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Semiempirical Molecular Orbital Studies of Phthalocyanines

I. The Electronic Structure and Excited States of Phthalocyanine, H_2Pc

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The π and σ lone pair electron system of the phthalocyanine molecule has been studied by a semiempirical SCF-MO method. Electronic transitions of both $\pi-\pi^*$ and $n-\pi^*$ types have been considered. The excited states have been calculated by means of the method of superposition of configurations where all singly excited states are included. Assignments for the electronic spectrum of phthalocyanine could be made in good agreement with experiment. The position of the lowest electronically allowed $n-\pi^*$ transition is predicted to be found in the region of the strong Soret band.

Das Elektronensystem der einsamen π- und σ-Elektronenpaare des Phthalocyaninmoleküls wurde mit Hilfe einer semiempirischen SCF-MO-Methode untersucht. Dabei wurden Elektronenübergänge vom $\pi-\pi^*$-Typ und vom $n-\pi^*$-Typ behandelt. Die angeregten Zustände wurden nach der CI-Methode unter Einschluß aller einfach angeregten Zustände berechnet. Die Zuordnung der Ergebnisse zum Elektronenspektrum des Phthalocyanins brachte gute Übereinstimmung mit dem Experiment. Die Lage des niedrigsten elektronisch erlaubten $n-\pi^*$-Übergangs wird für das Gebiet der starken Soret-Bande vorhergesagt.

Les électrons π et les paires libres σ de la molécule de phthalocyanine ont été étudiés par une méthode SCF MO semi-empirique. On envisage les transitions du type $\pi-\pi^*$ et $n-\pi^*$. Les états excités ont été calculés par la méthode de superposition des configurations incluant tous les états monoexcités. Les attributions du spectre électronique de la phthalocyanine sont en bon accord avec l'expérience. La position de la plus basse transition permise du type $n-\pi^*$ est prédite dans la région de la forte bande de Soret.

1. Introduction

Phthalocyanines have many important technological applications. They can be used as dyestuffs, catalysts and semiconductors. The literature contains several reviews of the chemistry and physics of these molecules [1–3]. In many respects the phthalocyanines resemble the biologically important porphyrins. It is therefore of great interest to perform a parallel study of phthalocyanines and porphyrins. Porphin and copper porphin have already been investigated by a semiempirical molecular orbital method at this laboratory [4, 5]. The present MO investigation of H_2Pc is the first in a series in progress studying phthalocyanines and metal phthalocyanines. Quite many Hückel calculations of these molecules have been reported in the literature [6–13].

Calculations with the free electron method have also been made [14]. Schaffer and Gouterman [15] used the extended Hückel method for a study of free base and metal phthalocyanines. SCF MO calculations with the Pariser-Parr-Pople (PPP)

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method were performed by Weiss, Kobayashi, and Gouterman [16]. They assumed D_{4h} symmetry and calculated the electronic spectra using a four orbital model. McHugh, Gouterman, and Weiss recently reported a full CI treatment with D_{4h} symmetry [17].

As far as we know the present investigation is the first PPP CI study of H_2Pc assuming D_{2h} symmetry. The calculated spectrum shows a very good agreement with the observed vapour phase spectra. Especially the splitting of the Q band is well reproduced. The positions of the $n-\pi^*$ transitions are predicted. The lowest allowed $n-\pi^*$ transition is found in the region of the strong Soret band. The theoretical model is the same one as used in previous porphin calculations [4, 5].

2. Theoretical Model and Details of the Calculations

Method

The PPP method in the SCF-MO-LCAO form was adopted. A parameter scheme devised at this laboratory [18, 19] was used. These fixed parameters have been tested on a number of conjugated molecules containing nitrogen [4, 18, 19] and the results are in good overall agreement with available experimental data.

Excited states were calculated by means of the method of superposition of configurations, where all singly excited configurations are included.

The oscillator strengths were determined from the standard formula of Mulliken and Rieke [20].

