Semi-empirical Calculations on Lumiflavin Regarding Electronic Structure and Spectra

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Calculations are made on the lumiflavin molecule in the oxidized and reduced states and on the half-reduced radical in three different dissociation states. A semi-empirical restricted Hartree-Fock SCF-MO-LCAO-CI method in the Pariser-Parr-Pople approximation is used. The numerical values of the parameters W and γ have been varied with charge. To get spin densities with different signs, an unrestricted Hartree-Fock method including annihilation has also been used. For comparison, calculations with a CNDO method have been made on iso-alloxazine.

In an earlier paper¹ calculations on lumiflavin in different oxidation and dissociation states with a semi-empirical restricted Hartree-Fock method (RHF) in the Pariser-Parr-Pople approximation have been reported. In the discussion in that paper it was indicated that further calculations were planned. The announced calculations are now given here.

In the actual calculations some parameter values have been varied with the charge on the atoms according to methods given in Refs. 2 and 3. In other respects the method is the same as in Ref. 1. To get spin densities with different signs, calculations have also been made with an unrestricted Hartree-Fock method (UHF) including annihilation, due to Amos and Snyder.⁴ The same parameters as in the restricted method have been used.

For comparison of electron densities, calculations have also been made with the CNDO method given by Höjer and Meza.⁵ The lumiflavin molecule was, however, too large, so the CNDO calculations have been made on isoalloxazine; *i.e.*, the three methyl groups on C(7), C(8), and N(10) in lumiflavin are replaced by hydrogen atoms.

The data machine programmes used have been written: restricted HF by B. Roos and M. Sundbom, unrestricted HF by T. Alm and modified by A. Fjellstad and H. H. Jensen and CNDO by G. Höjer and S. Meza.

NOTATIONS, NUMBERING AND STRUCTURE OF THE MOLECULES

The following notations of the molecules treated are used in accordance with Ref. 1.

As in Ref. 1 a hydrogen atom is bound to N(3) in all the molecules, and in $\dot{\text{L}}\text{fH}_2$ the second H is bound to N(5). (For the numbering of the atoms see Fig. 1.) In $\dot{\text{L}}\text{fH}_3^+$ and $\text{Lf}_{\text{red}}\text{H}_3$ a further H is bound to N(1), *i.e.*, they correspond to $\dot{\text{L}}\text{fH}_3^+$ (1,5) and $\text{Lf}_{\text{red}}\text{H}_3$ (1,5) in Ref. 1. The corresponding notations on isoalloxazine are obtained by substituting Ia for Lf.

In the PPP calculations all the molecules are assumed to be plane as in Ref. 1. In the CNDO calculations the coordinates used are obtained

Fig. 1. Lumiflavin in the oxidized state to show the numbering of the atoms and the polarization angle ϕ .

Table 1. Bond distances calculated with restricted Hartree-Fock, in A. Corrections of W and γ due to charges. For notations "Calc. A" and "Calc. B", see the text.

