectra of colored heterocyclic quinones and di- or triphenylmethane dyes and interpreted their spectra with the aid of PPP-MO calculations.

For the 2H-benzo[*b*]thiopyran-2-one (thiocoumarin) and the coumarin derivatives, which are colorless and used as fluorescent whiteners for polyester and polyamide fabrics, few theoretical treatments of absorption spectra by means of molecular orbital (MO) calculations have so far been reported. Minegishi *et al.*[6] interpreted the absorption spectra of two coumarin derivatives by means of MO calculations and polarized absorption spectra. Umemoto *et al.*[7] reported that the fluorescent character of benzocoumarin derivatives was affected by the position of annelation; however, no theoretical treatment for the absorption spectra was reported.

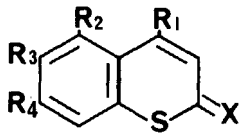
Recently, it was reported that PPP calculations with variable β approximation was the most convenient method to elucidate the annelation effect on the absorption spectra in anthraquinones.[8] In this paper, the change of absorption bands of the coumarin, the thiocoumarin and the 4H-benzo[*b*]thiopyran-4-one (thiochromone) series, an isomer of the thiocoumarin, with increasing ring size were reexamined by PPP calculations with variable β approximation.



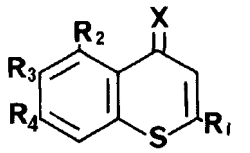
1a: $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$
1b: $R_2 = CH_3$, $R_1 = R_3 = R_4 = R_5 = R_6 = H$
1c: $R_2 = CH_3$, $R_5 = OCH_3$, $R_1 = R_3 = R_4 = R_6 = H$
1d: $R_2 = CH_3$, $R_5 = NH_2$, $R_1 = R_3 = R_4 = R_6 = H$
1e: $R_1 = R_2 = R_5 = R_6 = H$, $R_3 = R_4 = -(CH{=}CH)_2-$
1f: $R_1 = R_2 = R_3 = R_6 = H$, $R_4 = R_5 = -(CH{=}CH)_2-$
1g: $R_3 = R_4 = R_5 = R_6 = H$, $R_1 = R_2 = -(CH{=}CH)_2-$



2a: X = O
2b: X = S



3a: X = O, $R_1 = R_2 = R_3 = R_4 = H$
3b: X = O, $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$
3c: X = O, $R_1 = CH_3$, $R_2 = R_3 = H$, $R_4 = OCH_3$
3d: X = O, $R_1 = OH$, $R_2 = R_3 = R_4 = H$
3e: X = O, $R_1 = CH_3$, $R_4 = H$, $R_2 = R_3 = -(CH{=}CH)_2-$
3f: X = S, $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$



4a: X = O, $R_1 = R_2 = R_3 = R_4 = H$
4b: X = O, $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$
4c: X = O, $R_1 = CH_3$, $R_2 = R_3 = H$, $R_4 = OCH_3$
4d: X = O, $R_1 = CH_3$, $R_2 = R_4 = H$, $R_3 = OCH_3$
4e: X = O, $R_1 = CH_3$, $R_4 = H$, $R_2 = R_3 = -(CH{=}CH)_2-$
4f: X = O, $R_1 = C_6H_5$, $R_2 = R_3 = R_4 = H$
4g: X = O, $R_1 = C_6H_5$, $R_2 = R_4 = H$, $R_3 = OCH_3$
4h: X = S, $R_1 = CH_3$, $R_2 = R_3 = R_4 = H$

RESULTS AND DISCUSSION

The calculated and experimental absorption band data for various derivatives of the coumarin, thiocoumarin and thiochromone are summarized in Tables I, II and III.

