MOLECULAR ORBITAL CALCULATIONS ON PYRYLIUM SALTS—II

ELEMENTARY SCF THEORY AND SOLVENT EFFECTS

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Abstract—In an attempt to resolve an anomaly in the long-wavelength absorption spectra of methoxy and the corresponding hydroxy—substituted pyrylium salts, the visible spectra of 28 compounds have been measured in 10 solvents with widely varying physical properties. The measurements show that the discrepancy is most probably caused by solvent solute interaction. State functions for the molecules, to be used subsequently to calculate the solvent induced frequency shifts were obtained by the ω , $\omega\beta$ and the Pariser-Parr-Pople LCAO MO self consistent techniques. Using the correlation between calculated and observed transition energies as the criterion for the goodness of the state functions it is concluded that the $\omega\beta$ method leads to state functions showing better correlation with fewer parameters than the Pariser-Parr-Pople method.

INTRODUCTION

HÜCKEL theory has been applied to a series of 65 pyrylium salts by Bond and Singer,¹ who showed that a good correlation between calculated and observed transition energies for the longest wavelength transition could be obtained by a suitable choice of heteroatom parameters. An anomoly was found, in that experimentally, hydroxy substituted pyrylium salts absorbed at longer wavelength than their methyl ethers, whereas theory predicted the opposite. It is well known² that absorption frequencies in solution may be affected significantly by the solvent as a result of both general dielectric and specific short range interactions. The anomaly in the absorption spectra of the hydroxy and methoxy compounds could be due either to the inadequacy of the Hückel model or to solvent-solute interactions not allowed for in calculation.

To test these possibilities spectra have been measured in a wide variety of solvents to determine the effect of solvent on the position of the longest wavelength absorption band. Calculations have also been carried out using the ω technique,³ the $\omega\beta$ technique⁴ and the Pariser-Parr-Pople method⁵ to obtain state functions which could be used to calculate solvent solute interaction energies.

Three series of pyrylium perchlorates were studied. Series I is based on 2,6-diisopropyl-4-styrylpyrylium, II on flavylium and III on 2,4-diphenyl-6-styrylpyrylium. Details of preparations are given in the experimental part.

Thirteen compounds of Series I were prepared, seven of Series II and eight of Series III.

RESULTS OF SPECTRAL MEASUREMENTS

The experimental results for the longest wavelength absorption band of the 13 salts of Series I, the 7 salts of Series II and the 8 salts of Series III in 10 solvents are sum-

marized in Table 1. Some of the solution spectra could not be obtained because of the extremely low solubility of the salts.



FIG 1. Types of compound studied. R^1 , $R^2 = OH$, OMe or H

The solvents used in the investigation can be divided into three groups. Group I contains the strongly H-bonding and protonating compounds, perchloric, tri-fluoroacetic and formic acid;⁶ Group II contains benzene and dichloromethane, solvents which can be considered not to interact specifically with pyrylium cations and Group III contains acetic acid, dioxan, ethyl acetate, methyl cyanide and chloro-form, all compounds which can be regarded as intermediate between Group I and II in their ability to interact specifically with pyrylium ions.

The results in Table 1 show that the solvents in Groups I and II show absorption bands for the methoxy derivative at longer wavelengths than for the corresponding hydroxy compounds. Only the solvents in the third group give rise to the opposite, anomalous, behaviour.

A number of authors^{7–9} have discussed the effect of solvents on UV spectra. In terms of this work the observed solution spectra can be explained by assuming that the methoxy cations would indeed absorb at longer wavelength than the hydroxy compound *in vacuo*. The general dielectric effects on the spectra of the solutes would be expected to be similar for the two types of ion. Thus in the absence of specific ion-solvent interactions the vacuum order would also be observed in solution. This is the case for the solvents in Group II. The very strongly interacting solvents of the first group would swamp differences between the two types of ion so that in this case also, the theoretical order would be preserved. In the case of the Group III solvents, differences in the specific interaction between the methoxy and hydroxy substituted ions and the solvent are maximised and it is postulated that it is these differences which lead to the inversion in the expected order of the spectra.

The combination of data for absorption and emission spectra¹⁰ can show the presence of specific interactions. Investigations of emission and absorption spectra of a few of the salts in a wider variety of solvents has confirmed these preliminary conclusions. Discussion of the detailed results and the calculation of the non-specific solvent shifts is left to a subsequent paper.