Geometry

It is well known that crystalline H_2Pc exists in at least two polymorphic modifications: the stable β-form and the unstable α-form. The molecular geometry used in the calculations is based on the neutron diffraction data for the β-form [21]. These data show that the molecule can be considered as almost completely planar.

In the first calculation we have assumed D_{4h} symmetry for the carbon-nitrogen skeleton by taking the arithmetic means of the experimental values for equivalent bonds. These bond lengths are given in Table 3 (observed). The numbering of the atoms is shown in Fig. 1 together with the averaged bond angles.

The position of the protons attached to the inner ring atoms in H_2Pc has been the subject of much discussion [10, 11, 15]. According to the neutron diffraction data [21] the two protons are shared by all four nitrogens. UV- [22, 11] and IR-data [23], however, indicate that the symmetry of H_2Pc is D_{2h} and not D_{4h}.

In this study we have assumed that the two protons are located on two opposite nitrogens (2 and 4 in Fig. 1), leading to D_{2h} symmetry.

Schaffer and Gouterman [15] used extended Hückel calculations to study the location of free base protons. They concluded that the bonded structure, with two pyrrole and two *aza* nitrogens, is the most probable in the vapour.

Calculated bond distances were obtained from the calculated bond orders, $p_{\mu\nu}$, by means of the following bond order-bond length relations [18]:

$$R_{\mu\nu}(\mathrm{C,C}) = 1.517 - 0.18\, p_{\mu\nu}\,, \qquad (1)$$

$$R_{\mu\nu}(\mathrm{C,N}) = 1.458 - 0.18\, p_{\mu\nu}\,. \qquad (2)$$

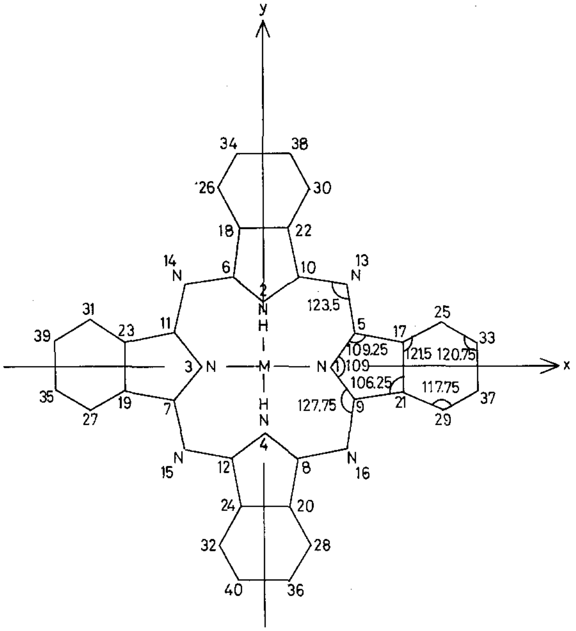

Fig. 1. The numbering system of phthalocyanine used in the present investigation. The bond angles are the averaged values from [21] giving the carbon-nitrogen skeleton D_{4h} symmetry. This geometry was used in the first calculation, cf. text

The calculation was repeated with the obtained values as input for the new geometry. After one iteration the calculated bond lengths deviated by less than ± 0.004 Å from the input value.

Calculations

The number of atomic orbitals that constitute the basis for the calculations is 46:40π orbitals and 6sp^2-hybridized nitrogen lone pair orbitals at the pyridine nitrogens. The number of electrons taken into account is 54.

The SCF molecular orbitals have been calculated by means of a computer program SCF-OPSZDO, written by Roos and Sundbom. This program also calculates the energy levels of excited states by mixing configurations obtained from single excitations. An IBM 360/75 computer was used for the present calculations.

3. Molecular Orbitals and Ground State Properties

The SCF molecular orbitals of H_2Pc are presented in Table 1, where the orbital energies, ε_i, and the electronic populations are given.