It is well known that the two longest-wavelength absorptions of coumarin 1a can be assigned to the π-π^* transition.[6] The longest-wavelength absorption of thiocoumarin (3a) and thiochromone (4a) is also a π-π^* transition.[9] Some PPP studies refer specifically to absorption spectral data determined in non-polar solvents to minimize solvent effects. Since the absorption maxima of the thiocoumarin and the coumarin series in ethanol were generally the same as those in cyclohexane, a non-polar solvent (Tables I and II), the former was used to avoid the low solubility in non-polar solvents.

The most critical parameters in any PPP calculation are the valence-state ionization potential (VSIP) and one-center electron repulsion integral (γ_{nn}) for each atom. The β values are secondary parameters.[5] In the coumarin series, calculated values of all β_{rs}'s decreased with increasing ring size. For examples, the β_{CO} between the carbon and oxygen atoms of the carbonyl group varied in the order: 1f (−2.63 eV) < 1a (−2.70 eV) < 2a (−2.86 eV). In the thiocoumarin series, the β_{CO} varied in the same order: 3e < 3a < 2b.

The two calculated longest-wavelengths λ_1 and λ_2 of the coumarin series were in good agreement with the experimental data (correlation coefficient between calculations and experimental data: λ_1; 0.9601, λ_2; 0.9639). In the thiocoumarin and thiochromone series, the agreement between experimental and calculated data was good for λ_1 (coefficient for thiocoumarin; 0.9586; for thiochromone; 0.9898). But

TABLE I

Calculated and experimental spectral data for the coumarin series

Compd	λ_{max} (calc)/nm	f[a] (calc)	λ_{max} (EtOH)	(exp)/nm (C_6H_{12})[b]	ε_{max} ($\times 10^4$) cm^{-1} mol^{-1}
1a	276	0.318	238[c]	—	1.25
	312	0.235	314		0.75
1b	276	0.316	274	279	0.82
	310	0.220	313	314	0.52
1c	289	0.270	310	310	0.94
	321	0.383	322	319	1.01
1d	301	0.249	355[c]	—	1.80
	332	0.477			
1e	320	0.249	349	356	0.75
	347	0.315	364	364	0.78
1f	323	0.404	323	—	2.08
	354	0.063	360[b]		0.16
1g	295	0.015	316	312	0.66
	320	0.160	326	328	0.40
2a	227	0.246	216[d]	—	0.23
	281	0.305	289		0.49

[a] Oscillator strength.
[b] Cyclohexane.
[c] See ref. 7.
[d] See ref. 12.

TABLE II

Calculated and experimental spectral data for the thiocoumarin series

Compd	λ_{max} (calc)/nm	f[a] (calc)	λ_{max} (EtOH)	(exp)/nm (C_6H_{12})[b]	ε_{max} ($\times 10^4$) cm^{-1} mol^{-1}
3a	295	0.339	—	338[c]	0.25[c]
	337	0.149			
3b	295	0.339	298	297	0.70
	333	0.149	342	337	0.29
3c	312	0.286	330	333	0.62
	336	0.287	343	342	0.61
3d	304	0.324	232	302[d]	0.84
	328	0.131	320	332	0.33
3e	333	0.239	333	331	1.21
	362	0.312	380[b]	380	0.23
3f	348	0.181	302	302	1.73
	437	0.677	420	419	1.12
2b	256	0.142	—	328[e]	0.29
	323	0.220		334	0.29
				349s	0.21

[a] Oscillator strength.
[b] Cyclohexane.
[c] See ref. 9, solvent *n*-hexane.
[d] Dioxane.
[e] See ref. 11.

TABLE III

Calculated and experimental spectral data for the thiochromone series

Compd	λ_{max} (calc) / nm	f [a] (calc)	λ_{max} (exp) [b] / nm	ε_{max} ($\times 10^4$) / cm^{-1} mol^{-1}
4a	279	0.063	287[c]	0.28
	319	0.231	336	1.07
4b	268	0.037	247	2.42
	315	0.221	335	1.14
4c	290	0.242	268	2.63
	317	0.153	328	1.12
4d	291	0.063	260	2.41
	337	0.225	357	0.88
4e	329	0.205	340	0.83
	345	0.133	356	0.52
4f	299	0.423	272	2.27
	333	0.325	345	1.10
4g	310	0.265	282	2.59
	351	0.229	362	0.85
4h	351	0.066	293	0.75
	417	0.760	412	2.10

[a] Oscillator strength.
[b] Ethanol.
[c] See ref. 13.

the calculated second-longest wavelength absorption of these series was not in good agreement with experimental data. The improvement of the limited configuration interaction treatment including 3*d*-orbital or more configurations might serve to elucidate this problem.

