

在不加对称性限制的条件下采用不同的半经验方法研究酞菁的电荷分布和几何构型

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在不加对称性限制的条件下采用不同的半经验方法 CNDO, INDO, MINDO/3, MNDO 和 Pm3 对自由酞菁 (H₂Pc) 进行几何构型最优化和电荷密度布居分析, 并将所得结果与 Am1 方法以及 X 射线衍射和中子衍射数据的数据进行比较。结果表明只有从 INDO 方法得到的是桥式构型, 而从 CNDO, MINDO/3, MNDO, Am1, Pm3 方法得到的都是键式构型。除 INDO 之外所有的这几种方法都对先前报道的几何构型扭曲给出进一步的支持证据。新近建立的半经验方法如 MNDO, Am1, Pm3 等看起来更适用于用来研究大分子如酞菁及其类似物的几何构型扭曲和电荷分布极化等问题。

关键词: 酞菁 几何构型 半经验方法 电荷分布
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The Electron Distribution and Geometry Investigation on Phthalocyanine with Different Semi-empirical Methods without any Symmetry Constraint

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Geometry optimization and electron density population analysis of free base phthalocyanine with different semi-empirical methods, namely CNDO, INDO, MINDO/3, MNDO and Pm3, were performed without any symmetry constraint and compared with that of Am1 method as well as the X-ray diffraction and neutron diffraction data. The optimized geometry of H₂Pc was found to be bridge-style configuration from INDO method and bond-style configuration from CNDO, MINDO/3, MNDO, Am1, Pm3 methods, respectively. All these methods except INDO give further evidence to support the geometry distortion as reported previously. The recently founded semi-empirical methods, say MNDO, Am1, Pm3, seem to be more suitable to investigate the distortion evidence of the geometry and the polarization of the electron distribution in the macromolecules such as phthalocyanine and its analogues.

Keywords: phthalocyanine geometry semi-empirical method electron distribution

0 Introduction

Phthalocyanines and their metal complexes are promising NLO (non-linear optical) materials^[1]. Inten-

sive research work in this field has led to significant progress in recent years^[2-8]. Regarding the work of phthalocyanine compounds as NLO materials, it is easy

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to understand that asymmetrical substituted phthalocyanines without symmetry center in the molecule show SHG response^[2,3]. However, the experiments revealed that free base phthalocyanine(H_2Pc) and some metal phthalocyanine complexes, namely $CuPc$, $CoPc$, and $ZnPc$ ^[4-6], also show SHG response, which really confused the researchers because of the well accepted D_{2h} and D_{4h} symmetry taken by the above-mentioned compounds. According to the theory of second order NLO materials, the SHG response is actually related to the electron distribution and the polarizability in the molecules or in the crystal composed by respective molecules. Some NLO experimental scientists claimed that the SHG response of $CuPc$ was correlated with the nonsymmetrical center in the microstructure formed by the $CuPc$ molecules. Further investigation for the electron distribution and the polarization of molecules of H_2Pc or $CuPc$ is therefore necessary.

During this work, we find an unusual phenomenon that the electron distribution over the phthalocyanine molecule derived from calculation according to the optimized geometry of H_2Pc molecule at $Am1$ ^[9] level without any symmetry constraint from the starting model based on previous method^[10] does not fully agree with that of D_{2h} symmetry^[11]. H_2Pc molecule approximately takes C_{2v} symmetry. However, since the two inner hydrogen atoms tilt to each side of the N-H-H-N axis and also point out to each side of the phthalocyanine mean plane, it is not really a C_{2v} symmetry. Therefore the molecule does not have a symmetry center. This noncentral symmetrical geometry may be part of the origin of the SHG response of free base phthalocyanine. Since there still is the possibility that this unsymmetrical result may be due to the $Am1$ method itself, further investigation of different methods is necessary. To conform the reliability of the calculation methods, we performed CNDO, INDO^[12], MINDO/3^[13], MNDO^[14], and Pm3^[15] calculations to compare with the results of $Am1$ calculation as well as the X-ray diffraction^[16] and neutron diffraction data^[17].