Bond	Exp.		Calculated		LfH ⁻		LfH ₂		LfH ₃ ⁺		Lf _{red} H ₃		Exp.	
	Oxidized ^a		Calc. A	Calc. B	Calc. A	Calc. B	Calc. A	Calc. B	Calc. A	Calc. B	Calc. A	Calc. B	Reduced ^b	
A1	1.303		1.318	1.315	1.338	1.332	1.322	1.319	1.382	1.379	1.398	1.399	1.391	
12	1.368		1.383	1.390	1.362	1.377	1.382	1.389	1.390	1.402	1.377	1.393	1.367	
22'	1.207		1.242	1.213	1.258	1.222	1.243	1.215	1.235	1.209	1.245	1.212	1.193	
23	1.410		1.381	1.395	1.379	1.394	1.381	1.392	1.380	1.392	1.377	1.393	1.391	
34	1.362		1.368	1.385	1.375	1.391	1.371	1.386	1.372	1.388	1.378	1.391	1.380	
44'	1.219		1.240	1.211	1.253	1.220	1.246	1.222	1.236	1.210	1.241	1.213	1.223	
4B	1.483		1.467	1.467	1.437	1.446	1.448	1.444	1.461	1.463	1.450	1.456	1.432	
AB	1.446		1.454	1.456	1.418	1.425	1.439	1.441	1.392	1.397	1.379	1.375	1.350	
B5	1.300		1.312	1.310	1.372	1.362	1.380	1.386	1.384	1.381	1.405	1.408	1.385	
5C	1.372		1.378	1.382	1.376	1.368	1.405	1.404	1.391	1.396	1.401	1.398	1.394	
DC	1.405		1.411	1.410	1.420	1.423	1.407	1.408	1.412	1.409	1.411	1.413	1.404	
C6	1.406		1.416	1.413	1.407	1.412	1.404	1.403	1.413	1.412	1.399	1.399	1.370	
67	1.371		1.387	1.389	1.401	1.401	1.396	1.397	1.388	1.389	1.403	1.404	1.386	
78	1.421		1.411	1.409	1.397	1.396	1.403	1.402	1.418	1.415	1.396	1.395	1.401	
89	1.376		1.391	1.392	1.404	1.408	1.396	1.397	1.389	1.390	1.404	1.405	1.402	
9D	1.397		1.411	1.410	1.402	1.399	1.406	1.404	1.411	1.411	1.397	1.397	1.380	
10D	1.380		1.387	1.389	1.389	1.390	1.398	1.398	1.394	1.397	1.410	1.406	1.438	
10A	1.360		1.383	1.387	1.396	1.397	1.389	1.393	1.379	1.377	1.395	1.397	1.386	

^a Norrestam — Stensland⁶ 3,7,8,10-tetramethylisalloxazine. ^b Norrestam — v. Glehn⁷ 9-bromo-1,3,7,8,10-pentamethyl-1,5-dihydroisalloxazine.

Table 3. Net charges added for larger parts of the molecule due to π -electrons in units of electronic charge e , calculated with restricted Hartree-Fock (RHF).

	Lf _{ox} H	LfH ⁻	LfH ₂	LfH ₃ ⁺	Lf _{red} H ₃
Corrections of W and γ : Calc. A					
Pyrimidine ring with A and B	-0.30	-0.90	-0.49	0.05	-0.25
Middle part: N5, N10 and CH ₃ 10'	0.30	0.13	0.62	0.81	0.44
Benzene ring with C and D	0.00	-0.24	-0.13	0.14	-0.19
Pyrimidine part without A and B (1,2,2',3,4,4')	-0.39	-0.72	-0.44	0.13	-0.02
Middle ring with A, B, C, and D	0.38	0.02	0.51	0.72	0.18
Benzene ring without C and D (6,7,7',8,8',9)	0.00	-0.30	-0.08	0.15	-0.16
A+B	0.09	-0.18	-0.05	-0.08	-0.23
C+D	0.00	0.06	-0.06	-0.01	-0.03
Corrections of W and γ : Calc. B					
Pyrimidine ring with A and B	-0.17	-0.76	-0.37	0.16	-0.22
Middle part: N5, N10 and CH ₃ 10'	0.22	0.08	0.54	0.77	0.44
Benzene ring with C and D	-0.05	-0.32	-0.17	0.07	-0.22
Pyrimidine part without A and B (1,2,2',3,4,4')	-0.31	-0.63	-0.37	0.18	0.01
Middle ring with A, B, C, and D	0.35	0.01	0.48	0.72	0.19
Benzene ring without C and D (6,7,7',8,8',9)	-0.04	-0.38	-0.12	0.11	-0.20
A+B	0.14	-0.13	-0.01	-0.02	-0.23
C+D	-0.01	0.06	-0.05	-0.04	-0.02

from Norrestam—Stensland—v. Glehn (personal communication) and this implies that the reduced form is bent, the angle being 150°. The structure used for the oxidized form is also used for $\dot{\text{IaH}}^-$ and $\dot{\text{IaH}}_2$. CNDO calculations for $\dot{\text{IaH}}_3^+$ did not converge.