The vertical ionization potential of H_2Pc, obtained from the energy of the highest filled orbital, is 5.7 eV. As fas as we know there are no observed gasphase ionization potentials for phthalocyanines. For the solid state several measure-

Table 1. Molecular orbitals of H_2Pc. Orbital energies ε_i in a.u. Population analysis. The numbering system as in Fig. 1

No.	MO Symmetry	ε_i	Population analysis[a]										
			N_1[b]	N_2	C_5	C_6	N_{13}[b]	C_{17}	C_{18}	C_{25}	C_{26}	C_{33}	C_{34}
Occupied													
1	$1b_{1u}$	−0.5074	0.0313	0.0621	0.0357	0.0537	0.0428	0.0131	0.0369	0.0035	0.0115	0.0012	0.0050
2	$1b_{3g}$	−0.4982		0.0893	0.0063	0.0702	0.0319	0.0004	0.0625	0.0001	0.0227	0.0000	0.0113
3	$1b_{2g}$	−0.4887	0.0810		0.0809	0.0137	0.0468	0.0438	0.0013	0.0156	0.0003	0.0070	0.0000
4	$2b_{1u}$	−0.4636	0.0507	0.0198	0.0413	0.0098	0.0035	0.0405	0.0387	0.0207	0.0267	0.0127	0.0209
5	$2b_{3g}$	−0.4368		0.0620	0.0078	0.0156	0.0220	0.0009	0.0199	0.0004	0.0610	0.0001	0.0913
6	$1a_u$	−0.4352			0.0431	0.0692	0.1133	0.0049	0.0122	0.0021	0.0052	0.0003	0.0008
7	$3b_{1u}$	−0.4327	0.0006	0.0757	0.0002	0.0158	0.0090	0.0152	0.0091	0.0256	0.0400	0.0313	0.0658
8	$2b_{2g}$	−0.4263	0.0138		0.0070	0.0169	0.0253	0.0274	0.0031	0.0670	0.0017	0.0945	0.0003
9	$4b_{1u}$	−0.4108	0.0700	0.0760	0.0294	0.0091	0.0036	0.0027	0.0001	0.0361	0.0055	0.0746	0.0160
10	$1a_g$	−0.3818					0.2500*n*						
11	$1b_{3u}$	−0.3818					0.2500*n*						
12	$1b_{2u}$	−0.3818					0.2500*n*						
13	$2a_g$	−0.3818	0.5000*n*										
14	$1b_{1g}$	−0.3818					0.2500*n*						
15	$2b_{3u}$	−0.3818	0.5000*n*										
16	$3b_{2g}$	−0.3756	0.0668		0.0160	0.0574	0.0164	0.0038	0.0342	0.0030	0.0538	0.0200	0.0121
17	$3b_{3g}$	−0.3715		0.1426	0.0652	0.0015	0.0560	0.0205	0.0009	0.0266	0.0002	0.0055	0.0024
18	$2a_u$	−0.3505			0.0160	0.0046	0.0051	0.0120	0.0331	0.0267	0.1159	0.0062	0.0305
19	$5b_{1u}$	−0.3391	0.0020	0.1322	0.0001	0.0004	0.0016	0.0001	0.0963	0.0000	0.0000	0.0002	0.0841
20	$4b_{3g}$	−0.3373		0.0945	0.0008	0.0001	0.0001	0.0022	0.1026	0.0074	0.0000	0.0019	0.0876
21	$3a_u$	−0.3277			0.0002	0.0061	0.0108	0.0265	0.0032	0.1265	0.0333	0.0334	0.0101
22	$4b_{2g}$	−0.3254	0.0168		0.0020	0.0250	0.0344	0.0186	0.0082	0.0000	0.1036	0.0178	0.0321