1 Calculation Details

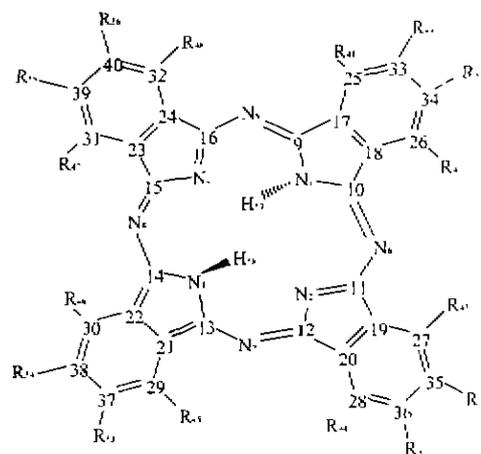


Fig. 1 Molecule structure and atom numbers of H_2Pc ($R = H$)

The calculation model is created according to previous method^[10] to eradicate any symmetry constraint and further optimization was made at CNDO, INDO^[12], MINDO/3^[13], MNDO^[14], Pm3^[15] level with the Gaussian-94W software^[18]. The algorithm for optimization is the Beryn algorithm using redundant internal coordinates and the population analysis is performed based on the optimized geometry^[18]. The numbering for atoms in phthalocyanine compounds is conducted as reported previously as shown in Fig. 1 for the purpose of comparing electron distribution and geometry variations of this molecule^[11]. All the peripheral hydrogen atoms are regarded as substituents and included. All calculations are performed on a Personal Computer (CPU K7-500, SDRAM 128MB, HD 13GB). The resulting bond lengths and bond angles are summarized in Table 1 and Table 2, respectively. The electron distribution data are comparatively listed in Table 3 to Table 7 according to the different methods used. In the literature concerning the X-ray molecular structure of H_2Pc ^[16], the corresponding researchers considered the molecule to be D_{2h} symmetry, therefore they only gave one fourth of the structural data for the whole molecule. In studying the molecular structure of H_2Pc by means of neutron diffraction method^[17], the investigators considered the geometry of the molecule to be centrosymmetrical and only gave half of the molecular structural data for the whole molecule. In Table 1 and Table 2, the data which were not directly given in the original

Table 1 Bond Lengths of H₂Pc (R = H)

methods	Am1	CNDO	INDO	MINDO/3	MNDO	Pm3	X-ray	neutron
H57-N1	0.9944	1.0709	1.2562	1.0232	0.9964	1.0023		(0.95)
H58-N3	0.9941	1.0713	1.1744	1.0261	0.9953	0.9963		0.95
H58-N2			1.2992					0.93
H57-N4			1.2022					(0.93)
N1-C9	1.4138	1.3916	1.3869	1.3914	1.4089	1.4282	1.34	(1.36)
N1-C10	1.4138	1.3916	1.3747	1.3914	1.4088	1.4281	1.34	(1.38)
N3-C13	1.3988	1.3835	1.3789	1.3717	1.3931	1.3974	(1.34)	1.36
N3-C14	1.3988	1.3835	1.3851	1.3717	1.3931	1.3974	(1.34)	1.38
N2-C11	1.3399	1.3415	1.3633	1.3023	1.328	1.3328	1.34	1.38
N4-C16	1.3399	1.3416	1.3722	1.3023	1.328	1.3328	(1.34)	(1.37)
N2-C12	1.4392	1.3925	1.3938	1.4178	1.4266	1.4528	(1.34)	1.37
N4-C15	1.4392	1.3925	1.3916	1.4178	1.4266	1.4528	(1.34)	(1.38)
C9-N5	1.3146	1.3181	1.3386	1.2774	1.3058	1.3115	1.34	(1.34)
C10-N6	1.3146	1.318	1.3362	1.2774	1.3058	1.3115	1.33	(1.31)
C13-N7	1.3777	1.36	1.3618	1.3547	1.3769	1.3921	(1.34)	1.34
C14-N8	1.3777	1.3599	1.3447	1.3547	1.3769	1.3921	(1.33)	1.31
C11-N6	1.3954	1.3731	1.3494	1.3703	1.3915	1.4031	(1.33)	1.30
C16-N5	1.3954	1.3732	1.3608	1.3703	1.3915	1.4031	(1.34)	(1.31)
C12-N7	1.3113	1.3253	1.3357	1.2696	1.3038	1.3015	(1.34)	1.31
C15-N8	1.3113	1.3252	1.3324	1.2696	1.3038	1.3015	(1.33)	(1.30)

