

X-ray Photoelectron and Optical Absorption Spectroscopic Studies on the Dye Chlorodiane Blue, Used as a Carrier Generation Molecule in Organic Photoconductors

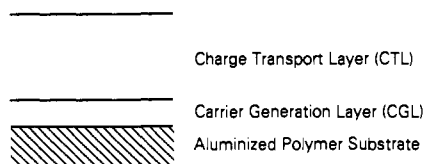
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Abstract: The dye chlorodiane blue, used as a carrier generation molecule in organic photoconductors, is characterized via optical absorption and X-ray photoelectron spectroscopy, and the results are interpreted on the basis of ab initio quantum mechanical molecular models. These data indicate that chlorodiane blue exists as azo-enol and hydrazone-quinone chemical structures and it is the hydrazone-quinone form that provides the higher xerographic gain in electrophotographic applications. Optimized geometries, atomic charges, and molecular orbital plots and energies are reported for both the azo-enol and hydrazone-quinone forms of chlorodiane blue. The two structural forms of the dye are experimentally distinguishable via both optical absorption and X-ray photoelectron spectroscopy, and the wavelength and chemical shifts, respectively, are interpreted via the theoretical results.

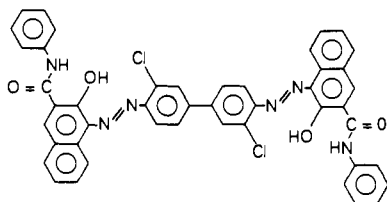
Introduction

Most modern day copiers and printers utilize an electrophotographic process to produce printed material. In order for the electrophotographic process to operate efficiently, organic layered photoconductors, a profile of which is shown below, were invented.



This design, that is a physical separation of the charge generators and hole transporters into two layers, allows each function to be independently optimized. An explanation of the electrophotographic process and of organic layered photoconductors is extant in the literature.¹

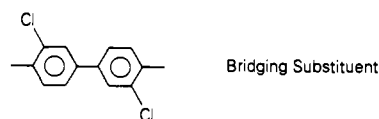
The organic materials in both the charge generation and hole transport layers are subjected to several hundred thousand charge and discharge cycles. For commercial acceptance, the photoconductor must remain a good electrical insulator in the dark and conductor in the light. This places severe demands on the organic materials used in the hole transport and carrier generation layers.^{2,3} Polyazo pigments like chlorodiane blue, the structure of which is shown below, represent just one family of molecules that may



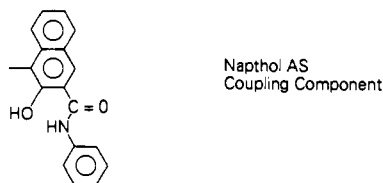
Chlorodiane blue (CDB)

be used as charge or carrier generation molecules in electrophotographic applications.² A major impetus for the use of polyazo dyes as an organic photoreceptor is that very fine particles are readily obtained. Fine particles lead to uniform coating which in turn minimizes electrical noise, important for high-resolution applications using liquid developers or dry toning with small particles. Additionally, polyazo dyes exhibit excellent spectral sensitivity to ≈ 700 nm, compatible with many of today's laser printheads.^{3,4}

It has recently been reported that the photosensitivity of polyazo-based photoreceptors are strongly dependent upon both chemical structure and morphology of the dye. With respect to the former, Nguyen et al.³ have divided the chemical structure of polyazo dyes like chlorodiane blue (CDB) into two basic structural components: a "bridging" substituent represented by the dichlorobiphenyl fragment in CDB above, and a "coupling"



Bridging Substituent



Naphthol AS Coupling Component

component which in CDB is Naphthol AS. A variety of structurally related bridging and coupling fragments useful in electrophotography are summarized by Nguyen and Weiss.³ From their studies, it is apparent that chlorodiane blue itself exhibits one of the highest sensitivities for photodischarge on a relative scale compared to other polyazo-based pigments. Apparently, a bridging substituent with high electron affinity enhances photosensitivity. Modification of the coupling moiety has also been observed to enhance sensitivity, for example by replacing the -CONH- amido structural moiety of the Naphthol AS coupling component in CDB with a -CONHN=CH-Ar group, Ar being an aromatic structural moiety.³