It was observed that an annelation of a benzene ring to a 2H-pyran-2-one (2a → 1a) produced a bathochromic displacement of the longest wavelength λ_1 (*ca.* 25 nm), and further, an annelation of a benzene ring to a coumarin also produced a bathochromic shift of λ_1, dependent on the position of annelation (*ca.* 10 to 50 nm). These annelation effects are predicted well by the calculation. A good linear correlation existed between the calculated first-excited energies (ΔE_1) and the singly-excited configurational energies ($E_{HO\text{-}LU}$). The dependence of ΔE_1, LUMO energy level (ε_{LU}) and HOMO energy level (ε_{HO}) of the coumarin series is illustrated in Figure 1. The bathochromic shift by the annelation to 2a was roughly due to a reduction of LUMO energy level. The 3,4-annelation to the coumarin increased both HOMO and LUMO energy levels, and consequently brought about only a small spectral shift. The 5,6-annelation to the coumarin reduced the LUMO energy level and increased the HOMO energy level, and a pronounced bathochromic shift (*ca.* 50 nm) of λ_1 was consequently observed. In the linear-annelated compound 1f, the weak broad absorption band was observed at the longer wavelength. From the calculation including a configuration interaction, this absorption is approximately the π-π^* transition from the second occupied MO, whose excited wave function was as follows; $\Psi_1 = -0.3660\Phi_{8,9} + 0.7238\Phi_{7,9} + \cdots$. This effect may be due to a smaller difference (0.377 eV) between the HOMO and the second occupied MO of 1f than that of other benzocoumarins (*ca.* 0.6–1.0 eV). In the thiocoumarin series, the

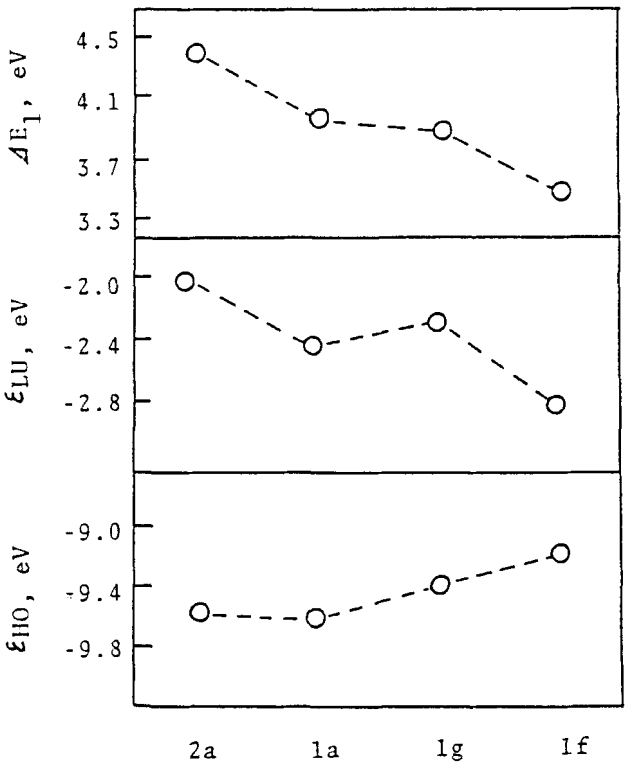


FIGURE 1 Relationship between ΔE_1, ε_{LU} and ε_{HO} for the coumarin series.

same annelation effect on absorption spectra was observed: an annelation of a benzene ring to 2b and 3a produced a bathochromic displacement of λ_1. These shifts in the thiocoumarin series as well as the coumarin series appear to be due to a reduction of LUMO energy level and/or increase of HOMO energy level, as shown in Table IV.