Table 2 Bond Angles of H₂Pc (R = H)

methods	Am1	CNDO	INDO	MINDO/3	MNDO	Pm3	X-ray	neutron
H57-N1-C9	123.6289	124.6715	107.9053	120.4696	123.0002	124.5881		123
H57-N1-C10	123.6426	124.8549	145.7859	120.4716	123.007	124.62		129
H58-N3-C13	124.2553	124.6905	110.5909	121.4474	123.9361	124.68		(123)
H58-N3-C14	124.271	124.851	141.418	121.4484	123.9443	124.7024		(129)
C9-N1-C10	112.7285	110.4734	106.3088	119.0588	113.9928	110.7919	(108.5)	108
C13-N3-C14	111.4737	110.4585	107.9911	117.1042	112.1195	110.6175	(108.5)	(108)
C11-N2-C12	109.4386	103.0314	105.6722	112.1451	109.4446	109.1725	(108.5)	(110)
C16-N4-C15	109.4389	103.0303	107.3424	112.1451	109.4447	109.1726	108.5	110
N1-C9-N5	130.1438	127.3805	122.9054	128.4005	129.2057	128.8706	{331}	127
N1-C10-N6	130.1469	127.4915	129.4403	128.4002	129.206	128.8768	(131)	128
N3-C13-N7	128.6686	125.498	121.1077	124.4256	127.3671	127.9913	(131)	(127)
N3-C14-N8	128.6719	125.5952	128.1875	124.4248	127.3675	127.9954	(131)	(128)
N2-C11-N6	128.232	127.2065	129.0718	123.6171	125.3336	125.3244	(131)	(131)
N4-C16-N5	128.2342	127.158	121.9409	123.6156	125.3332	125.3256	131	127
N2-C12-N7	128.594	127.2318	122.8669	124.3146	126.6764	125.9856	(131)	(127)
N4-C15-N8	128.592	127.2887	128.4381	124.3153	126.6766	125.9855	131	131
C9-N5-C16	122.0543	121.7055	116.2349	132.3483	126.2271	124.9265	115	122
C10-N6-C11	122.0535	121.9233	132.9453	132.3507	126.2261	124.929	(119)	125
C12-N7-C13	123.8446	124.1513	117.2992	137.1185	127.6913	126.7706	(115)	(122)
C14-N8-C15	123.8447	124.3631	136.8763	137.1221	127.691	126.7731	119	(125)

literatures^[16,17] are noted in brackets according to their symmetry.

2 Results and Discussions

2.1 Bond Lengths

To clarify the accuracy of these six semi-empirical methods, the bond lengths and bond angles are

checked first in this and the subsequent section. The lengths of the N-H bonds in the center of this macrocycle and some of the N-C bonds are listed in Table I together with the data obtained from X-ray diffraction^[16] and neutron diffraction measurement^[17]. The data of N-H bond lengths with differences less than 0.05 Å from that of neutron diffraction^[17] and those of N-C