Conversely, the morphological aspects of polyazo dyes seem somewhat less understood, and it is reported that the α -form of the bisazo pigment exhibits the highest sensitivity.³ Khe et al.⁵ have also reported on how the sensitivity of chlorodiane blue depends upon structure and morphology and, in addition, have published an optical absorption spectrum of the most efficient polyazo dye but without relating it to a specific structural form of the dye. They reported that as the optical absorption spectrum of chlorodiane blue shifted toward shorter wavelengths, the efficiency for carrier generation and/or injection diminished.

To our knowledge, there is very little information in the literature characterizing the solid-state structure of the polyazo dye chlorodiane blue and its relevance in photoconduction. In this

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report, we continue our studies on organic photoconductors with particular emphasis on the chemical components contained in organic layered photoconductors.⁶ This effort is designed to ultimately obtain an understanding of the origins of photoconductor electrical fatigue which is incurred by organic photoconductors after extensive use in electrophotographic applications and/or exposure to room light.^{6,7} Elucidation of the cause and effects of electrical fatigue in organic photoconductors is presently an important area of research^{2,3,6,7} and mandates complete characterization of its chemical components to provide a direction for improving their long-term stability. Chlorodiane blue represents a particularly challenging problem because of the largely intractable nature of the material. We describe herein spectroscopic studies of the polyazo dye chlorodiane blue, in an effort to understand the importance of its structural parameters with respect to spectral sensitivity and photoconductivity. Accordingly we report the solid-state X-ray photoelectron spectra and liquid- and solid-state optical absorption spectra of chlorodiane blue and interpret these results where suitable with ab initio quantum mechanical molecular models. These results indicate that chlorodiane blue may exist primarily as a mixture of azo-enol and hydrazone-quinone forms in the solid state. However, when solid-state films of chlorodiane blue are exposed to acidic and/or acid-containing solvents, the solvent contact causes the hydrazone-quinone form to be preferentially formed at the interface between the carrier generation and hole transport layers, in an organic layered photoconductor architecture. The hydrazone-quinone form absorbs light at longer wavelengths, and it is this form that demonstrates the greatest photoconductivity effect.

Experimental Section

Chlorodiane blue was obtained from commercial sources. For XPS measurements, samples of chlorodiane blue or CDB were spin coated onto polished Si wafers (2000 Å) from a 3% by weight solution of CDB in ethylenediamine (EDA) and dried (in the dark) at 50 °C for 2 weeks. Another set of samples were spin coated similarly and dried for 1 week and then exposed to tetrahydrofuran (THF) solvent for 1 min, followed by additional drying at 50 °C for an additional week. Treatment with tetrahydrofuran changes the chemical structure of chlorodiane blue, and thus these samples are designated CDB/EDA and CDB/THF, respectively. XPS measurements were made on a VG Scientific 5000 ESCA spectrometer with an Al K α source ($E = 1486.7$ eV). Data were typically acquired with a 20 eV pass energy, and pressure in the sample chamber was typically 1×10^{-9} Torr.

Curve fitting to determine binding energies and relative intensities was performed with an iterative least-squares computer program using a combination of Gaussian and Lorentzian line shapes to best fit the experimental envelope. Prior to the curve fitting, the spectra were corrected for the inelastic background shape by subtracting the contribution of the inelastic electrons using the Shirley method.⁸ All binding energies were referenced to the lowest energy C_{1s} line at 284.6 eV (aromatic CC bonds) as is standard practice for (organic) insulating materials.⁹ The magnitude of the charge correction was 0.1 and 1 eV for CDB/EDA and CDB/THF, respectively. Collection times for the C_{1s}, N_{1s}, O_{1s}, and Cl_{2p} core lines were typically 10–20 min (10–20 scans) while valence levels required ≈ 2 h (150 scans). As a check for radiation damage, the constancy of the ratios of the core level peak intensities and positions were taken as evidence that no significant radiation damage occurred.