The calculation of solvent induced frequency shifts requires that a state function

¹ FOR PYRYLJUM SALTS IN DIFFERENT SOLVENTS	
IN CM	ima in cm
ON MAXIN	tion max
ABSORPTI	of absorp
WAVE	tency (
HE LONGEST	Frequ
Y OF TI	
PREQUENCY	
OBSERVED	
TABLE 1.	

t.					8	olvent		·		
Compound	CF3COOH	нсоон	HCIO,	CH1CI1	C ₆ H ₆	CHCI3	сн ₅ соон	dioxan	CH ₃ CN	сн,соос,н,
					Series I					
Unsubstituted	24400	25100	25300	23900	24500	23900	25000	25100	25500	25100
4'-OH	22400	22100	23600	21300	ł	20500	21600	21300	22300	21100
4'-OMe	21600	22000	23500	21200	20800	20800	21900	21600	22400	22100
3'-OH	24500	24800	25500	23500	****	24200	24500	24600	24900	24600
3'-OMe	24800	24800	25400	23400	24300	23000	24600	24600	25100	24500
2'-OH	22700	22800	24400	21800	22100	21000	22300	22800	22800	22800
2'-OMe	22300	22600	24200	21400	21600	21600	22600	22800	23100	23100
3',4'-OH	22100	21800	22900	20200	****	19400	20700	20200	20600	20600
3',4'-OMe	21200	21400	22500	19800	19700	19700	21100	20500	20700	20700
3'-OMe-4'-OH	21300	21300	23000	20200	19800	19900	20700	20000	20500	21200
3'-OH-4'-OMe	21400	21500	22600	20400	20300	20400	21200	20900	21200	20500
2',4'-OH	21100	20700	22600	20000		18900	20000	20300	19900	00661
2',4'-OMe	20500	20600	ł	19600	20000	19900	20600	20600	20700	20700
ĸ					Series II					
Unsubstituted	24900	25100	25100	24600	24600	24600	25400	25200	25400	25400
4'-OH	22700	22600	23400	21800		21500	22400	22500	22700	22600
4'-OMe	22200	22600	23100	21600	22100	21700	22500	22700	22600	22900
3'-OH	25300	25600	24900	25000	all sources	24600	25700	25600	25800	25800
3'-OMe	25500	25800	25100	25300	25100	25400	25800	25700	25900	26100
2'-OH	22600	22800	23400	21800	ł	20900	22600	22800	22900	22700
2'-OMe	22200	22600	22600	21900	*****	22100	22700	22800	22800	23000
					Series III					
4'-OH	20000	19700	21000	18700		19000	19600	19000	19700	19000
4'-OMe	19800	00961	20600	19500	19000	18600	19300	19300	19900	19300
3'-OH	21600	21400	21700	20600		20300	21300	20900	21600	20900
2'-OMe	19900	20300	١	19500	19300	19000	20400	20700	20500	20700
3',4'-OH	19200	19200	20500	18300		17200	19100	18100	19200	18100
3'-OMe-4'-OH	19500	19200	20300	18300	ł	17800	18700	18000	19100	18000
3'-OH-4'-OMe	19400	19300	20000	18500		18500	19200	18900	19300	18900
2',3'-OMe	18600	18500	18000	17700	-	17800	18400	18200	18900	18200

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for the solute be available. Such state functions for aromatic molecules can be obtained very simply using such modifications of the Hückel method as the ω and $\omega\beta$ technique or by the use of the more sophisticated SCF techniques as exemplified by the Pariser-Parr-Pople scheme.

In view of the fact that a number of solvents gave the expected order of spectra it was felt that a suitable test for the different calculation methods was to use the correlation between calculated and observed absorption spectra. The state function which gave the best correlation could then be used for further work.

For the Hückel type calculations, using the same nomenclature as in Ref 1, the Coulomb and resonance integrals for a heteroatom are given by

$$\alpha_{\rm X} = \alpha_{\rm C} + h_{\rm X} \beta_{\rm CC} \tag{1}$$

$$\beta_{\rm CX} = k_{\rm CX} \beta_{\rm CC} \tag{2}$$

and the calculated frequency of the longest wavelength transition is

$$v_{\max} = \frac{\Delta m \beta_{\rm CC}}{hc} \tag{3}$$

The relation between bond order, p_{rs} , and resonance integral, β_{rs} , used was $\beta_{rs} = \beta_{CC} \exp(0.4829 \ p_{rs} - 0.3219)$. Two sets of simple Hückel calculations, three sets of ω calculations and three sets of $\omega\beta$ calculations were performed using different parameter values for the Coulomb integrals for O⁺ and the OH and OMe group for each set. In all the calculations alkyl groups were treated on the basis of the inductive model with h_{alkyl} equal to -0.3^1 and k_{CO+} and k_{CO} equal to 1.0 and 0.8 respectively. The remaining parameter values are summarized in Table 2.