The observed λ_1 of the coumarin and the thiocoumarin was not shifted when one methyl group was inserted in the 4 position. When the inductive (I) effect of the

TABLE IV

Orbital Energies of the MO in the coumarin, the thiocoumarin and the thiochromone series

Coumarin series			Thiocoumarin series			Thiochromone series		
Compd	HOMO/eV	LUMO/eV	Compd	HOMO/eV	LUMO/eV	Compd	HOMO/eV	LUMO/eV
2a	−9.589	−1.995	2b	−9.439	−2.348	4a	−9.325	−2.354
1a	−9.629	−2.434	3a	−9.421	−2.536	4c	−9.172	−2.141
1c	−9.184	−2.215	3c	−9.072	−2.330	4d	−8.959	−2.235
1d	−8.850	−2.130	3d	−9.178	−2.266	4e	−9.050	−2.602
1e	−9.138	−2.704	3e	−9.027	−2.779	4f	−9.199	−2.646
1f	−9.242	−2.823	3f	−8.548	−3.453	4g	−8.902	−2.554
1g	−9.436	−2.256				4h	−8.467	−3.435

methyl group was considered in the PPP calculations of 1b and 3b, the calculated λ_1 was 310 and 333 nm, respectively. The difference between parent compounds and 4-methyl derivatives was very small, 2 and 4 nm, respectively. Thus, the methyl group was ignored for calculation of 4-methylcoumarin and thiocoumarin derivatives (1c, 1d, 3c, 3e and 3f). A donor substitution in the 7 position of the coumarin series strongly raised the energy of the HOMO (0.46–0.75 eV) rather than that of the LUMO (0.2–0.3 eV). In the thiocoumarin series, this substitution effect was also shown in the HOMO and LUMO, but an increase of the energy of the HOMO was smaller. In 3c, the π-π^* transition was characterized by release of π-electrons from the lone pair of the sulfur atom upon the lowest-energy excitation. This change of π-electrons was not shown in the coumarin. Thus, only in the coumarin is a bathochromic shift produced by the donor substitution in the 7 position. From comparison of λ_1 of the thiocoumarin and the coumarin, it was found that a bathochromic shift produced by the exchange of an oxygen atom of the hetero ring to a sulfur atom was *ca.* 20–30 nm. This shift was in good agreement with the calculations (*ca.* 15–25 nm) and may be mainly due to an increase of HOMO and a reduction of LUMO in the thiocoumarin series.

Thiocoumarins and thiochromones are well known as structural isomers. We previously proposed distinguishing them by means of their mass, NMR and IR spectra and methylation of these compounds.[10] From the results shown in Tables II and III, it was found that the absorption maxima (λ_1) of the thiocoumarin appeared at longer wavelengths (*ca.* 10–20 nm) than those of the corresponding thiochromones. This provides a method of distinguishing them by the UV spectra. This bathochromic shift was roughly due to a reduction of the LUMO energy level in the thiocoumarin. Since the effect of the methyl group on λ_1 was very small from comparison of 4a with 4b, the methyl group was also ignored for calculations of thiochromone derivatives. A methoxyl substitution in the 6 position, but not in the 7 position, of 4a strongly raised the energy of the HOMO (0.4–0.7 eV) and the additional phenyl substitution in the 2 position of 4a reduced the energy of LUMO (0.2 eV). Consequently, a bathochromic shift was produced in 4g by these substitutions (*ca.* 26 nm). Replacement of the carbonyl group of thiocoumarin 3b and thiochromone 4b by the thiocarbonyl group was accompanied by a pronounced bathochromic shift. This shift amounted to 78 and 77 nm on going from 3b to 3f and from 4b to 4h, respectively. Thiocarboxylation to 3b and 4b strongly raised the energy of the HOMO and reduced the energy of the LUMO (*ca.* 1.0 eV). Consequently, the energy gap between the frontier orbitals is smaller for structures of thiocarbonyl types 3f and 4h. These compounds exhibited lower excitation energies than 3b and 4b, respectively.

