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CLEVELAND OHIO DEPT OF CHEMISTRY A B ANDERSON ET AL.
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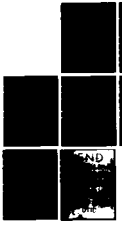

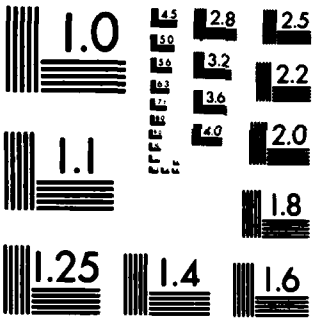
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Electronic and Redox Properties of Stacked-Ring Silicon Phthalocyanines from Molecular Orbital Theory

by

Alfred B. Anderson*, Teresa L. Gordon and Malcolm E. Kenney*

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Abstract

It is shown that the multi-peaked cyclic voltammograms for silicon phthalocyanine monomer-oligomer sets may be predicted from initial state molecular orbital energy levels if field shifts are used to allow for the charges of the anions and cations. The theory should have broad application for the understanding of the redox properties of other cofacial macrocyclic ring systems and the conductivity of doped cofacial polymers. The molecular orbital energy levels also produce the features of the optical and photoemission spectra of silicon phthalocyanine monomer-oligomer sets in the HOMO-LUMO energy regions, showing the importance of direct (π) - Pz overlap. For the dimers a 45° staggered conformation is predicted to be slightly more stable than the eclipsed conformation.

Introduction

Oxygen-bridged stacked silicon phthalocyanine ring systems are members of a class of molecular and linear-chain solid state compounds with interesting bonding[1-4] and conducting[5,6] properties. In this paper the focus is on silicon phthalocyanine monomers, dimers, and trimers. Only one monomer-dimer set has been examined by photoemission spectrosopy[7], while two monomer-oligomer sets have been examined by optical spectroscopy.[8-10] One purpose of the present study is to analyze these data on the basis of molecular orbital theory. However, the main theme of our work is to provide theoretical understanding for the interesting multi-peaked cyclic voltammograms of monomer-oligomer sets.[11,12] The model developed in this study appears to provide a method for treating and understanding redox properties of phthalocyanine ring systems in general.

The stacked silicon phthalocyanine ring systems considered here are bridged by oxygen anions and capped by $OSiR_3$ or similar groups. A representative monomer structure is shown in Fig. 1. The cap in this structure is the one used in our molecular orbital study.

The low-energy Q band of the optical absorption spectrum has, on the basis of a molecular orbital study, been assigned to $2a_{1u} \rightarrow 6e_g$ HOMO-LUMO transitions.[8] In the monomer examined by Hush[8] the main peak occurs at 1.86 eV while in the corresponding dimer it is shifted 0.11 to 1.97 eV, with evidence for weak shoulders at 1.65 and 1.82 eV. Both the monomer and dimer show high-energy shoulders which are found in many ring compounds and are due to vibrational excitations accompanying the electronic excitation.[13] The corres-

ponding trimer and tetramer show further blue shifting and shoulder widening of the band.[9] The explanation given for the main Q band peak by Hush is in terms of a model with no ring-ring orbital overlap.[8] Our discussion is in terms of π overlap. The higher energy Soret band is composed of a variety of excitations. Since they are not excitations between the π systems important to the cyclic voltammetry results, we shall not elaborate on them here.

The monomer photoemission spectrum has an emission from the $2a_{1u}$ orbital at 6.42 eV, which in the dimer splits into two emissions at 6.19 and 6.51 eV, the average value being shifted 0.07 eV to 6.35 eV.[7] The splitting is recognized to be a result of "through-space" overlap. The onset of emissions from the lower orbitals begins at ~7.9 eV for the monomer and ~7.5 eV for the dimer. The $\sigma - \pi$ emission band continues at least to ~17 eV for both molecules and shows a multi-peaked structure.[7] Our initial-state energy level calculations (which omit orbital relaxations in the cations produced on ionization) will be seen to be in good qualitative agreement with these photoemission features and the dimer splitting will be related to the multi-peaked redox properties.