TABLE 2. PARAMETER VALUES FOR THE CALCULATIONS

Calculation	Parame	Parameter values in units of β_{CC}						
type	h _{o+}	ћ _{он}	home					
Hückel 1	2.5	1.2	0-9					
Hückel 2	2.5	1.8	0-9					
ω1	3-2	2.0	1.8					
ω2	3.4	2-0	1.8					
ω 3	3-0	2.0	1.8					
ωβ1	3-0	2.0	1.8					
ωβ2	3-0	1.9	1.6					
ωβ3	2.5	1.9	1.6					

The value of ω was taken as 1.4, that recommended by Streitwieser, although recently¹¹ this has been criticized on theoretical grounds as being too high. However, the justification for values of empirical parameters in empirical theories is that good results can be obtained using them. Using $\omega = 1.4$ gives a worthwhile improvement in our correlation.

The correlation between the calculated Δm values for each set of parameters and the observed frequencies was measured by calculating the standard deviation, σ , of

Table 3. Standard deviations in cm⁻¹ of regression curves of Δm on wave number for different parameter sets and methods of calculation for 28 compounds

						Solvent				
Calculation										
2	CF ₅ CO ₂ H	нсо _з н	HCIO,	CH ₃ Cl ₃	C ₆ H ₆	сн ₃ со ₂ н	СНСІЗ	dioxan	CH ₃ CN	CH3CO2C2H3
Hückel 1	1163	1269	1030	1307	1493	1383	1506	1431	1390	1510
Hückel 2	1274	1420	1185	1458	1601	1568	1709	1661	1595	1731
œl	992	1037	853	1122	1264	1168	1298	1217	1253	1215
m 2	992	1038	849	1122	1267	1169	1297	1218	1253	1217
0 3	985	1030	859	1122	1250	1160	1289	1208	1246	1206
op1	865	806	290	1036	1131	1054	1207	1083	1090	1109
თ β2	848	893	582	1021	1044	1055	1197	1082	1072	1119
arb3	842	888	615	1014	1113	1047	1214	1073	1065	1115

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the plot of Δm against observed frequency for each solvent. The parameter set which gave the lowest overall σ value was taken as the best set. The results of these calculations are given in Table 3.

It is clear that Hückel 1 gives the best fit for the simple calculation whilst $\omega 3$ and $\omega\beta 3$ gave marginally the best set of parameters for the self consistent calculations. It is clear that for all the solvents, considering the overall correlation, both the ω and $\omega\beta$ techniques gave appreciably better results than the simple Hückel method with the $\omega\beta$ technique the better of the two. The improvements for the solutions in the strong acids are particularly outstanding amounting to nearly 50% for the case of the perchloric acid solutions. It is worth noting that in the case of the $\omega\beta$ technique used on a molecule containing a number of hetero-atoms this improvement is achieved with a reduced number of empirical parameters compared to the Hückel and ω techniques. This is because the value of the k_{CX} parameter need not be estimated as the self-consistent nature of the calculation always leads to the same final value of this parameter whatever its starting value.

The values of Δm for each of the 28 compounds calculated with the best parameter set of each kind are summarized in Table 4. Closer examination of these results shows that the greatest part of the discrepancy between observed and calculated values is due to Series II, the flavylium compounds. This can be seen from Table 5 where the standard deviations of the correlations for each series separately are given for the best parameter sets and selected solvents.

When the series are considered separately, correlation for the flavylium series is very poor since both 3'-substituted compounds absorb at much shorter wavelength than predicted. The absorption peak for these compounds is very broad, and there may be more than one transition giving rise to the peak. If this were so, the frequency of the absorption maxima could not be correlated in the same way as that for other compounds. The standard deviation for the other two series are low. A very real improvement over simple calculations is obtained. For example, a standard deviation of 228 cm⁻¹ for the ω 3 set for Series III in formic acid is obtained and many others are nearly as good.

Unfortunately, the ω type calculations appear to give points which lie on two distinct, nearly parallel lines, one for Series III, the other for Series I and II together. Thus, although the correlation within the series is improved, the overall pattern is worse. For the simple calculations, the points do at least straddle the best line, even though they are widely scattered. The $\omega\beta$ calculations reproduce this sort of pattern much better, with much less scatter. We must conclude that inclusion of β variation together with ω type variation give more realistic results for these compounds than using ω variation alone even though the latter may be better for a series of very similar compounds.