PARAMETER VALUES

Most parameters used are the same as in Ref. 1. The one-electron integrals W_μ and the one-center two-electron integrals $\gamma_{\mu\mu}$ have, however, been varied with the charge for those atoms where the calculated charge is >0.2 . This implies that W_μ and $\gamma_{\mu\mu}$ have been varied for the oxygen atoms, the carbons bound to the oxygens, and for the nitrogens.

For the carbon and oxygen atoms in the C=O bonds, two different parameter sets have been used. In Calc. A the values of W_μ for neutral atoms and the variation of W_μ with charge are according to Alt. 2 $F_2(Z_{\text{eff}})$ in Ref. 3, and in Calc. B they are according to Alt. 1 $F_1(q)$ in the same reference.

For the nitrogen atoms, the values of W_μ for neutral atoms and the variation of W_μ with charge are according to Alt. 1 $F_2(Z_{\text{eff}})$ in Ref. 3 for pyridine N and according to Alt. 2 $F_2(Z_{\text{eff}})$ for pyrrole N in the same reference.

For the numerical values of the one-center two-electron integrals $\gamma_{\mu\mu}$ and their variation with charge, see Refs. 2 and 3.

RESULTS

The bond lengths calculated with restricted Hartree-Fock (RHF) are given in Table 1 together with experimental values given by Norrestam *et al.*^{6,7} Charges on the atoms calculated with RHF are given in Table 2. The calculations with unrestricted Hartree-Fock (UHF) have in most cases given the same results. When they differ >0.03 from the RHF calculations, they are given in parentheses. To show how the charges are dislocated, charges on larger parts of the molecule are given in Table 3.

Table 4. Spin densities obtained with restricted Hartree-Fock (RHF) and with unrestricted Hartree-Fock (UHF) after annihilation.

Atom	Corrections of W and γ due to charges according to					
	Calc. A			Calc. B		
	RHF	UHF		RHF	UHF	
	$\dot{\text{L}}\text{FH}^-$	$\dot{\text{L}}\text{FH}_3$	$\dot{\text{L}}\text{FH}_3^+$	$\dot{\text{L}}\text{FH}^-$	$\dot{\text{L}}\text{FH}_3$	$\dot{\text{L}}\text{FH}_3^+$
A	0.05	0.01	0.06	0.05	0.01	0.08
N1	0.02	0.06	0.02	0.04	0.08	0.03
2	0.02	0.02	0.00	0.01	0.00	0.00
O2'	0.01	0.02	0.00	0.03	0.04	0.01
N3	0.00	0.01	0.00	0.00	0.00	0.00
4	0.04	0.05	0.01	0.02	0.02	0.00
O4'	0.02	0.06	0.02	0.07	0.16	0.04
B	0.09	0.44	0.13	0.14	0.46	0.19
N5	0.51	0.23	0.32	0.36	0.16	0.29
C	0.00	0.00	0.08	0.02	0.00	0.06
6	0.09	0.01	0.01	0.11	0.01	0.01
7	0.00	0.00	0.03	0.00	0.00	0.02
8	0.04	0.01	0.04	0.06	0.01	0.03
9	0.02	0.00	0.00	0.02	0.00	0.00
D	0.03	0.01	0.08	0.03	0.01	0.06
N10	0.05	0.05	0.19	0.04	0.03	0.19
S*						
			0.79		0.78	0.75
					1.45	1.38
						1.15

Spin densities on the CH_3 -groups are = 0.00 except on $\text{CH}_3\text{10'}$ in $\dot{\text{L}}\text{FH}_3^+$, where it is 0.01.