23	$5b_{3g}$	−0.3184		0.0135	0.0075	0.0003	0.0310	0.0178	0.0110	0.1312	0.0001	0.0367	0.0078
24	$6b_{1u}$	−0.3049	0.0429	0.0043	0.0022	0.0001	0.0073	0.1232	0.0012	0.0032	0.0000	0.0885	0.0008
25	$5b_{2g}$	−0.3007	0.1094		0.0056	0.0067	0.0016	0.1008	0.0000	0.0035	0.0059	0.0689	0.0022
26	$7b_{1u}$	−0.2637	0.1308	0.0653	0.0015	0.0120	0.1083	0.0001	0.0180	0.0000	0.0021	0.0000	0.0099
27	$4a_u$	−0.2096			0.0940	0.0878	0.0021	0.0052	0.0102	0.0158	0.0154	0.0089	0.0108
Unoccupied													
28	$6b_{3g}$	−0.0391		0.0552	0.0906	0.0420	0.0237	0.0241	0.0026	0.0071	0.0122	0.0133	0.0068
29	$6b_{2g}$	−0.0215	0.0732		0.0058	0.0566	0.0696	0.0003	0.0474	0.0025	0.0059	0.0013	0.0240
30	$5a_u$	0.0415			0.0246	0.0057	0.0559	0.0376	0.0585	0.0013	0.0005	0.0246	0.0413
31	$8b_{1u}$	0.0451	0.0253	0.0193	0.0061	0.0290	0.0094	0.0006	0.0117	0.0101	0.1202	0.0031	0.0376
32	$7b_{3g}$	0.0569		0.0030	0.0042	0.0056	0.0175	0.0135	0.0243	0.0001	0.1341	0.0102	0.0390
33	$9b_{1u}$	0.0714	0.0195	0.0005	0.0077	0.0007	0.0028	0.0299	0.0062	0.1335	0.0190	0.0352	0.0051
34	$7b_{2g}$	0.0718	0.0188		0.0075	0.0003	0.0034	0.0317	0.0098	0.1400	0.0001	0.0368	0.0109
35	$6a_u$	0.1002			0.0038	0.0223	0.0043	0.0386	0.0276	0.0029	0.0079	0.0674	0.0752
36	$8b_{2g}$	0.1029	0.0113		0.0043	0.0395	0.0094	0.0072	0.0378	0.0126	0.0141	0.0028	0.1167
37	$8b_{3g}$	0.1074		0.0116	0.0157	0.0249	0.0008	0.0514	0.0116	0.0083	0.0133	0.1152	0.0029
38	$10b_{1u}$	0.1223	0.0385	0.0389	0.0192	0.0932	0.0130	0.0116	0.0292	0.0131	0.0244	0.0026	0.0049
39	$7a_u$	0.1363			0.0360	0.0199	0.0401	0.0038	0.0000	0.0190	0.0164	0.0731	0.0416
40	$9b_{3g}$	0.1593		0.0272	0.0188	0.0842	0.0558	0.0018	0.0140	0.0183	0.0062	0.0363	0.0010
41	$9b_{2g}$	0.1853	0.0532		0.0517	0.0036	0.0066	0.0082	0.0615	0.0034	0.0465	0.0005	0.0412
42	$8a_u$	0.1975			0.0000	0.0269	0.0062	0.0106	0.0988	0.0085	0.0530	0.0076	0.0384
43	$11b_{1u}$	0.2069	0.0884	0.0058	0.1068	0.0263	0.0487	0.0131	0.0026	0.0041	0.0006	0.0006	0.0001
44	$10b_{2g}$	0.2120	0.0557		0.0691	0.0303	0.0365	0.0081	0.0467	0.0024	0.0181	0.0003	0.0106
45	$10b_{3g}$	0.2220		0.0012	0.0330	0.0056	0.0144	0.1174	0.0005	0.0505	0.0001	0.0308	0.0000
46	$9a_u$	0.2225			0.0323	0.0076	0.0123	0.1110	0.0075	0.0473	0.0023	0.0286	0.0012

[a] Formal population of the virtual orbitals. N_i and C_i denotes π orbitals on nitrogen and carbon.