The very real improvement in correlation that can be obtained by using a simple self-consistent method of calculation is shown in Figs 2, 3 and 4 where the data for perchloric acid solution are plotted. The decrease in scatter for compounds of different structural types when the $\omega\beta$ technique is used is particularly pleasing in view of the fact that this is produced with a reduction in the number of empirical parameters required compared to the Hückel method.

The Pariser-Parr-Pople⁵ calculations require values for the one centre repulsion integrals γ_{rr} , which are usually expressed as the difference between the valence state

		Δm (β units)	
Compound	Hückel 1	ω3	ωβ3
		Series I	
Unsubstituted	0-9695	0.8463	0-8760
4'-OH	0-8781	0-7996	0-7915
4'-OMe	0-8238	0.7917	0.7668
3'-OH	0-9346	0.8323	0-8477
3'-OMe	0-8620	0-8294	0-8327
2'-OH	0-8900	0.8148	0-8158
2'-OMe	0-8293	0-8080	0-7922
3',4'-OH	0-8050	O-7767	0-7524
3'.4'-OMc	0-7046	0-7630	07111
3'-OMc-4'-OH	0-7530	0-7722	0-7371
3'-OH-4'-OMe	07482	0-7677	0.7262
2′.4′-OH	0-8530	0.7774	0.7540
2',4'-OMe	0-8011	0·7669	0.7240
,		Series II	
Content Content Content V.4'-OMe 0-8011 0-7669 0 Series II 0 0 0 Jnsubstituted 1-0317 0-8923 0 V-OH 0-8935 0-8401 0 V-OHe 0-8103 0-8284 0 V-OH 0-8803 0-8585 0			0-8618
OH 0.8935 0.8401 0.79 -OMe 0.8103 0.8284 0.70 -OH 0.8803 0.8585 0.83 -OMe 0.7653 0.8440 0.71 -OH 0.8967 0.8570 0.83 -OMe 0.8052 0.8450 0.71		0.7900	
4'-OMe	0-8103	0-8284	0-7665
3'-ОН	0-8803	0.8585	0-8183
3'-OMe	0-7653	0.8440	0-7840
2'-OH	0-8967	0.8570	0-8127
2'-OMe	0-8052	0-8450	0-7864
		Series III	
4'-OH	0.7051	0-6432	0-6511
4'-OMe	0.6675	0-6386	0-6349
3'-OH	0.7500	0.6635	0-6894
2'-OMe	0-6749	0-6475	0-6520
3'.4'-OH	0.6584	0.6307	0.6277
3'-OMc-4'-OH	0-6190	0-6285	0-6188
3'-OH-4'-OMe	0-6101	0.6250	0-6085
2',4'-OMe	0-6412	0-6200	0-6005

TABLE 4. CALCULATED Δm values in units of β_{CC} for different parameters and different methods of calculation

ionization potential, I_r , and the valence state electron affinity, E_r , as well as the two centre repulsion integrals, γ_{rs} , the bond integrals β_{rs} and the effective nuclear charge Z_r for the atoms in the molecule.

For the molecules studied in the present work I_r , E_r and Z_r values were required for the atoms C and O⁺ and for the groups -OH, $-OCH_3$ and the diisopropyl group. Bond integral values for C-C, C-O⁺, C-OH and C-OCH₃ bonds were also needed. It was decided to use the same bond integral value for the C-OH and C-OCH₃ bond and this will be written β_{CO} .

The values, $I_C = 11.16$, $E_C = 0.03$, $I_{O+} = 34.15$ and $E_{O+} = 15.30$ eV are well established and are obtained from promotion energies given by Hinze and Jaffe.¹² On the other hand, values of E_{OH} ranging between 35.73 and 23.5 eV and of γ_{OH} between 21.53 and 16.86 eV have been used by different authors.^{13, 14} The values of these parameters to be used in the present work must, therefore, be in doubt.