In Table 4 the spin densities obtained with RHF and UHF are given. The expectation values of the S^2 operator after annihilation are also given. The S^2 values in Calc. A are near 0.75, so the wave functions after annihilation are close to spin eigenfunctions, and in these cases the agreement between RHF and UHF values on the charges on the atoms (Table 2) is very good. For Calc. B the deviations of S^2 from 0.75 are large, thus further annihilation is desirable. From Table 2 it is seen that in these cases there are large differences between values obtained from RHF and UHF for charges on some of the atoms. Fjeldstad and Jensen⁸ have tested the UHF program on some π -electron radicals. In most of their calculations the values on S^2 are near 0.75, but in two cases they have also obtained large values on S^2 (1.10 and 1.37).

In Table 5 charges on the atoms and spin densities obtained with CNDO calculations on isalloxazine are given. Convergence was not obtained for $\dot{\text{Ia}} \text{H}_3^+$.

Ionization potentials obtained with restricted HF are given in Table 6 and in Tables 7a-e calculated values on transition energies, oscillator strengths, and direction of the transition moments are given, *viz.* singlet-singlet π - π^* transitions for the molecules with paired spins in the ground state and doublet-doublet π - π^* transitions for the radicals with one unpaired electron in the ground state. Experimental values obtained by different workers are also given, but for more detailed references to experimental values see Ref. 1.

Comparisons with the results in Ref. 1 and with the CNDO calculations

Bond lengths. The results in Calc. A are very close to those obtained in Ref. 1, but in Calc. B the bond lengths in the C=O bonds and C(2)-N(3) are much closer to the experimental values than those obtained in Ref. 1 and in Calc. A.

Table 5. Charges on atoms and spin densities calculated with the CNDO method on isalloxazine. The notations in accordance with those of lumiflavin.

Atom	Charges								Spin densities	
	$\dot{\text{Ia}}_{\text{ox}}\text{H}$ total	π	$\dot{\text{Ia}}\text{H}^-$ total	π	$\dot{\text{Ia}}\text{H}_2$ total	π	$\dot{\text{Ia}}_{\text{red}}\text{H}_3$ total	π	$\dot{\text{Ia}}\text{H}^-$	$\dot{\text{Ia}}\text{H}_2$
A	0.21	0.20	0.21	0.23	0.22	0.19	0.18	0.13	0.02	-0.06
N1	-0.25	-0.38	-0.33	-0.47	-0.25	-0.37	-0.24	0.28	0.03	0.12
2	0.32	0.19	0.32	0.22	0.32	0.19	0.37	0.19	-0.01	-0.04
02'	-0.27	-0.39	-0.36	-0.47	-0.28	-0.39	-0.28	-0.43	0.03	0.07
N3	-0.28	0.24	-0.29	0.24	-0.27	0.23	-0.27	0.28	-0.02	-0.04
4	0.28	0.18	0.27	0.21	0.26	0.16	0.29	0.18	-0.03	-0.11
04'	-0.25	-0.35	-0.34	-0.45	-0.26	-0.35	-0.27	-0.42	0.11	0.22
B	-0.09	-0.09	-0.19	-0.34	-0.12	-0.20	-0.13	-0.22	0.17	0.44
N5	0.01	0.12	-0.14	-0.23	-0.08	0.42	-0.12	0.80	0.50	0.32
C	0.00	-0.10	0.05	0.02	0.04	-0.06	0.07	0.03	-0.15	-0.06
6	-0.05	0.05	-0.11	-0.05	-0.09	-0.02	-0.10	-0.04	0.16	0.06
7	-0.10	-0.06	-0.09	-0.04	-0.08	-0.03	-0.06	0.01	-0.12	-0.04
8	-0.02	0.07	-0.09	-0.06	-0.05	0.01	-0.08	-0.02	0.17	0.06
9	-0.13	-0.09	-0.12	-0.07	-0.11	-0.07	-0.08	-0.01	-0.09	-0.04
D	0.12	0.09	0.06	0.00	0.10	0.02	0.04	-0.02	0.14	0.06
N10	-0.16	0.32	-0.18	0.26	-0.19	0.26	-0.18	0.81	0.08	0.05
H1'								0.17		
H3'	0.16		0.11		0.16			0.17		
H5'					0.18			0.11		
H6'	0.09		0.05		0.08			0.08		
H7'	0.08		0.03		0.08			0.07		
H8'	0.08		0.03		0.08			0.08		
H9'	0.08		0.04		0.08			0.07		
H10'	0.16		0.11		0.16			0.14		