[b] The letter *n* after the number indicates a nitrogen σ lonepair orbital.

Table 2. The total electron population of the atomic orbitals in H_2Pc. For comparison the population for porphin, H_2P, and pyrrole are also included. The numbering of the atoms is given in Fig. 1

AO[a]	H_2Pc	H_2P[b]	Pyrrole[c]
N_1	1.232	1.217	1.656
N_2	1.675	1.673	
C_5	0.925	0.956	1.072
C_6	0.952	0.968	
N_{13}	1.146	1.057	
C_{17}	0.959	1.029	1.099
C_{18}	1.003	1.051	
C_{25}	1.030		
C_{26}	1.010		
C_{33}	1.019		
C_{34}	1.003		

[a] N_i and C_i denotes π orbitals on nitrogen and carbon.

[b] From previous calc. [4].

[c] From previous calc. [18].

Table 3. Observed and calculated bond lengths of H_2Pc. The numbering of the atoms as in Fig. 1. All values in Å

Bond	Bond lengths		
	H_2Pc		Pyrrole
	Observed[a] [21]	Calculated	Observed [27]
5–1	1.373	1.349	1.374
6–2	1.373	1.379	
13–5	1.315	1.351	
14–6	1.315	1.338	
17–5	1.470	1.463	1.381
18–6	1.470	1.448	
21–17	1.405	1.409	1.417
22–18	1.405	1.412	
25–17	1.388	1.403	
26–18	1.388	1.409	
33–25	1.390	1.394	Benzene:
34–26	1.390	1.389	1.397
37–33	1.425	1.402	
38–34	1.425	1.407	
M[b]–1	1.959	2.040[c]	
M–2	1.959	1.946[c]	

[a] The observed values are the arithmetic means of the values of equivalent bonds, assuming the geometry has D_{4h} symmetry.

[b] M denotes the center of the phthalocyanine molecule.

[c] Cf. text.

ments have been performed (see Ref. [3], Table 6.7 for a review). According to Komp and Fitzsimmons [24] the bulk ionization potential of H_2Pc is 6.1 eV, whereas the surface ionization potential is 5.3 eV.

The two highest occupied orbitals have symmetries b_{1u} and a_u and the two lowest empty orbitals are b_{3g} and b_{2g} orbitals.

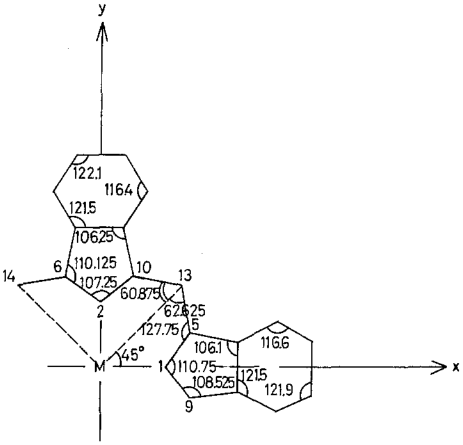

Fig. 2. The finally adopted bond angles, cf. text

The total electron population of the atomic orbitals is given in Table 2. The highest π-electron density is found on atoms N_1 and N_2 closely followed by atom N_{13}, whereas the lowest π-electron density is found for C_5 and C_6. This ordering is in accordance with most of the previous calculations.

The computed bond lengths are collected in Table 3 together with experimental data. For comparison the observed bond distances for pyrrole and benzene are also included. The computed bond distances from the first calculation were used to construct a new geometry in the following way: The angles 1-M-13 and 2-M-14 were assumed unchanged (45°). New structures were then tried using the computed bond distances and with the main angular change in the angles 5-1-9 and 6-2-10. A reasonable structure was obtained for an increase of the 5-1-9 angle by 1.75° and a decrease of the 6-2-10 angle by the same amount. The finally adopted bond angles are shown in Fig. 2. This structure has a somewhat larger hole size than the experimentally determined structure [21]. This is to be expected since the MO calculations describe a free molecule, whereas the neutron diffraction measurements give information about the structure of the molecule in a crystal.