Optical absorption studies of solid films of chlorodiane blue were prepared simultaneously and identically with the XPS samples, only a quartz substrate was substituted for the Si wafer. The optical absorption spectra of these two samples mirror the XPS samples, with one sample being spin coated from ethylenediamine and the other subsequently exposed to tetrahydrofuran. These samples were dried as described above for the XPS samples. Additionally, to normalize all data, we have prepared films of chlorodiane blue, 0.2 μm thick, on aluminized poly(ethylene terephthalate) such as used in organic photoconductor applications.⁶ Finally, liquid-state spectra of CDB in a variety of solvents were prepared in the following manner. Due to the low solubility of CDB in the solvents, a saturated solution of CDB in solvent (pyridine, ethanol,

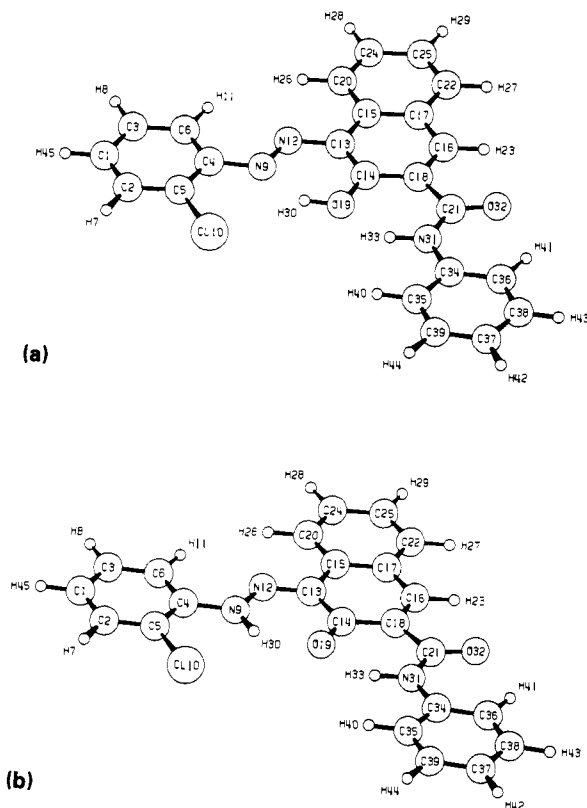


Figure 1. RHF/3-21G optimized geometries for (a) HCDBA and (b) HCDBH.

trifluoroethanol, tetrahydrofuran, and glacial acetic acid) was stirred and filtered through a small silica gel column followed by Whatman filter paper to remove particulates, i.e., undissolved chlorodiane blue, and spectra were then recorded immediately. For the optical absorption studies, a Perkin-Elmer Lambda Array 3840 UV-visible spectrophotometer equipped with a Model 7700 computer was used. The chemical solvents used in these studies were obtained from commercial sources in their highest grade and used without further purification.

Computational Details

Molecular orbital calculations on chlorodiane blue were performed with the vectorized IBM version of the Gaussian 88 computer code.¹⁰ The optimized geometries for half of the CDB molecule, for both the azo-enol and hydrazone-quinone forms, are reported and have been assigned the acronyms HCDBA and HCDBH, respectively (for example, HCDBA having the meaning Half CDB, Azo). The optimized geometries are shown in Figure 1. The calculations for the half CDB structures were performed at the SCF level of theory utilizing the computationally efficient and reliable 3-21G basis set. The ab initio geometry optimizations for HCDBA and HCDBH required 500 and 565 h of CPU time, respectively, using the Gaussian 88 IBM/AIX3 version with an IBM RS6000 Model 530 work-station. Neither analytical nor numerical second derivative calculations for their frequencies were attempted because of the size of the calculations. No symmetry constraints were placed on the geometry optimizations. As shown in Figure 1, both HCDBA and HCDBH are planar molecules. These results are consistent with crystal structure data of structurally analogous molecules.^{11–14} The HF/3-21G total energy for the hydrazone HCDBH, -44735.01 eV, is lower than the azo HCDBA, -44734.73 eV, by approximately 0.3 eV. The major changes observed in bond lengths and bond angles are attributable to differences in the azo-enol versus hydrazone-quinone structures.¹⁵ Additionally, complete geometry optimizations were per-