Table 6. Vertical ionization potentials of π -electrons calculated with restricted Hartree-Fock (RHF). Notation o singnifies ionization of the odd electron, t = triplet, s = singlet, the state after ionization.

	Corrections of W and γ due to charges according to									
	Calc. A					Calc. B				
	$Lf_{ox}H$	LfH^-	LfH_2	LfH_3^+	$Lf_{red}H_3$	$Lf_{ox}H$	LfH^-	LfH_2	LfH_3^+	$Lf_{red}H_3$
Ionization potential, eV										
		o 2.29	o 7.64	o 12.73	6.14		o 0.81	o 6.82	o 12.03	5.53
		t 2.81	t 7.39	t 12.69	8.40		t 1.68	t 6.67	t 11.95	7.80
7.72		s 4.36	s 9.25	s 14.36		6.91	s 3.86	s 8.16	s 13.47	
		t 3.94	t 8.90	t 13.19	8.77		t 2.97	t 7.51	t 12.12	8.08
8.89		s 5.88	s 10.92	s 15.30		8.01	s 4.06	s 9.03	s 12.45	
		t 4.38	t 8.94	t 13.29	9.47		t 3.42	t 8.49	t 12.80	8.17
9.19		s 4.63	s 9.70	s 13.46		8.59	s 4.70	s 9.94	s 15.03	
		t 5.37	t 9.71	t 14.05	9.78		t 4.70	t 9.20	t 13.43	9.10
9.82		s 6.13	s 10.21	s 15.12		9.26	s 5.51	s 9.66	s 14.60	

Table 7a. Electronic singlet-singlet transitions of Lf_{ox}H below 60 kK with restricted Hartree-Fock (RHF).

Corrections of W and γ according to						Observed absorption			
Calc. A			Calc. B			Riboflavin in dioxane, Koziol ^b			
ν , kK	f	pol. ϕ^a	ν , kK	f	pol. ϕ^a	max. λ , nm	ν , kK	min. ν , kK	$\varepsilon \times 10^{-3} \text{M}^{-1} \text{cm}^{-1}$
26.7	0.51	165	26.7	0.54	167	440	22.7	20 ^b	12.1
34.1	0.02	55	33.6	0.02	123	344	29.1	26.5	8.4
35.7	0.01	157	35.4	0.05	80			33.5	33.1
39.6	1.17	25	38.8	0.74	27	271	36.9		
40.8	0.07	12	40.8	0.44	16			42.1	
44.6	0.17	35	44.2	0.26	24				
47.1	0.11	139	45.9	0.11	158				
48.9	0.32	161	46.6	0.03	49				
50.8	0.54	144	49.6	0.35	151	224	44.6		31.0
51.5	0.10	166	50.4	0.05	91				
51.8	0.12	29	51.3	0.38	3				
54.7	0.01	159	52.7	0.48	101				
56.3	0.81	55	54.0	0.67	53				
57.0	0.13	79	55.1	0.10	172				
57.9	0.21	106	57.0	0.07	107				
59.6	0.00		59.1	0.06	70				

^a The angle ϕ , see Fig. 1. ^b The start of the band.Table 7b. Electronic doublet-doublet transitions below 50 kK of the lumiflavin radical LfH⁻ with restricted Hartree-Fock (RHF).