There have been other molecular orbital studies of stacked phthalocyanine systems. Most closely related to our present work is an extended Huckel tight-binding calculation of the a_{1u} and e_g band widths as a function of ring spacing and rotation using a model in which the benzene-like rings are clipped off the phthalocyanine ring (the ring formed is that used in our minimal models - see Fig. 2).[4] The resulting a_{1u} and e_g bands had respective widths of 0.9

and 0.8 eV with the rings being staggered. An SCF INDO tight-binding calculation of a tetraazaporphyrin polysiloxane chain (the ring employed is that used in our intermediate models, Fig. 2) produced a_{1u} and e_g band widths of 2.00 and 1.52 eV, respectively.[3] A variety of other tight-binding calculational results have been reviewed recently,[2] as has the structure dependence of through-space splittings in various systems.[1]

In the present study it is possible to compare the calculated electronic structures within the full, minimal and intermediate models of Fig. 2. It will be seen that all three do a comparable qualitative job of describing HOMO and LUMO energy levels. Thus, the minimal models are adequate for understanding the ring optical, photoemission, and redox properties of silicon phthalocyanine monomers, dimers, and trimers.

Results and Discussion

Molecular Orbital Interpretation of Monomer and Dimer Photoelectron Spectra and Prediction for the Trimer

For the monomers our calculations place the lowest unoccupied (e_g) orbitals and the highest occupied (a_{1u}) and next occupied (framework) orbital on our energy scale as shown in Table I. Planar views of the a_{1u} and e_g π orbitals are given in Fig. 3. Our initial-state calculations do not produce relaxation shifts, which nearly uniformly decrease orbital ionization potentials, so it is understandable that the numbers in Table I are uniformly 4-5 eV too large. (Further discussion of the theoretical procedure is given in the Appendix.) Taking into account the relaxation shifts, the electronic energy level structures in Table I can be compared

with the experimental spectra given in Ref. 8. The σ-a_{1u} gap calculated for the monomer full model is 1.59 eV, agreeing well with ~1.5eV in the spectrum. The minimal model overestimates this, producing 2.68 eV and the intermediate model underestimates it at 1.37 eV.

Dimer energy levels based on minimal and intermediate dimers in eclipsed conformations are given in Table II. The g and u notations refer to bonding and antibonding combinations of the a_{1u} and e_g π orbitals. It may be seen that the σ-a_u gap closes due to the splittings. This is physically evident in the photoelectron spectrum of the dimer[7], where the gap between emissions decreases from ~1.5 eV to ~1 eV. Further, the a_{1u} splitting observed to be 0.32 eV in the dimer is predicted accurately in the calculations as 0.32 eV for the minimal dimer and 0.29 eV for the intermediate dimer. The 0.07 eV shift of the average a_{1u} energy as indicated by the spectrum is probably a relaxation effect because the splitting is symmetric in our calculations.

In Table III are given our predicted a_u splittings based on the minimal trimer. The overall splitting is 0.45 eV. These splittings should be accurate since the dimer splitting is exact within our structure and computational models.

We have examined the effects of rotating a ring out of the eclipsed conformation using the intermediate dimer. We find a monotonic increase in stability on going from an eclipsed conformation to a 45° staggered conformation, but the stability gain is only 1.0 kcal/mole, and thus we do not predict any angle preference. If this is correct, then it appears that crystal packing or solution coordination forces will determine the rotational conformations of

stacked phthalocyanine systems. An X-ray study of a solid trimer[14] shows the two outer rings rotated 16° in the same direction with respect to the inner ring. This is almost certainly the result of packing forces.

Our calculations using the intermediate model predict the a_{1u} splitting decreases from 0.28 eV to 0.02 eV on rotating 22.5° and increases to 0.25 eV at 45°, in qualitative agreement with earlier work.[4] The rotational conformation of none of the known dimers in the solid state has been published. The observed splitting of Ref. 7 could be accounted for by 0° or 45° rotation in the gas phase dimer. It seems certain that few molecules are rotated 22.5° in the gas phase as the a_{1u} splitting would then be very small. It is noted that the predicted strength of the through-space splitting seems to depend on the calculational method, extended Huckel splittings being small[4], CNDO being large[3] and DV-Xα[1] in between. If our calculations, and the extended Hückel calculations, are underestimating the through-space overlap and a_{1u} splitting, then the observed 0.32 eV splitting in the photoemission spectrum of Ref. 7 might correspond to fixing the dimer at an average intermediate rotational angle. At present there is no reason to suppose this happens.