Table 3 Electron Population of Phthalocyanine (R = H, CNDO)

atom	charge	atom	charge	atom	charge	atom	charge
H57	0.223373	H58	0.198794				
N1	-0.353522	N3	-0.296113	N2	-0.328383	N4	-0.328510
N5	-0.288817	N7	-0.250424	N6	-0.289024	N8	-0.250605
C9	0.299199	C13	0.221332	C11	0.269376	C16	0.269233
C10	0.299325	C14	0.221343	C12	0.238551	C15	0.238629
C17	-0.014682	C21	-0.011327	C19	-0.032725	C24	-0.032745
C18	-0.014642	C22	-0.011272	C20	-0.014810	C23	-0.014788
C25	0.001421	C29	-0.008745	C27	0.000241	C32	0.000246
C26	0.001407	C30	-0.008766	C28	-0.010501	C31	-0.010524
C33	-0.007257	C37	-0.016077	C35	-0.018503	C40	-0.018515
C34	-0.007253	C38	-0.016068	C36	-0.008070	C39	-0.008066
R41	0.026479	R45	0.007141	R43	0.006642	R48	0.006646
R42	0.026488	R46	0.007151	R44	0.010693	R47	0.010683
R49	0.021826	R53	0.005413	R51	0.008098	R56	0.008091
R50	0.021824	R54	0.005411	R52	0.007848	R55	0.007833

Table 4 Electron Population of Phthalocyanine (R = H, MINDO/3)

atom	charge	atom	charge	atom	charge	atom	charge
H57	0.125026	H58	0.078323				
N1	-0.295283	N3	-0.061892	N2	-0.368382	N4	-0.368379
N5	-0.340082	N7	-0.232076	N6	-0.340091	N8	-0.232076
C9	0.361649	C13	0.117736	C11	0.347180	C16	0.347170
C10	0.361656	C14	0.117732	C12	0.283528	C15	0.283524
C17	-0.037390	C21	-0.021417	C19	-0.058975	C24	-0.058973
C18	-0.037392	C22	-0.021411	C20	-0.022277	C23	-0.022275
C25	0.035679	C29	0.022845	C27	0.034227	C32	0.034227
C26	0.035679	C30	0.022839	C28	0.018882	C31	0.018880
C33	0.013663	C37	-0.005029	C35	0.001349	C40	0.001347
C34	0.013662	C38	-0.005024	C36	0.014456	C39	0.014456
R41	0.002089	R45	-0.024520	R43	-0.019943	R48	-0.019943
R42	0.002090	R46	-0.024518	R44	-0.009429	R47	-0.009428
R49	0.002287	R53	-0.018543	R51	-0.010203	R56	-0.010202
R50	0.002287	R54	-0.018544	R52	-0.010384	R55	-0.010384

Table 5 Electron Population of Phthalocyanine (R = H, MNDO)

atom	charge	atom	charge	atom	charge	atom	charge
H57	0.318323	H58	0.300656				
N1	-0.487404	N3	-0.310163	N2	-0.402106	N4	-0.402102
N5	-0.353328	N7	-0.234773	N6	-0.353331	N8	-0.234766
C9	0.384397	C13	0.147205	C11	0.278486	C16	0.278484
C10	0.384412	C14	0.147213	C12	0.192274	C15	0.192270
C17	-0.085716	C21	-0.054371	C19	-0.105875	C24	-0.105878
C18	-0.085721	C22	-0.054369	C20	-0.061735	C23	-0.061731
C25	-0.014774	C29	-0.042014	C27	-0.015073	C32	-0.015071
C26	-0.014771	C30	-0.042017	C28	-0.035774	C31	-0.035776
C33	-0.091013	C37	-0.107002	C35	-0.108677	C40	-0.108679
C34	-0.091015	C38	-0.107001	C36	-0.086250	C39	-0.086248
R41	0.129483	R45	0.107140	R43	0.116320	R48	0.116320
R42	0.129483	R46	0.107140	R44	0.122952	R47	0.122950
R49	0.111757	R53	0.091855	R51	0.102711	R56	0.102712
R50	0.111758	R54	0.091855	R52	0.103182	R55	0.103180