Corrections of W and γ according to						Observed absorption			
Calc. A			Calc. B			Lumiflavin 3-CH ₃ COOC ₂ H ₅ in nonaqueous dimethylformamide, semiquinone anion Ehrenberg, Müller and Hemmerich ¹⁰			
ν , kK	f	pol. ϕ^a	ν , kK	f	pol. ϕ^a	max. λ , nm	ν , kK	min. ν , kK	$\varepsilon \times 10^{-3} \text{M}^{-1} \text{cm}^{-1}$
14.6	0.00		9.6	0.00					
16.7	0.06	14	11.4	0.00					
21.1	0.02		15.7	0.03	11			18 ^b	1.5
22.7	0.20	176	18.1	0.10	2	477	21.0	5.9	3.5
26.3	0.03							23.3	
28.7	0.09	179	22.2	0.22	170	400	25.0 (peak)	11.5	
								25.6	11
31.9	0.07	172	25.5	0.04	75	373	26.8	17.6	5
33.8	0.00		28.2	0.04	2			29 ^c	
35.9	0.08	109	31.8	0.03	132				
37.9	0.36	36	36.2	0.23	22				
40.5	0.23	7	36.9	0.28	62				
40.7	0.20	40	38.2	0.04	149				

Table 7b. Continued.

41.0	0.06	20	39.4	0.04	48
41.5	0.15	3	41.0	0.17	7
44.0	0.28	154	41.4	0.16	178
45.8	0.01		42.5	0.04	
46.4	0.15	168	45.2	0.34	168
47.2	0.04		45.6	0.03	
48.3	0.01		47.4	0.01	
49.3	0.10	15	47.9	0.02	
			48.7	0.08	160
			49.9	0.08	11

^a The angle ϕ , see Fig. 1. ^b Start of the band. ^c End of the recorded curve.

Table 7c. Electronic doublet-doublet transitions below 50kK of the lumiflavin radical $\dot{\text{L}}\text{fH}_2$ with restricted Hartree-Fock (RHF).

Corrections of W and γ according to Calc. A			Calc. B			Observed absorption Neutral semiquinone of glucose oxidase, pH 6.3 Palmer and Massey ¹¹			
ν , kK	f	pol. ϕ^a	ν , kK	f	pol. ϕ^a	max. λ , nm	ν , kK	min. ν , kK	$\epsilon \times 10^{-3} \text{M}^{-1} \text{cm}^{-1}$ ^b
10.5	0.06	177	9.6	0.01					
			15.0	0.02				15 ^c	0.3
20.4	0.01		19.3	0.03	172	~ 600	~ 17	18.5	1.9
22.6	0.00					450	22.2	24	5.5
24.6	0.03		25.9	0.00		382	26.2		9.3
26.1	0.01		27.6	0.00		(shoulder)			
26.6	0.07	23							
28.3	0.00		30.2	0.04		360	27.8		10.1
31.6	0.09	166	32.5	0.01				30 ^d	7.5
35.0	0.18	178	35.6	0.23	161				
37.8	0.13	16	37.5	0.14	18				
38.5	0.45	39	39.1	0.09	75				
39.6	0.06		40.9	0.28	10				
39.8	0.07		42.1	0.06	47				
41.9	0.09	159	42.7	0.04					
42.6	0.06	160	44.7	0.02					
43.4	0.01		45.9	0.05					
44.9	0.36	169	46.7	0.34	167				
45.7	0.04		47.2	0.17	6				
47.4	0.11	106	48.1	0.11	151				
48.3	0.04		50.0	0.04	56				
49.0	0.20	141							
49.6	0.06								

^a The angle ϕ , see Fig. 1. ^b Estimated from curve in Palmer and Massey,¹¹ and based on value 14.1 at 450 nm in Massey and Palmer.¹² ^c Start of the band. ^d End of the recorded curve.