Molecular Orbital Interpretation of Optical Q Band

Our calculations underestimate the Q band energy in the monomer. As seen in Table I, all three models produce somewhat over half of the measured monomer value of 1.86 eV.[8] For the dimer the observed main Q band peak shifts to 1.97 eV, a result of orbital relaxations in the final state cation which are not pro-

duced in our initial-state calculations, as seen on comparing Tables I and II. The presence of a single main peak for the dimers, despite the splitting of the a_{1u} and e_g orbital levels into $a_{1u}(g)$, $a_{1u}(u)$ and $e_g(g)$ and $e_g(u)$ energy levels ($a_{1u}(g)$ and $e_g(u)$ are the bonding combinations), is a result of selection rules. Only (g)→(u) and (u) → (g) are allowed in x-y polarized light. These transitions are determined to have nearly the same energy for the intermediate dimer (1.15 eV and 1.14 eV) and for the minimal dimer (1.03 and 1.00 eV), consistent with a single strong peak. Based on the intermediate dimer calculation, the forbidden $a_u(u) \rightarrow e_g(u)$ transition lies 0.29 eV towards the red and may be responsible for the observed weak low energy shoulder at 0.32 eV to the red. A similar forbidden $a_g(g) \rightarrow e_g(g)$ transition calculated to be 0.28 eV toward the blue may be obscured by the vibrational shake-up bands. The other observed shoulder 0.15 eV to the red from the main peak may be due to vibrational shake-up of the lowest energy transition. The low energy shoulder would merge well into the main peak if the rings were rotated 22.5°. The fact it is shifted relatively far into the red means the average angle probably lies near the 0 or 45° extremes.

Energy Level and Field Shift Model for Monomer, Dimer and Trimer Redox Potentials

A number of electron transfer steps are evident in cyclic voltammograms of silicon phthalocyanine monomer-oligomer sets.[11,12] (see Table IV). It might be supposed that each electron transfer step corresponds to adding one or more electrons to an e_g orbital (reduction) or removing one or more electrons from an a_{1u} orbital

(oxidation). The reversible voltammograms indicate such processes are themselves reversible. Will initial state energy levels, perhaps with an added field shift for multiple oxidations or reductions, explain the spacings of the redox potentials for these systems? This section shows that they will.

In the monomers, the oxidation and reduction waves are one-electron in nature,[11,12] and in the dimers they represent two-electron steps.[12] As will be discussed below, we suspect two-electron waves are seen for the trimers as well. For the monomer examined by Armstrong the 1.89 V gap between the first oxidation and first reduction peak matches well the splitting of 1.86 eV between the a_{1u} and e_g levels seen in Ref. 8. The second reduction peak is 0.56 V in the cathodic direction from the first peak and probably corresponds to creating a double occupancy of the degenerate e_g set yielding a triplet state, which by Hund's Rules, probably has the $(e_{gx})^1(e_{gy})^1$ configuration, though the formation of a singlet state through antiferromagnetic coupling cannot be ruled out.

Two-electron processes become allowed for the dimers and trimers because of charge delocalization among the rings. For these oligomers it is possible to relate the oxidation and reduction peak spacings to the spectra and calculated energy levels by imposing field shifts. The field shifts are the result of the charges on the molecular anions and cations. These shifts are small because of the shielding effect of the dielectric electrolyte in which the redox reactions are performed. The counter ions necessary for charge neutrality also serve to make them small. Similar valence state

field shifts have been discussed for cations in ferrous and ferric oxides.[15] Such shifts are the basis of oxidation state determinations using ESCA.