	So	blvent	
HCO₂H	HClO₄	CH ₂ Cl ₂	CH₃CO₂H
1092	712	879	1228
532	263	347	618
611	361	424	753
	Series II		
	So	blvent	
HCO₂H	HClO4	CH ₂ Cl ₂	CH₃CO₂H
1669	1091	1864	1785
1462	933	1619	1524
1490	943	1657	1565
	Series III		
	So	blvent	
HCO₂H	HClO₄	CH ₂ Cl ₂	CH ₃ CO ₂ H
550	970	644	581
228	709	361	296
284	693	442	351
	HCO ₂ H 1092 532 611 HCO ₂ H 1669 1462 1490 HCO ₂ H 550 228 284	Sc HCO ₂ H HClO ₄ 1092 712 532 263 611 361 Series II Series II 1669 1091 1462 933 1490 943 Series III Series III 550 970 228 709 284 693	$\begin{tabular}{ c c c c c } \hline Solvent \\ \hline HCO_2H & HClO_4 & CH_2Cl_2 \\ \hline 1092 & 712 & 879 \\ 532 & 263 & 347 \\ 611 & 361 & 424 \\ \hline \\ \hline Series II & \\ \hline \\ \hline Series II & \\ \hline \\ \hline HCO_2H & HClO_4 & CH_2Cl_2 \\ \hline 1669 & 1091 & 1864 \\ 1462 & 933 & 1619 \\ 1490 & 943 & 1657 \\ \hline \\ $

TABLE 5. STANDARD DEVIATIONS FOR EACH SERIES SEPARATELY

In order to reduce the number of arbitrary parameters, it was decided to take alkyl substituents, both on carbon and oxygen atoms, into account by using an inductive model. As in the work in the $\omega\beta$ method, no distinction was made between methyl and diisopropyl groups. Flurry,¹⁵ in calculations on methyl substituted benzenes has suggested that the effect of an alkyl group is to reduce the valence state ionization potential of the carbon atom to which it is attached by 1.8 eV and the effective nuclear charge by 0.11. Those parameters were used in the present work to take into account alkyl substituents, both on C and O atoms. The C—C and C—O bond integrals were not changed to take alkyl substituents into account.

The two centre repulsion integrals were calculated using the charged sphere approximation. Some later calculations using the Mataga¹⁶ and Ohno¹⁷ approximations shows that these affected calculated transition energies only very little.

The bond integral, β_{CC} , was taken as -2.29 eV. However uncertainty existed as to the best value for $\beta_{CO+}^{13, 14}$ and β_{O} .

Thus, in order to carry out calculations on our molecules, it was necessary first to establish the correct values for E_{OH} , γ_{OH} , β_{CO+} and β_{CO-} . This was done by carrying out a number of calculations on model compounds and adjusting these parameters till a fit with experimentally observed absorption spectra was obtained. These optimised parameters were then used for subsequent calculations. Table 6 gives the



parameter values that were used in the calculation and Table 7 the comparison of observed and calculated transition energies for pyrylium, flavylium, 3'-hydroxy flavylium and 4'-hydroxyflavylium perchlorates obtained with these parameter sets. It is clear from these results that sets 1 and 3 using relatively low values for I_{OH} and E_{OH} give poor results. It is difficult to decide between the remaining sets, however, set 5 gave the correct transition energy for pyrylium itself and appeared to give marginally better results for the other molecules. This set was, therefore, adopted for the calculations on the full set of 28 molecules. Table 8 lists the final parameter values used. The results are plotted in Fig 5 and summarized in Table 9.

The results are clearly disappointing. Correlation within separate series appears to be better than the overall correlation but the results are not even an improvement on



Series III ——— Regression line for Seri ———— Overall Regression line.

 TABLE 6. PARAMETER VALUES USED IN THE PRELIMINARY CALCULATION SETS

 All values are in eV

Calculation set	I _{OH}	E _{OH}	βα	β _{co} +	Всон
114	26.14	7.32	- 2.29	- 2.29	- 1.95
213	35.73	14.61	- 2.39	- 2.80	-3.11
3	26.14	7.32	- 2.39	-2.80	-3.11
4	35.73	14-61	- 2·29	- 2.29	- 1-95
5	35.73	14-61	- 2·29	- 2.50	- 1.80
6	35.73	14.61	- 2·29	- 2-80	- 1.50
7	35.73	14.61	- 2·29	- 2.50	- 2.80

For all calculations $I_0 + = 34.15$, $E_0 + = 15.30$, $I_c = 11.16$, $E_c = 0.03$.



the simple Hückel correlation. In an attempt to improve the correlation, the calculations were repeated with the inclusion of configuration interaction. Twelve excited states resulting from all possible single excitations from the 3 highest energy occupied orbitals to the 4 lowest energy unoccupied orbitals were used. These results are included in Table 9 and plotted in Fig 6. The correlation is again most disappointing and appreciably worse than the $\omega\beta$ results.