Table 7d. Electronic doublet-doublet transitions below 50 kK of the lumiflavin radical $\dot{\text{L}}\text{fH}_3^+$ with restricted Hartree-Fock (RHF).

Corrections of W and γ according to Calc. A			Calc. B		
ν , kK	f	pol. ϕ^a	ν , kK	f	pol. ϕ^a
16.4	0.05	161	10.4	0.02	
18.5	0.10	20	17.6	0.10	168
19.7	0.06	155	19.4	0.01	
23.7	0.01		20.3	0.08	1
26.0	0.01		21.1	0.04	72
27.2	0.04	156	25.3	0.00	
29.4	0.06	39	26.6	0.03	
31.1	0.01		30.4	0.07	27
34.4	0.03	164	32.7	0.01	
38.4	0.02		34.2	0.03	
39.0	0.00		36.4	0.00	
40.4	0.00		39.1	0.01	
40.9	0.21	48	40.4	0.11	51
41.6	0.29	30	40.6	0.14	41
43.0	0.04		41.8	0.01	
43.8	0.34	176	43.3	0.10	151
44.8	0.01		43.9	0.12	14
45.9	0.26	148	46.1	0.32	169
47.5	0.05		47.1	0.01	
48.1	0.17	168	48.3	0.06	
48.8	0.03		48.6	0.64	180
49.4	0.05	8	50.0	0.03	

^a The angle ϕ , see Fig. 1.Absorption spectrum of flavin semiquinone $\dot{\text{F}}\text{lH}_3^+$ has maxima at about 490 nm (ca. 20 kK) and at about 360 nm (ca. 28 kK), according to Ehrenberg and Hemmerich.¹³Table 7e. Electronic singlet-singlet transitions below 60 kK of $\text{Lf}_{\text{red}}\text{H}_3$ with restricted Hartree-Fock (RHF).

Corrections of W and γ according to Calc. A			Corrections of W and γ according to Calc. B			Observed absorption Flavohydroquinone $\text{Fl}_{\text{red}}\text{H}_3$ in H_2O Ehrenberg and Hemmerich ¹³ (see also Hemmerich <i>et al.</i> ¹⁴)			
ν , kK	f	pol. ϕ^a	ν , kK	f	pol. ϕ^a	max. λ , nm	ν , kK	min. ν , kK	$\epsilon \times 10^{-3} \text{M}^{-1} \text{cm}^{-1}$
19.6	0.04		20.4	0.04					
30.0	0.20	4	28.8	0.24	2	~ 400	~ 25 shoulder		ca. 2
35.1	0.23	114	33.4	0.22	113	~ 300	~ 33 »		» 6
39.9	0.14	26	39.0	0.18	22				
			41.1	0.12	174				
42.0	0.83	4	43.1	0.54	172	250	40.0		30
43.9	0.17	132	44.2	0.30	54				
			45.8	0.27	158				
46.5	0.07	146	46.8	0.01				43.5	12
47.2	0.24	75	48.2	0.03					

Table 7e. Continued.

48.1	0.04							
50.1	0.04							
53.1	0.56	88	50.6	0.92	65	204	49.0	30
53.6	0.50	29	52.5	0.19	157			
54.9	0.22	147	53.2	0.08	101			
55.8	0.06		55.1	0.27	131			
56.1	0.04		55.6	0.40	43			
56.8	0.26	44	58.0	0.13	106			
59.4	0.30	96	59.4	0.03				
			59.8	0.02				

^a The angle ϕ , see Fig. 1.

In the experimental curve given by Ehrenberg and Hemmerich,¹³ the absorption ($\epsilon \times 10^{-3}$) increases continuously from about 1 at 22 kK (450 nm) to about 30 at 40 kK (250 nm). According to Dudley *et al.*,¹⁶ the intensity in the 500–700 nm range appears to be a measure of molecular planarity.