In the dimer and trimer examined by Armstrong the first reduction peaks lie at about the same voltage (-1.29 V and -1.35 V respectively) as the corresponding peak of the monomer (-1.29 V). The first oxidation peak shows a decrease from 0.60 to 0.27 to 0.08 V for the set. The 0.33 V decrease in gap between the first reduction and first oxidation potentials on going from monomer to dimer is not reflected in the optical a_{1u} to e_g excitation energy, which increases 0.11 eV.[8] However, our calculations show a decrease of 0.30 eV for the minimal model and 0.28 eV for the intermediate model; the decrease is a consequence of the splitting of the a_{1u} and e_g levels due to the inter-ring orbital overlaps. The experimental dimer to trimer decrease of 0.13 V is reproduced in our minimal dimer and trimer calculations where the decrease is 0.13 eV. Thus the calculated initial state energy levels provide an adequate basis for predicting changes in the difference between first oxidation and first reduction potentials, and the optical spectra do not. This is probably because of complicated orbital relaxations which occur in the optically excited systems, while final state relaxations accompanying the ionization processes are more uniform .

Although the above shows that the addition or subtraction of a single electron from the monomer and the addition or subtraction of pairs of electrons from the dimer and trimer are well described within the initial state one-electron framework, not a surprising result because of the ability of such calculations to deal with

photoemission spectra, field shifts must be superimposed on the level differences when additional electrons are added or subtracted. In the dimer the oxidation peaks are separated by 0.46 V. Our calculated splitting for the minimal model is 0.32 eV (agreeing exactly with the photoemission spectrum). We assign the 0.14 V difference as an "anionic field shift" due to the greater difficulty of removing a second pair of electrons, this time from the $a_u(g)$ orbital of the +2 anion in the dielectric medium. The final state of the +4 anion then has no a_u electrons. The first two dimer reduction peaks are separated by 0.36 V, compared to 0.29 eV calculated for the $e_g(g)$, $e_g(u)$ level separation, leading to a "cationic field shift" of 0.07 V. The final state, if it is high-spin, should be a quintet, but in any event it has the $(e_{gx}(u))^1(e_{gy}(u))^1(e_{gx}(g))^1(e_{gy}(g))^1$ configuration. A third reduction at 0.54 V cathodic to the second one is, as for the second reduction of the monomer, due to adding additional electrons to the degenerate e_g set.

The above field shifts are used to predict redox potentials for the trimer in conjunction with the minimal trimer model energy levels. The trimer has three oxidation peaks which must correspond to $(a_u(u_l))^2(a_u(g))^2$, $(a_u(u_l))^2$, and empty a_u orbital final state configurations. The first two are separated by 0.39 V. Adding the 0.14 V field shift to the calculated 0.23 eV $a_u(u)$, $a_u(g_2)$ level splitting produces 0.37 eV, which is in good agreement with this value. The middle and third oxidation peaks are separated by 0.46 V. The simplest approximation is to double the field shift to 0.28 V, which, when added to the calculated spacing

of 0.22 eV produces 0.50 eV, in reasonable agreement.

The first three reduction peaks correspond to $(e_{gx}(g_1))^1$ $(e_{gy}(g_1))^1$, $(e_{gx}(g_1))^1(e_{gy}(g_1))^1(e_{gx}(u))^1$ $(e_{gy}(u))^1$, and $(e_{gx}(g_1))^1(e_{gy}(g_1))^1(e_{gx}(u))^1(e_{gy}(u))^1(e_{gx}(g_2))^1(e_{gy}(g_2))^1$ final states. The first pair is spaced 0.24 V and adding the 0.07 V anionic field shift to the 0.20 eV calculated splitting yields 0.27 eV, in good agreement. Doubling the field shift for the second pair results in a prediction of 0.36 eV, in close agreement with 0.38 V from experiment. The fourth reduction peak lies 0.36 V in the cathodic direction and corresponds to an additional reduction step.

Conclusions

Our calculations illustrate the adequacy of truncated models and initial state molecular orbital theory for producing certain features of photoemission, optical, and redox potential measurements on stacked-ring silicon phthalocyanines. Through-space orbital overlaps are seen to be responsible for splittings in the photoemission and optical spectra and to provide a basis for a partial understanding of the multi-peaked cyclic voltammograms. We find in the dimer a very small dependence of total energy on ring rotation angles, with the 45^o staggered form favored by 1 kcal/mole. This implies that ring rotations which occur in molecular crystals[14] or infinite stacked chains[16] are most likely caused by steric interactions which accompany crystal packing forces. NMR solution studies suggest free rotation in the oligomeric species on the NMR time scale.[17]

Our most novel and interesting finding is the relationship of photoemission and optical spectra and our calculated energy levels

with the redox potentials of the monomer, dimer and trimer. We have shown that on oxidation and reduction it is possible to identify ionic field shifts for use in conjunction with experimental and theoretical energy level data to predict the current peaks in cyclic voltammetry. The fundamental simplicity of the theory required to understand the oxidation and reduction of the silicon phthalocyanines should hold for other similar systems. Hopefully, these findings will play a role in future understanding of electrochemical processes and catalysis by macrocyclic complexes.