4. Excited States

All singly excited configurations were included in the calculation of the transition energies. The results of the present CI treatment are presented in Tables 4 and 5. In Table 4 the allowed singlets (< 55 kK) are given together with the four lowest triplets. A detailed presentation of the configuration mixing for some of the excited states is found in Table 5. Only those configurations which contribute to the wave function with coefficients larger than 0.2 are given in the table. Table 5 shows that the four lowest triplets and the two lowest singlets can almost be completely described by a four orbital model. Most of the singlets are however, characterized by a more extensive configuration mixing. Edwards and Gouterman [25] recently measured vapour absorption spectra of phthalocyanine

Table 4. Calculated electronic transitions in H_2Pc. The four lowest triplets. All allowed transitions below 55 kK. The strongest transitions in the region 55 – 65 kK[a]. For choice of symmetry axes, see Fig. 1

Calculated				Observed [25] vapour		
Symmetry	pol.	ν (kK)	f	Notation	ν (kK)	range
$^3B_{3u}$		3.2				
$^3B_{2u}$		9.6				
$^3B_{3u}$		14.1				
$^1B_{2u}$	y	14.3	0.11		14.6	14 – 15
$^3B_{2u}$		14.9		Q		
$^1B_{3u}$	x	15.9	0.53		16.1	15 – 17
$^1B_{2u}$	y	26.6	1.09			
$^1B_{3u}$	x	32.2	2.38			
$^1B_{2u}$	y	32.8	2.92	B	29.4	26 – 34
$^1B_{1u}$	z[b]	33.1				
$^1B_{3u}$	x	34.2	0.08			
$^1B_{3u}$	x	35.4	0.42			
$^1B_{1u}$	z[c]	35.7			35.7[d]	
$^1B_{2u}$	y	36.0	0.22	N		34 – 38
$^1B_{2u}$	y	38.6	0.004			
$^1B_{3u}$	x	38.8	0.01		37.0	
$^1B_{3u}$	x	39.3	0.59			
$^1B_{1u}$	z[b]	41.9				
$^1B_{2u}$	y	42.6	0.23	L	41.7	40 – 43
$^1B_{3u}$	x	43.0	0.05			
$^1B_{2u}$	y	44.6	0.007			
$^1B_{3u}$	x	45.2	0.02			
$^1B_{2u}$	y	46.3	0.26			
$^1B_{3u}$	x	46.7	0.56		45.5[d]	
$^1B_{2u}$	y	46.7	0.01			
$^1B_{3u}$	x	49.4	0.002	C		43 – 50
$^1B_{2u}$	y	50.3	0.000			
$^1B_{2u}$	y	51.0	0.71		47.6	
$^1B_{2u}$	y	52.5	0.000			
$^1B_{3u}$	x	52.9	0.31			
$^1B_{3u}$	x	53.6	0.003			
$^1B_{3u}$	x	54.6	0.14			
$^1B_{2u}$	y	55.1	0.13			
$^1B_{3u}$	x	56.3	0.62	X_1	55.6	52 – 56
$^1B_{2u}$	y	57.3	0.40			
$^1B_{2u}$	y	58.7	0.40			
$^1B_{2u}$	y	59.2	0.89	X_2	62.5	59 – 64
$^1B_{3u}$	x	61.8	0.67			
$^1B_{2u}$	y	64.6	0.24			

[a] In this region transitions with f-values lower than 0.2 have been omitted.

[b] $n \rightarrow \pi^*$ transition from lone pairs of the bridge nitrogens.

[c] $n \rightarrow \pi^*$ transition from the inner ring nitrogen lone pairs.