It was shown that the small π-π^* transition shift of the absorption maxima, even in the UV region, was reproduced well by the PPP calculations.

EXPERIMENTAL

Method of MO calculation. The Parier–Parr–Pople method was used with the variable β approximation, changing with increasing ring size. The resonance integrals (β_{rs}) and the bond lengths (R_{rs}) were adjusted at every iteration of the SCF calculations in accordance with the following equations proposed by Nishimoto and Foster.[14]

Pyran thiopyran	Coumarin thiocoumarin thiochromone	Benzocoumarin benzothiocoumarin benzothiochromone
β_{CC} = −2.04–0.51P	−1.90–0.51P	−1.84–0.51P
β_{CO} = −2.44–0.56P	−2.27–0.56P	−2.20–0.56P
β_{CN} = —	−2.09–0.53P	—

$R_{CC} = 1.517–0.18P_{CC}$
$R_{CN} = 1.451–0.18P_{CN}$
$R_{CO} = 1.410–0.18P_{CO}$

where P_{rs} is the π-bond order between the r and s atoms. The β_{CS} between carbon and sulfur atoms was fixed as −1.00 eV.[15] The two-center repulsion integrals (γ_{rs}) were calculated by means of the Nishimoto–Mataga equation, using the R_{rs} values. In the PPP calculations of all compounds containing sulfur atoms, one *p*-orbital for the sulfur atom was assumed. Electronic excitation energies were refined by a limited configuration interaction (CI) treatment involving the twenty-five singly-excited configurations obtained by promoting an electron from the five highest occupied orbitals to the five lowest unoccupied orbitals. For these calculations, planar structures were assumed and the molecular geometry of the compounds studied was taken as follows: bond lengths; C—C 1.40 Å, C=O 1.15 Å, C—O 1.37 Å, C—S 1.72 Å, C=S 1.66 Å, C—N 1.40 Å. All the valence angles were assumed to be 120°, except for the valence angle between carbon and hetero atoms in the heterocyclic ring. The valence-state ionization potentials (VSIP) and the one-center repulsion integrals (γ_{rr}) used are given in Table V. Calculations were performed on the ACOS-77-NEAC System 700 Computer in University of Osaka Prefecture by the program[8] used previously.

Materials and UV spectra. All compounds used, except 2a, 2b, 3a, and 4a, were previously prepared in our laboratory.[7,10,18] All these compounds were recrystallized from ethanol and their mp's were in agreement with reported values, within ±1°C. 2-Phenylthiochromone 4f and 6-MeO-2-phenylthiochromone 4g were prepared by Bossert's method.[19] 4f: mp 125–127°C (lit 124–127°C), 4g: mp 155–157°C (lit 157°C). Absorption spectra were reexamined in ethanol and cyclohexane (or dioxane) at the concentration of 1.0×10^{-4} mol/l using a Hitachi EPS-3T recording spectrophotometer.

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TABLE V

Parameters used in the PPP-MO calculations

Atom	VSIP[a]/eV	γ_{rr}[b]/eV
C[c]	11.16	11.13
N	26.7	17.44
O (OH)	32.9	21.53
O (OCH_3, —O—)	33.0[d]	21.53
O (=O)	17.7[d]	15.23
S	22.2[d]	13.05
S (=S)	12.7[e]	9.94

[a] Valence-state ionisation potential.
[b] One-center electron repulsion integrals.
[c] VSIP[16] and γ_{CC} of the carbon atom affected by the I-effect of the methyl group were 10.53 and 10.30 eV, respectively.
[d] See ref. 15.
[e] See ref. 17.

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