Appendix

Our calculations employ the atom superposition and electron delocalization theory with a molecular orbital approximation to the electron delocalization energy.[18] The ASED theory is derived from the Hellmann-Feynman formula for electrostatic forces on nuclei in molecules. In this theory the molecular charge density is partitioned into atomic and electron delocalization (bonding) parts.[19] The atom superposition energy is calculated exactly by integrating the force due to atom superposition. The electron delocalization[20] energy is conveniently approximated by a one-electron molecular orbital energy using a molecular hamiltonian similar to the extended Huckel hamiltonian. Parameters used in this study are in Table V.

Acknowledgment

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Table I. Energies of the HOMO (a_{1u}), LUMO (e_g), and σ orbitals using minimal, intermediate, and full models of the monomer (eV). Δ indicates energy level separation (eV).

Orbital	minimal		intermediate		full	
	energy	Δ	energy	Δ	energy	Δ
e_g	-9.42	1.01	-10.51	1.14	-10.08	0.98
a_{1u}	-10.43	2.68	-11.65	1.37	-11.06	1.59
σ	-13.11		-13.02		-12.65	

Table II. As in Table I, for dimer (eV).

	minimal		intermediate	
Orbital	energy	Δ	energy	Δ
$e_g(g)$	-9.27		-10.36	
		0.29		0.28
$e_g(u)$	-9.56		-10.64	
		0.71		0.86
$a_u(u)$	-10.27		-11.50	
		0.32		0.29
$a_u(g)$	-10.59		-11.79	
		2.54		0.65
σ	-13.13		-12.44	

Table III. As in Table I for minimal trimer.

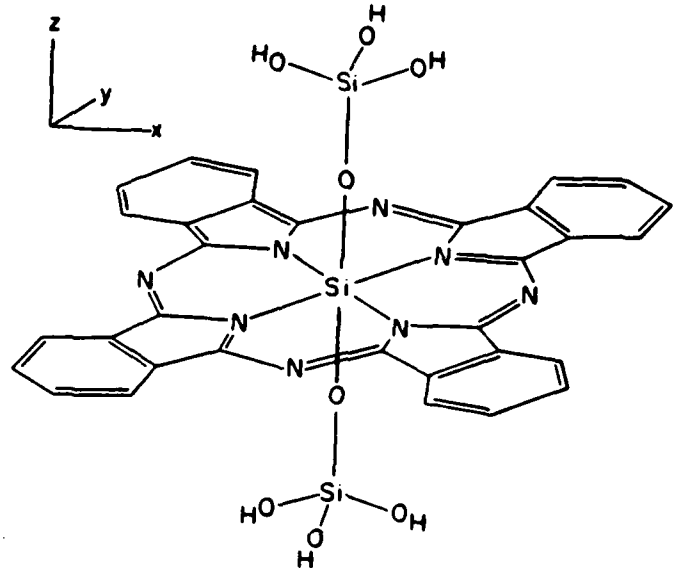
orbital	minimal energy	Δ
$e_g(g_2)$	-9.20	
		0.22
$e_g(u)$	-9.42	
		0.20
$e_g(g_1)$	-9.62	
		0.58
$a_u(u_2)$	-10.20	
		0.23
$a_u(g)$	-10.43	
		0.22
$a_u(u_1)$	-10.65	
		2.49
σ	-13.14	

Table IV. Oxidation and reduction potentials from Ref. 11 (vs. $Ag/AgClO_4$).