The plots shown in Figs 5 and 6 compare the calculated transition frequencies with those observed in perchloric acid solution. These plots are not readily comparable with those of the previous calculations. To make the comparison easier, the calculated transition frequencies were converted into " β units" by division by 25,000 cm⁻¹. The resultant graph of the CI results for the perchloric acid solutions is shown in Fig 7. The validity of drawing a least square line here is somewhat questionable; however,

ion		pyrylium	flavylium	3'-OH- flavylium	4'-OH- flavylium
observed wavelength		270	401	395	440
set1	singlet	278·2	349·1	640-5	373·1
	triplet	481·5	465·5	782-1	697·0
set 2	singlet	254-6	324·5	350-3	333·5
	triplet	408-0	418·0	408-6	435·6
set 3	singlet	254·6	324·5	575·3	358-9
	triplet	408-0	418-0	729·4	583-9
set 4	singlet	278-2	349-1	347-6	350-8
	triplet	481-5	465-5	418-9	466-1
set 5	singlet	270-3	341-7	338-8	343-2
	triplet	452-7	449-4	40 6 -8	448-6
set 6	singlet	261·1	331-0	326-6	332-0
	triplet	423·3	427-3	392·7	424-6
set 7	singlet	270-3	341·7	359-3	348-0
	triplet	452-7	449·4	424-0	462·7

TABLE 7. COMPARISON OF OBSERVED AND CALCULATED WAVELENGTHS IN 1114 FOR THE TRIAL PARAMETER SETS

TABLE 8. FINAL PARAMETER VALUES

(a) Beta Values (eV).

 $\beta_{\rm CC} = -2.29$ $\beta_{\rm CO} + = -2.50$ $\beta_{\rm CO} = -1.80$.

(b) Ionisation Potentials, Electron Affinities and Effective Nuclear Charges.

atom	С	C-<	0+	ОН	OCH3
I (eV)	11.16	9.98	34.15	35.73	34.55
E (eV)	0-03	0.00	15.30	14 .6 1	14-61
z	3.25	3.14	4.55	4.55	4-44

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for the sake of comparison, the standard deviations calculated for the non CI and CI results from these plots are 1227 and 2246 cm^{-1} . These values do not compare favourably with the values summarized in Table 3.

Undoubtedly, the inclusion of configuration interaction does give an improvement in individual cases. For example, in perchloric acid solution, the 3'-OH-substituted compound absorbs at a longer wavelength than unsubstituted flavylium and this feature is reproduced by the CI calculation but not by the one omitting configuration interaction. In Series I, the non CI results give the same transition frequency for the 2'-OH- and the 2'-OMe- compounds whilst the CI calculations show a slightly lower frequency for the methoxy compound in agreement with experiment. Again in

		Calculated	frequency	
Compound	No	n CI	Includ	ing CI
-	Singlet	Triplet	Singlet	Triplet
	, _	Series I		
Unsubstituted	27716	19825	25131	15487
4'-OH	27397	19908	24881	15078
4'-OMc	27397	19908	24881	15078
3'-OH	28066	21431	25258	15375
3'-OMe	28066	21431	25258	15375
2'-OH	27277	19657	24968	15078
2'-OMe	27277	19661	24962	15085
3',4'-OH	27434	20631	24612	14892
3',4'-OMe	27434	20644	24612	14900
3'-OMe-4'-OH	27434	20631	24624	14900
3'-OH-4'-OMe	27434	20644	24612	14900
2',4'-OH	26860	19080	24539	14731
2'.4'-OMe	26860	19094	24540	14738
		Series II		
Unsubstituted	29265	22251	28719	21132
4'-OH	29137	22291	28304	20777
4'-OMc	29137	22316	28304	20772
3'-OH	29515	24582	27980	21039
3'-OMe	29524	24642	27980	21039
2'-OH	29044	23218	27910	20837
2'-OMe	29036	23218	27894	20837
		Series III		
4'-OH	25420	20433	24200	17774
4'-OMe	25420	20437	24200	17790
3'-ОН	25906	21039	24324	17937
2'-OMe	25195	20012	24010	17680
3'.4'-OH	25753	21092	24055	17717
3'-OMo-4'-OH	25753	21092	24055	17717
3'-OH-4'-OMe	25753	21101	24055	17727
2',4'-OMe	25125	20084	23912	17624

TABLE 9. CALCULATED PPP TRANSITION FREQUENCIES IN CM⁻¹ FOR PYRYLIUM SALTS WITH AND WITHOUT CONFIGURATION INTERACTION

this series, the observed shift to higher frequency is found for the 3'-OMe-4'-OH-salt compared to the 3',4'-OMe compound. On the other hand all these features are also reproduced, though perhaps in exaggerated form, in the simple calculations.