[d] Shoulder.

and metallophthalocyanines. They identified five bands, denoted by Q, B, N, L and C. In the far UV two broad bands (X_1 and X_2) were observed.

In free base H_2Pc the Q band splits into two, which can be ascribed to the reduction of symmetry from D_{4h} to D_{2h}. The observed data from Ref. [25] are quoted in Table 4 and Fig. 3 for comparison with the calculated transitions.

Table 5. Configuration mixing for some of the excited states of H_2Pc

v (kK)	Wave function[a]
3.2	$0.90(4a_u-6b_{3g})^T+0.28(7b_{1u}-6b_{2g})^T+\cdots$
9.6	$0.95(4a_u-6b_{2g})^T+\cdots$
14.1	$0.86(7b_{1u}-6b_{2g})^T+0.37(4a_u-6b_{3g})^T+\cdots$
14.3	$0.75(4a_u-6b_{2g})+0.62(7b_{1u}-6b_{3g})$
14.9	$0.94(7b_{1u}-6b_{3g})^T+\cdots$
15.9	$0.89(4a_u-6b_{3g})-0.42(7b_{1u}-6b_{2g})+\cdots$
26.6	$0.62(6b_{1u}-6b_{3g})+0.51(7b_{1u}-6b_{3g})-0.47(4a_u-6b_{2g})-0.22(5b_{2g}-5a_u)+\cdots$
32.2	$0.79(7b_{1u}-6b_{2g})+0.37(4a_u-6b_{3g})+0.29(3a_u-6b_{3g})+0.21(5b_{1u}-6b_{2g})+\cdots$
32.8	$-0.66(6b_{1u}-6b_{3g})+0.50(7b_{1u}-6b_{3g})-0.38(4a_u-6b_{2g})+\cdots$
35.4	$0.66(4a_u-7b_{3g})-0.35(3a_u-6b_{3g})-0.33(5b_{2g}-9b_{1u})-0.32(6b_{1u}-7b_{2g})-0.24(6b_{1u}-6b_{2g})+\cdots$
36.0	$\begin{cases}0.44(5b_{1u}-6b_{3g})-0.37(4b_{3g}-8b_{1u})+0.33(4a_u-7b_{2g})+0.32(2a_u-6b_{2g})-0.29(5b_{1u}-7b_{3g})\\+0.27(7b_{1u}-7b_{3g})+0.23(4b_{2g}-5a_u)+0.22(3a_u-6b_{2g})+0.21(4a_u-8b_{2g})+\cdots\end{cases}$
39.3	$0.71(5b_{1u}-6b_{2g})+0.41(6b_{1u}-6b_{2g})-0.33(3a_u-6b_{3g})-0.29(4b_{3g}-5a_u)+\cdots$
42.6	$0.81(5b_{1u}-6b_{3g})-0.25(2a_u-6b_{2g})-0.24(7b_{1u}-7b_{3g})-0.22(3a_u-6b_{2g})+\cdots$
46.7	$\begin{cases}0.55(4a_u-8b_{3g})+0.38(4a_u-9b_{3g})-0.27(6b_{1u}-7b_{2g})+0.23(3a_u-6b_{3g})-0.21(5b_{2g}-9b_{1u})\\+0.21(2a_u-7b_{3g})-0.21(2a_u-6b_{3g})+\cdots\end{cases}$
51.0	$\begin{cases}0.41(5b_{1u}-7b_{3g})+0.40(4b_{3g}-8b_{1u})+0.39(7b_{1u}-7b_{3g})+0.27(2a_u-6b_{2g})-0.26(4b_{1u}-6b_{3g})\\+0.24(5b_{2g}-5a_u)-0.20(3a_u-7b_{3g})+\cdots\end{cases}$

[a] T stands for triplet. The singlet configurations have no special notation.