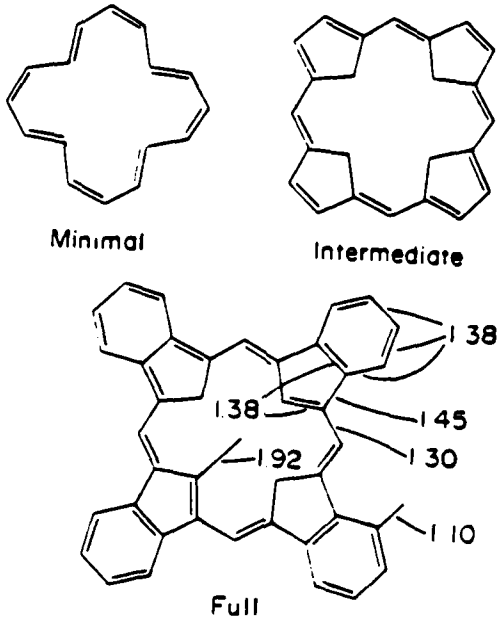
	Oxidation Potential,(V)			Reduction Potential(V)			
Monomer			0.60	-1.29	-1.85		
Dimer		0.73	0.27	-1.29	-1.65	-2.19	
Trimer	0.93	0.47	0.08	-1.35	-1.59	-1.97	-2.33

Table V. Parameters used in the calculations: principal quantum number (n), ionization potential (IP) in eV, orbital exponents (ζ) in a.u.

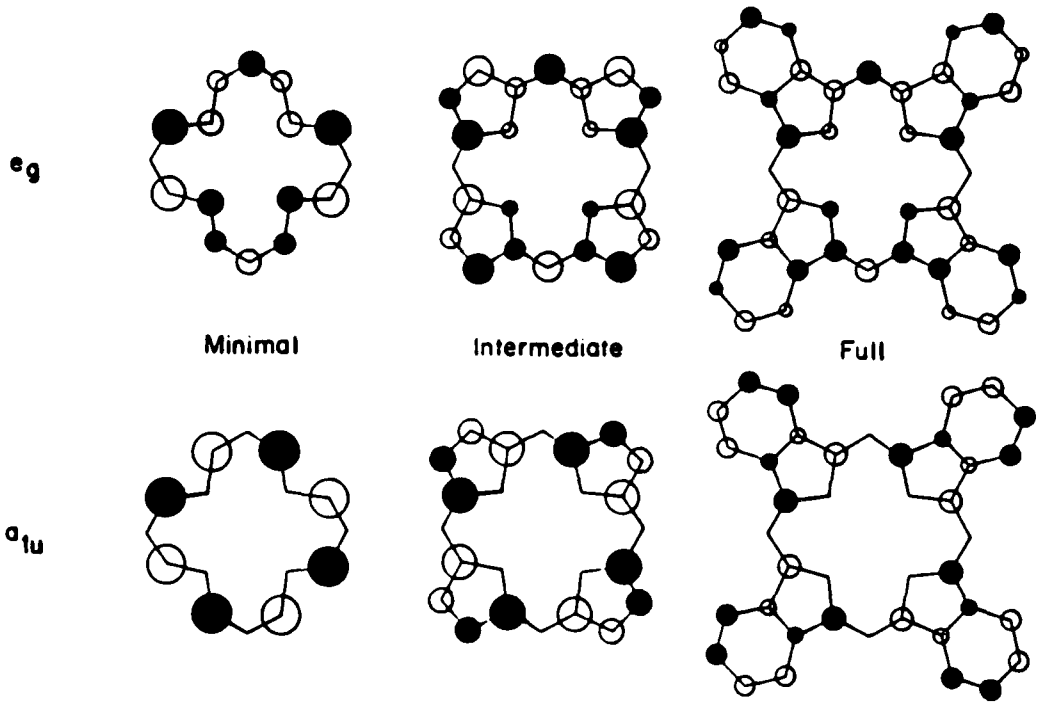
Atom	s			p		
	n	IP	ζ	n	IP	ζ
Si	3	13.46	1.634	3	8.15	1.428
O	2	28.48	2.246	2	13.62	2.227
N	2	20.33	1.924	2	14.53	1.917
C	2	20.00	1.658	2	11.26	1.618
H	1	13.6	1.3	-	-	-



1. Silicon phthalocyanine monomer structure based on the X-ray study of the trimer in Ref. 14. Hydroxyl groups in the caps are models. The particular oligomer of Ref. 14 has, in place of the hydroxyls, a $-CH_3$ and two $-OSi(CH_3)_3$ groups. The Si-O distance is 1.66 Å and ring spacing is 3.32 Å.