Table 6 Electron Population of Phthalocyanine (R = H, Pm3)

atom	charge	atom	charge	atom	charge	atom	charge
H57	0.219820	H58	0.163000				
N1	0.000685	N3	0.383974	N2	-0.278831	N4	-0.278818
N5	-0.133748	N7	0.066741	N6	-0.133771	N8	0.066754
C9	0.075036	C13	-0.249033	C11	0.130882	C16	0.130860
C10	0.075108	C14	-0.249011	C12	-0.026739	C15	-0.026746
C17	-0.096911	C21	-0.054474	C19	-0.123034	C24	-0.123037
C18	-0.096920	C22	-0.054478	C20	-0.061344	C23	-0.061341
C25	-0.116653	C29	-0.140322	C27	-0.112641	C32	-0.112638
C26	-0.116652	C30	-0.140324	C28	-0.143750	C31	-0.143753
C33	-0.183511	C37	-0.197347	C35	-0.203740	C40	-0.203742
C34	-0.183510	C38	-0.197346	C36	-0.173477	C39	-0.173475
R41	0.221429	R45	0.207696	R43	0.212761	R48	0.212760
R42	0.221432	R46	0.207697	R44	0.216812	R47	0.216812
R49	0.200169	R53	0.189112	R51	0.196512	R56	0.196512
R50	0.200169	R54	0.189111	R52	0.194637	R55	0.194637

Table 7 Electron Population of Phthalocyanine (R = H, INDO)

atom	charge	atom	charge	atom	charge	atom	charge
H57	0.336409	H58	0.324177				
N1	-0.470423	N3	-0.404801	N2	-0.461061	N4	-0.429956
N5	-0.366844	N7	-0.342657	N6	-0.400749	N8	-0.330264
C9	0.357405	C13	0.310877	C11	0.387690	C16	0.344881
C10	0.391235	C14	0.298161	C12	0.331915	C15	0.309936
C17	-0.030031	C21	-0.032750	C19	-0.042957	C24	-0.040787
C18	-0.037234	C22	-0.017159	C20	-0.023205	C23	-0.013101
C25	0.024590	C29	0.022371	C27	0.030085	C32	0.028878
C26	0.028344	C30	0.012665	C28	0.018838	C31	0.011770
C33	0.012727	C37	0.001573	C35	0.004536	C40	0.000467
C34	0.009271	C38	0.009851	C36	0.014762	C39	0.015442
R41	-0.008374	R45	-0.017837	R43	-0.012480	R48	-0.014968
R42	-0.008584	R46	-0.017084	R44	-0.010511	R47	-0.012434
R49	-0.008107	R53	-0.014920	R51	-0.009971	R56	-0.011563
R50	-0.007885	R54	-0.016040	R52	-0.010813	R55	-0.013299

bond lengths with differences less than 0.04 Å from those of X-ray^[16] or neutron diffraction^[17] measurement are emphasized in the dark leaning style. It has been found that the data of N-H bonds calculated with Am1, MNDO and Pm3 methods are close to those obtained by neutron diffraction measurement^[17]. While the data derived from other calculation methods seem to be somewhat too large. The four N-H bond lengths obtained from INDO are close to each other but much larger than those from other methods, indicating the configuration of the geometry from INDO to be bridge-style which contrasts to the bond-style geometry deduced from the other methods. Moreover, the values of the N-C bonds calculated from INDO, CNDO, MINDO/3 and MNDO methods are close to the experimental data of X-ray^[16]

and neutron diffraction^[17] while the data due to other methods do not correspond so well with the experimental results.