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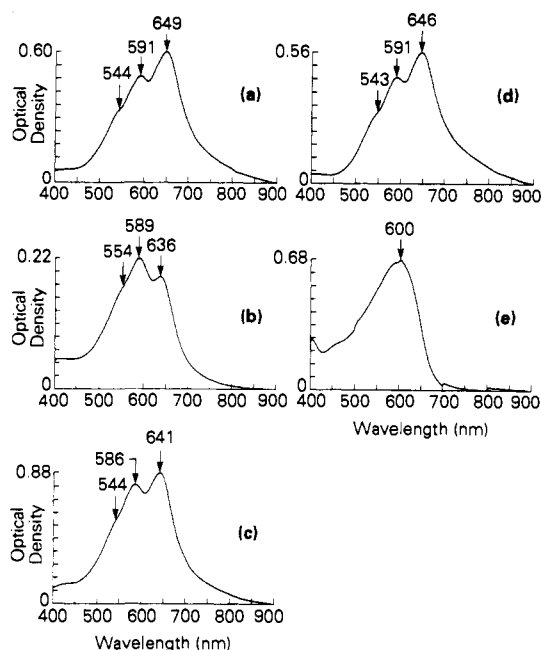
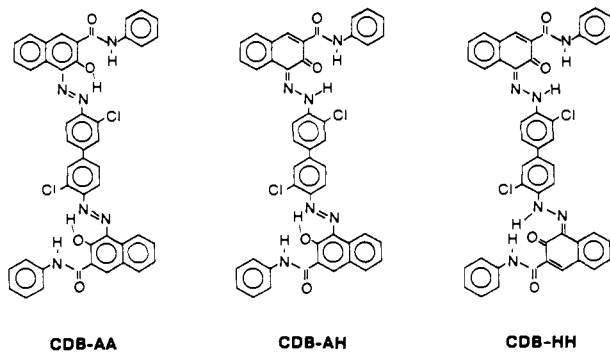


Figure 2. Liquid-state optical absorption spectra of chlorodiane blue as a function of solvent. Chlorodiane blue in (a) glacial acetic acid, (b) pyridine, (c) tetrahydrofuran, (d) ethanol, and (e) ethylenediamine (EDA).

formed on the full azo and hydrazone forms of CDB using the semi-empirical restricted closed shell AM1¹⁶ formalism; they are not presented here.¹⁵

Results and Discussion

Optical Absorption Studies on CDB. (a) Liquid Phase. The complexity of the chlorodiane blue (CDB) chemical structure necessitates a discussion of liquid-phase optical absorption data before solid-state spectra may be understood. The complexity arises from the azo-enol and hydrazone-quinone tautomeric forms that exist for this class of molecules, i.e., arylazonaphthols like CDB; three possible forms are shown below. It is important to characterize the structure of the chlorodiane blue dye in the liquid state because commercial photoconductors using CDB are typically coated from amine bases, or solvent-amine base mixtures, and it has been shown that photosensitivity of the organic photoconductor is strongly dependent upon the chlorodiane blue morphology and/or structure that finally prevails in the carrier generation layer.^{3-5,17} Photosensitivity is defined as the *gain*, or number of mobile carriers generated per absorbed photon, and it is desirable to maximize the gain of a photoconductor system. Chlorodiane blue or CDB is traditionally thought of as an azo dye with the characteristic -N=N- linkage; however, as shown below, may