2. Structures of minimal, intermediate, and full models. Indicated bond lengths are based on Ref. 14. C_6 ring angles are set equal to 120°, and the phthalocyanine ring system is flattened out.



3. Highest occupied a_{1u} and one of the degenerate set of lowest unoccupied e_g orbitals for the minimal, intermediate and full modes.

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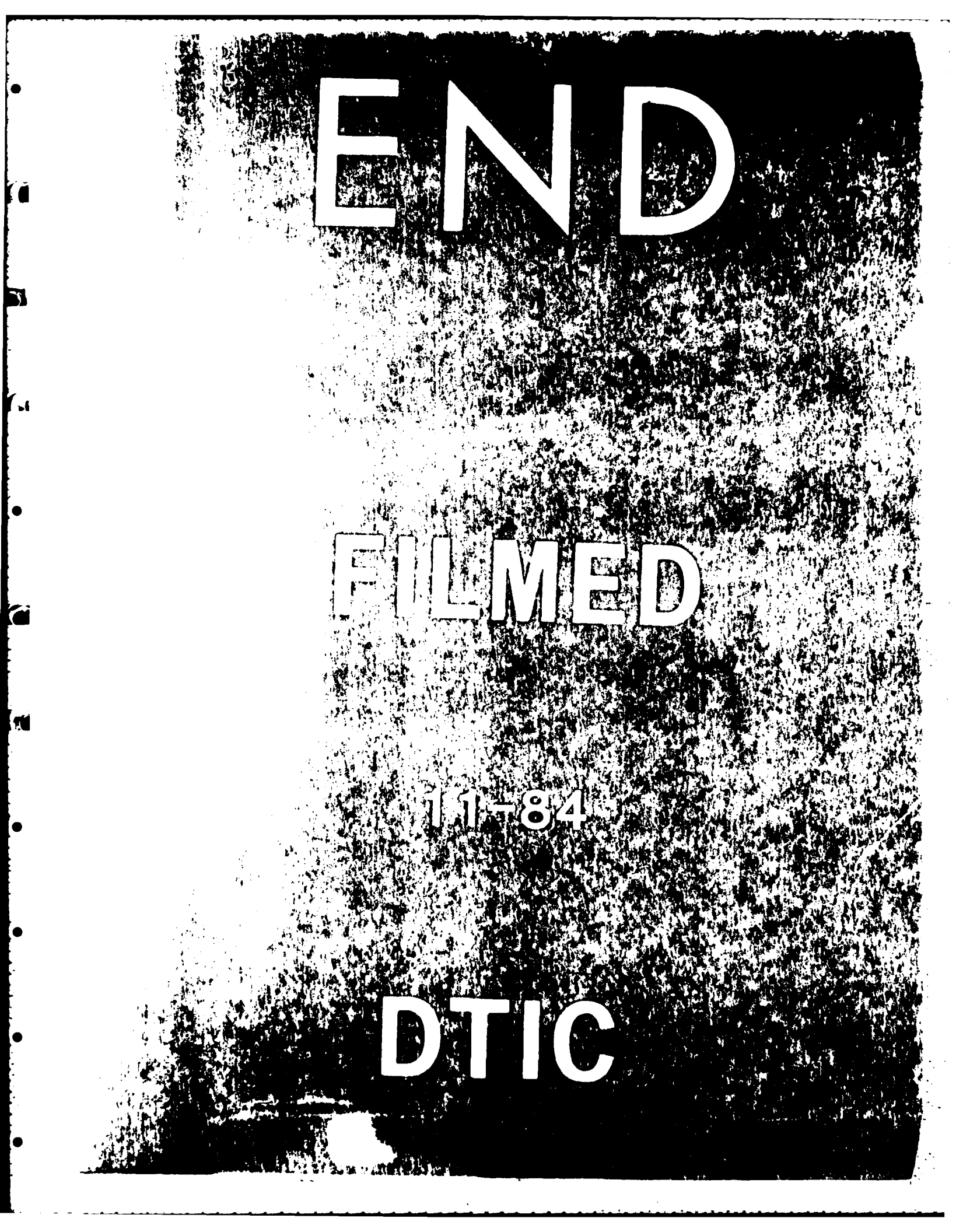
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