As in Ref. 1 the bond lengths in the benzene ring are alternating long and short in $\text{Lf}_{\text{ox}}\text{H}$, and LfH_3^+ but approximately equal within the ring in LfH^- , LfH_2 , and $\text{Lf}_{\text{red}}\text{H}_3$.

Charges on the atoms due to π -electrons. Calc. A gives approximately the same values for charges on the atoms as those obtained in Ref. 1. In Calc. B, however, much smaller charges have been obtained on C(2), O(2'), C(4), and O(4') than in the other calculations. In CNDO the charges on C(2), O(2'), C(4), and O(4') are between those obtained with Calc. A and B. The oxygen atoms are the most negatively charged atoms both in Calc. A and B as in Ref. 1. The CNDO calculations give about the same negative values on N(1) as on O(2') and O(4') except in $\text{Lf}_{\text{red}}\text{H}_3$ where N(1) is positively charged.

The pyrimidine ring compared to the other parts of the molecule is more negatively charged in $\text{Lf}_{\text{ox}}\text{H}$, LfH^- and LfH_2 as also was obtained in Ref. 1. The values in Calc. B are, however, smaller than those in Calc. A and Ref. 1.

The middle part is positively charged in all the calculations in all molecules. The relatively large variation in charge of the benzene ring in different oxidation and dissociation states, pointed out in Ref. 1, is obtained also in Calc. A and B.

Ionization potentials. Most values on ionization potentials obtained are smaller than those obtained in Ref. 1. In most cases Calc. B gives smaller values than Calc. A.

Electronic spectra. The calculated spectra are compared with experimental ones and with those calculated in Ref. 1. Calc. A gives about

equally good agreement with experimental spectra as the calculations in Ref. 1. Calc. B gives poorer agreement with experiments in all the molecules except $\text{Lf}_{\text{ox}}\text{H}$, where the results are equally good.

Spin densities. With the RHF method Calc. A and B give about the same values on spin densities except on N(5) in LfH^- (Calc. A 0.51, Calc. B 0.36) and on O(4') in LfH_2 (Calc. A 0.06, Calc. B 0.16), in spite of very different values for charges on some atoms.

With the UHF method there are differences between Calc. A and B for N(5), C(2), O(2'), C(4), and O(4') in all three radicals and on C(A) in LfH^- and on C(B) in LfH_2 . Furthermore, the RHF and the UHF methods according to Calc. B give significantly different values for the charges on these atoms. Since the S^2 values in Calc. B (see Table 4) differ a lot from 0.75, these UHF wave functions are not pure eigenfunctions of S^2 , and thus the UHF results are uncertain.

According to experimental data the spin density is large on N(5) and small on N(1).¹⁵ From Tables 4 and 5 it is seen that large values on N(5) are obtained in all the calculations except for the UHF Calc. B in LfH_2 and that small values on N(1) are obtained in all the calculations except for the UHF Calc. A and B in LfH_2 . It is to be pointed out that in Calc. B UHF for LfH_2 , the value of S^2 is 1.38, and thus the wave functions are not pure eigenfunctions, and thus the obtained spin densities are uncertain.

According to experimental data the spin density on N(10) should be about half of the

density on N(5).¹⁵ As is seen from Tables 4 and 5, this result is not obtained by the calculations: for LfH^- and LfH_2 the ratio of spin density on N(10) and N(5) is smaller than 0.5 and for LfH_3^+ it is larger.

DISCUSSION

From Table 1 it is seen that the parameter values used in Calc. B are the best for determining the bond lengths and that they are better than those used in Ref. 1. The CNDO calculations give values for the charges due to the π -electrons which are between those obtained by Calc. A and B. The spectra are best reproduced with the parameter set used in Calc. A which is in agreement with the results on smaller molecules.^{2,8}

Calc. B seems to be preferable as far as ground state properties are concerned, and Calc. A in case of excited states. If possible, both types of calculations should be carried out.

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