The PPP calculation scheme does allow separation of singlet and triplet transitions. The results here give some support to the hypothesis that the broad absorption bands observed for the flavylium salt solutions could be caused by overlapping of the singlet and triplet absorptions. The separation of the bands in this series is calculated to be rather less than that in the other two series studied.

One of the difficulties in attempting to carry out PPP calculations on the molecules of interest in this work must be the very large number of semi-empirical parameters which must be established, another is the difficulty of deciding the number and type of excited states to include in a CI calculation. It is clear that it is possible to carry out



FIG 5. Correlation for $\overline{\nu}$ in perchloric acid solution against calculated transition frequency for PPP calculations without CI



very extensive calculations without obtaining a real improvement over a large range of molecules.

We conclude that for our purpose, taking into account the number of parameters to be established and the amount of computing to be done, very satisfactory state function for a large number of molecules can be obtained using the $\omega\beta$ technique.

EXPERIMENTAL

MO calculations. The Hückel, ω and $\omega\beta$ calculations were carried out on an Elliott 4120 computer, using an Algol program. For the ω calculations, self consistency in the eigenvalues to 0-0005 was obtained after 5 iterations, while $\omega\beta$ calculations required 8 iterations for the same degree of self consistency.

Spectroscopic measurements. UV and visible spectra were recorded at room temp in 1 cm stoppered quartz cells on a Unicam SP700A spectrometer. Solns of approximately 10^{-5} moles litre⁻¹ concentration were used, giving an extinction coefficient for the long wavelength absorption band of approximately 10^4 .



FIG 6. Correlation for $\bar{\nu}$ in perchloric acid solution against calculated transition frequencies for PPP calculations including CI.



No attempt was made to measure this accurately. A value as high as this is quite consistent with the bands being due to $\pi \to \pi^*$ transitions. Some hydroxy compounds were either insoluble or very sparingly soluble in certain solvents.

Solvent purification. Analar 72% perchloric acid and GPR trifluoroacetic acid were used without purification. Alkyl halides and MeCN were distilled from P_2O_5 . Analar formic acid and Analar EtOAc were distilled from a molecular sieve. Dioxan was distilled first from anhyd SnCl₂ to remove peroxides, and then from Na. AcOH was distilled from a mixture of AcOH and Ac₂O. Analar benzene was distilled from Na. All distillations were carried out using a 50 cm column packed with glass helices.

Preparations-series I

2,6-Diisopropyl-4-styrylpyrylium perchlorates. These were prepared by the published¹⁸ method.

Series II

Flavylium perchlorates. These were prepared by condensing appropriate acetophenone derivatives with salicylaldehyde at 0° in dry ether saturated with dry HCl, using 72% perchloric acid as condensing agent.¹⁹



FIG 7. Regression line for $\overline{\nu}$ in perchloric acid solution against Δm for PPP calculation including CI. (β assumed equal to 25,000 cm⁻¹).

\odot	Series	I
0	Series	II
∆	Series	Ш

The solns were left to stand at 0° overnight when crystals of the flavylium perchlorate formed which were re-crystallized from glacial AcOH. The following new compounds were prepared :

		SUBSTITUTED FL.	AVYLIUM P	ERCHLORA	TES (Series	11)		
Compound	Ma	Econulo	R	equired (?	%)		 Found (%)
Compound	M.p.	rormua	С	н	Cl	С	н	Cl
3'-ОН	217-219°	C15H11CIO6	55.81	3.41	11-01	55.64	3-49	10-85
3'-OMe	176°	C ₁₆ H ₁₃ ClO ₆	57-06	3·86	10-54	56·83	3·98	10-38
2'-OH	218-220°	C15H11ClO6	55.81	3.41	11-01	55-63	3.43	10-78
2'•OMe	208-210°	C ₁₆ H ₁₃ ClO ₆	57-06	3.86	10-54	56-97	4-04	10-42

Three other salts of this series were prepared which had been characterized previously.

flavylium perchlorate m.p. 184–185° (lit.¹⁹ 186–187) 4'-hydroxyflavylium perchlorate m.p. 229–231° (lit.²⁰ 229–231°) 4'-methoxyflavylium perchlorate m.p. 198–199° (lit.²⁰ 196–197°)

Series III

2,4-Diphenyl-6-styrylpyrylium perchlorates. These were prepared by condensing appropriate benzaldehyde derivatives with 2,4-diphenyl-6-methylpyrylium chloride^{21, 22} by heating a threefold excess of the benzaldehyde derivative with the methylpyrylium salt on a steam bath for 4-5 hr. If the m.p. of the benzaldehyde derivative was below 100°, the condensation was done directly, otherwise a few ml AcOH were added. The resulting oily mixture was washed well with ether, and then dissolved in AcOH. The pyrylium perchlorate was precipitated by carefully adding the required amount of perchloric acid. The crude salts were recrystallized many times from AcOH. The following new compounds were prepared.