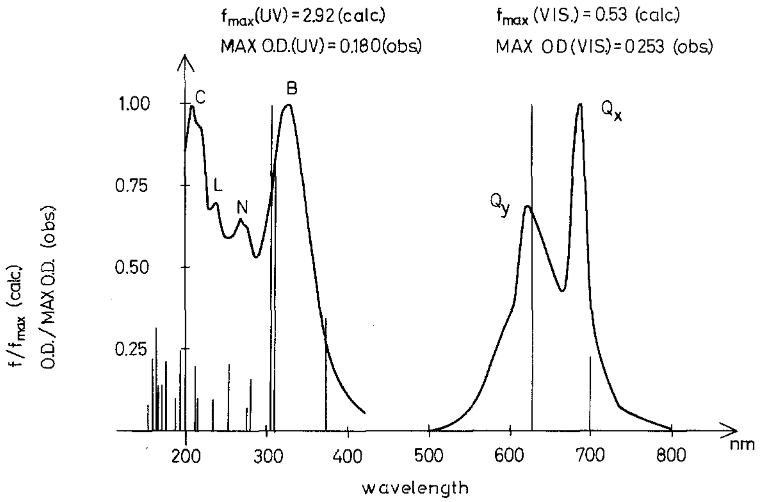

Fig. 3. Observed vapor-phase absorption spectra of H_2Pc from [25]. Calculated $\pi-\pi^*$ singlets with $f>0.2$, cf. Table 4

The Q Band. The calculated position and splitting of the Q band (14.3 and 15.9 kK) are in very good agreement with the experimental findings (14.6 and 16.1 kK). According to our calculations, the lower energy Q band (14.3 kK) is polarized along the NH-NH axis (y axis in Fig. 1), as was also the case for porphin [4].

The B Band. The present calculation gives three allowed $\pi-\pi^*$ transitions in the *B* band region: at 26.6 kK, 32.2 kK, and 32.8 kK.

The lowest allowed $n-\pi^*$ transition (33.1 kK) might also be found within the *B* band. This transition arises from the lone pairs of the bridge nitrogens.

The N, L, and C Bands. At higher energies than the *B*-band, observations show several bands: *N*, *L*, and *C*. On both the *N* and the *C* band a shoulder can clearly be distinguished.

According to our calculations, many transitions are expected to occur in the region between 35 and 50 kK. It is consequently difficult to make unambiguous assignments of the bands in this region. We suggest the following assignments: The $\pi-\pi^*$ transitions at 35.4, 36.0, 38.6, and 39.3 are assigned to the *N* band. An allowed $n-\pi^*$ transition at 35.7 kK is also expected to be found in this band. It is a transition from the inner ring nitrogen lone pairs.

The $\pi-\pi^*$ transitions at 42.6 and 43.0 kK and the $n-\pi^*$ transition (from the lone pairs of the bridge nitrogens) at 41.9 kK are assigned to the *L* band. As much as twelve allowed $\pi-\pi^*$ transitions are predicted to be found in the *C* band region, 44–55 kK.

The X_1 and X_2 Bands. In the high energy region, 55–65 kK, the calculation also gives many allowed $\pi-\pi^*$ transitions. Transitions with *f*-values lower than 0.2 have been omitted in Table 4. The strong transition at 56.3 kK can be attributed to the X_1 band. The two bands at 59.2 and 61.8 kK are assigned to the X_2 band.

Triplets. The parameter values in our parameter scheme are taken so as to give agreement between calculated and observed singlet transitions of a chosen set of small molecules [18, 19]. The parametrization implicitly takes into account part of the correlation. But since correlation effects are different for singlet and triplet states, our parameters will give too low values (around 2–7 kK [19]) for triplets. The calculated triplets at 14.1 and 14.9 kK will probably be above the lowest singlet.

Rieckhoff and Voigt [26] observed a phosphorescence band of H_2Pc in various solvents at 77°. It occured at 11–12 kK. The present calculation indicates the possibility of two triplets below the lowest singlet (Table 4).

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