2.2 Bond Angles

The position of the two inner hydrogen atoms is suggested to be very important towards the symmetry of the whole phthalocyanine molecule according to previously reported results^[11]. Its influence on the bond angles in the molecule has also been comparatively investigated for further clarification. The bond angles of H57-N1-C9, H57-N1-C10, H58-N3-C13, H58-N3-C14, C-N-C and N-C-N deduced from different methods are listed in Table 2 together with the experimental data of X-Ray^[16] and neutron diffraction measurement^[17]. The data with differences less than 2° from

that of X-ray^[16] or neutron diffraction^[17] measurement are emphasized in a dark leaning style as shown in Table 2. It has been found that the data of the H-N-C angles obtained from Am1, MNDO, Pm3 and CNDO methods agree well with the neutron diffraction^[17] measurement results and the data of C-N-C and N-C-N angles from Am1, Pm3, CNDO and MNDO correspond well with the X-ray^[16] and neutron diffraction^[17] measurement results.

2.3 Electron Distribution

The electron distribution data in the molecule were then checked. In order to get corresponding information, the nitrogen, carbon and hydrogen atoms in the molecule of H₂Pc are also divided into several subgroups (circles) according to their distance from the molecule center like that used in previous Am1 calculation^[11]. It was found that all the data of CNDO, MINDO/3, MNDO and Pm3 give further supporting evidence to the generalization deduced from Am1 calculation method^[11]. The charges of two inner hydrogen atoms are not identical. In the first nitrogen subcircle N1 is largely different from N3 while N2 is very close to N4. In the second nitrogen subcircle N5 is close to N6 and N7 is close to N8 while the later two atoms are largely different from the former ones. In the first carbon subcircle C9 is close to C10 and C13 is close to C14 which is largely different from that of C9 and C10. C11 is close to C16 and C12 is close to C15 while C12 and C15 are largely different from C11 and C16. The charges of atoms in other carbon subcircles and the hydrogen subcircles also agree with this generalization. This suggests that the generalization first observed from Am1 method^[11] is also general to CNDO, MINDO/3, MNDO and Pm3 methods.

Similar evidence could not be generalized from the data obtained from INDO method. The charge differences between atom pairs are very large and they do not show any significant symmetry. This indicates that INDO method is not appropriate for calculating the electron distribution. This conclusion actually relates with the nature of INDO calculation method, which is known as Intermediate Neglect of Differential Overlap method.

The differential overlap in all electron-interaction integrals except those involving one center are all neglected^[12]. This neglect thus limits the accuracy of the electron distribution calculation by means of this method.

3 Conclusions

(1) The geometry of free base phthalocyanine molecule is optimized at CNDO, INDO, MINDO/3, MNDO and Pm3 level without any symmetry constraint. The bond lengths of the inner N-H bonds calculated from different methods are compared with the data from neutron diffraction^[17] measurement and the data of Am1, MNDO and Pm3 are found to correspond well with the experimental results. The bond lengths of N-C bonds from different methods are compared with X-ray diffraction^[16] as well as neutron diffraction results^[17]. The data used INDO and CNDO methods seem to be more acceptable. The bond angles of H-N-C from Am1, MNDO and Pm3 agree with those provided by neutron diffraction^[17] measurement and the bond angles of C-N-C and N-C-N from Am1, MNDO and Pm3 are also in accordance with those of neutron diffraction^[17] and X-ray diffraction^[16] results.

(2) The electron distribution of H₂Pc derived from all the five semi-empirical methods is found not to be precisely symmetrical. The data obtained by four of the aforementioned method except INDO give corresponding result generalized from Am1 method^[11]. The unsymmetrical phenomenon of electron distribution for H₂Pc molecule therefore is not caused by the Am1 method itself but due to the intrinsic nature for the H₂Pc molecule according to current accuracy.

(3) To further confirm the proposition from this series of research work^[11], similar calculations on tetraporphyrin and substituted phthalocyanine using Am1, MNDO or Pm3 method is in progress. It is worth noting that although the accuracy of these three methods on the N-C bond lengths are not very good, it does not affect their usefulness because the bond lengths are not sensitive to the geometry distortion and the electron density polarization^[11].

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