SUBSTITUTED 2,4-DIPHENYL-6-STYRYLPYRYLIUM PERCHLORATES (Series III)

Compound	М.р.	Formula	Required (%)			Found (%)		
			с	н	Cl	С	н	Cl
3'-ОН	242-243°	C ₂₅ H ₁₉ ClO ₆	66-59	4·22	7.85	66.53	4.63	7.82
2'-OMe	217–219°	C ₂₆ H ₂₁ ClO ₆	67·17	4·52	7.64	66 ∙87	4·72	7.49
4'-OH-3'-OH	255–258°	C23H19C107	64·31	4-07	7.60	64.18	3.93	7.50
4'-OH-3'-OMe	252256°	C ₂₆ H ₂₁ ClO ₇	64.93	4.37	7.38	64.60	4.55	7.32
4'-OMe-3'-OH	253–254°	C26H21C107	64.93	4.37	7.38	64.97	4.36	7.50
4'-OMe'2'-OMe	236-238°	C27H23C107	65·52	4.65	7.17	65-16	5-06	7.04

In addition two salts of this series which had been characterized previously were prepared.

2,4-diphenyl-4-4'-hydroxystyrylpyrylium perchlorate

m.p. 251-254° (lit. 254°)²²

2,4-diphenyl-6-4'-methoxystyrylpyrylium perchlorate

m.p. 221-223° (lit 228-229°)22

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REFERENCES

- ¹ Part I, G. V. Boyd and N. Singer, *Tetrahedron* 21, 1263 (1965)
- ² For a recent review see S. Basu, Adv. in Quantum Chem. 1, 145 (1964)
- ³ A. Streitwieser, Molecular Orbital Theory for Organic Chemists p. 115. Wiley, New York (1961)
- ⁴ G. V. Boyd and N. Singer, J. Chem. Soc. (B), 1017 (1966)
- ⁵ R. Pariser and R. G. Parr, J. Chem. Phys. 21, 466 (1953); J. A. Pople, Trans. Faraday Soc. 49, 1375 (1953)

⁶ G. C. Pimentel and A. L. McClellan, The Hydrogen Bond pp. 196, 23. Freeman, London (1960)

- ⁷ For recent discussion see W. P. Hayes and C. J. Timmons, Spectrochim. Acta 21, 529 (1965); M. E. Baur and M. Nichol, J. Chem. Phys. 44, 3337 (1966)
- ⁸ N. S. Bayliss and E. G. McRae, Ibid. 58, 1002 (1954)
- 9 Y. Ooshika, J. Phys. Soc. Japan 9, 594 (1954)
- ¹⁰ H. M. Rosenberg and E. Eimutis, Spectrochim. Acta 21, 1751 (1966); L. Bilot and A. Kawski, Z. Naturforsch. 17a, 621 (1962)
- ¹¹ H. Looyenga, Mol. Phys. 11, 337 (1966)
- ¹² J. Hinze and H. H. Jaffe, J. Am. Chem. Soc. 84, 540 (1962)
- ¹³ G. Bendz, O. Martensson and E. Nilsson, Ark. Kemi. 27, 65 (1967)

- ¹⁴ W. E. Kiurtin and Pill-Soon Song, Tetrahedron 24, 2255 (1968)
- ¹⁵ R. L. Flurry, Theoret. Chim. Acta 9, 96 (1967)
- ¹⁶ N. Mataga and K. Nishimoto, Z. physik. Chemie 13, 140 (1957)
- ¹⁷ K. Ohno, Theoret. Chim. Acta 2, 219 (1964)
- ¹⁸ J. Kelemen and R. Wizinger, Helv. Chim. Acta 45, 1918 (1962)
- ¹⁹ D. D. Pratt and R. Robinson, J. Chem. Soc. 121, 1577 (1922)
- ²⁰ Ch. Michaelidis and R. Wizinger, Helv. Chim. Acta 34, 1761 (1951)
- ²¹ W. Dilthey, J. prakt. Chem. 94, 53 (1916)
- ²² W. Dilthey and J. Fischer, Ber. Dtsch. Chem. Ges. 57B, 1653 (1924)