well exist in at least three different forms,¹⁸ an azo-azo (CDB-

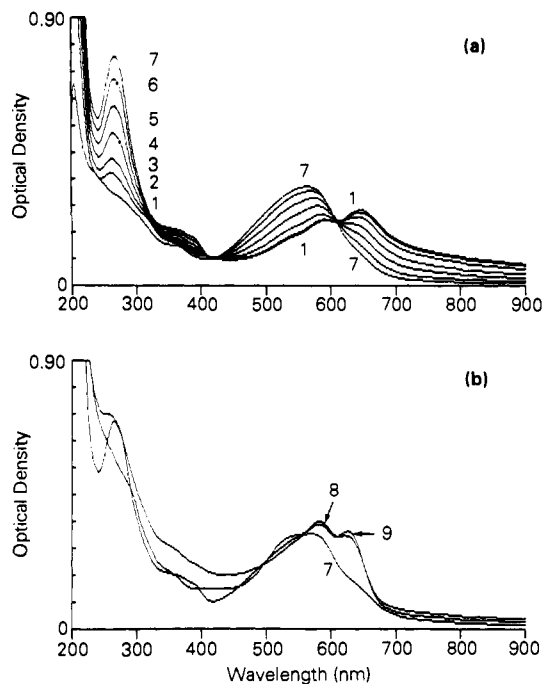


Figure 3. The effect of basicity or acidity on the optical absorption spectrum of chlorodiane blue in 2% by volume of water in ethanol. In (a), trace 1 is CDB in 2% H₂O/EtOH; traces 2-7 show the effect of adding a basic solvent (NaOH, H₂O, and EtOH mixture). In (b) acidic solvent (HCl, H₂O, and EtOH mixture) is added to trace 7. Traces 8 and 9 show the effect of adding the acidic solvent.

AA), an azo-hydrazone (CDB-AH), and a hydrazone-hydrazone (CDB-HH) form, depending upon the polarity or basicity of the solvent.¹⁹ In strongly alkaline solutions, the anion of the azo form is believed to occur^{19,20} while in strong acids either the hydrazone itself^{19,20} or a protonated form²¹ prevails. Liquid-state optical absorption spectra of CDB in a variety of solvents are shown in Figure 2. The spectrum for CDB in glacial acetic acid, Figure 2a, reveals an absorption maximum at 648 nm with two additional and distinct shoulders at 591 and \approx 545 nm. In glacial acetic acid, the hydrazone form of chlorodiane blue predominates.¹⁹ Conversely, the spectrum for CDB in pyridine, Figure 2b, reveals an absorption maximum at 589 nm with two additional peaks at 638 and \approx 550 nm. Clearly the absorption maximum for CDB has blue-shifted; in accordance with literature data,¹⁹ the spectrum for CDB in pyridine corresponds predominantly to the azo structure of the dye. Overall, the visible absorption maxima of CDB are considerably red-shifted compared to the structurally analogous 1-phenylazo-2-hydroxy-3-naphthalide,²⁰ by \approx 100 nm. A comparison of spectra a and b in Figure 2 together with previous literature data on hydroxyazo aromatics¹⁷⁻²² suggest, however, that the hydrazone may be identified by the 640-nm band while the azo is characterized by the 590-nm absorption band. Figure 2 shows the optical absorption spectrum of CDB in several other solvents. In tetrahydrofuran and ethanol, the shapes of the absorption curves are virtually identical to the one observed in glacial acetic acid, consequently we conclude that the hydrazone form of CDB prevails in these solvents also. Conversely, the shape of the electronic absorption spectrum of chlorodiane blue in ethylenediamine resembles much more the shape observed in pyridine but without the 638-nm absorption band, and thus the azo form of CDB must predominate here. Ethylenediamine is, of course, somewhat basic ($\text{p}K_b \approx 4$), and in order to preclude assignment of the optical absorption maximum at 590 nm to an anionic form

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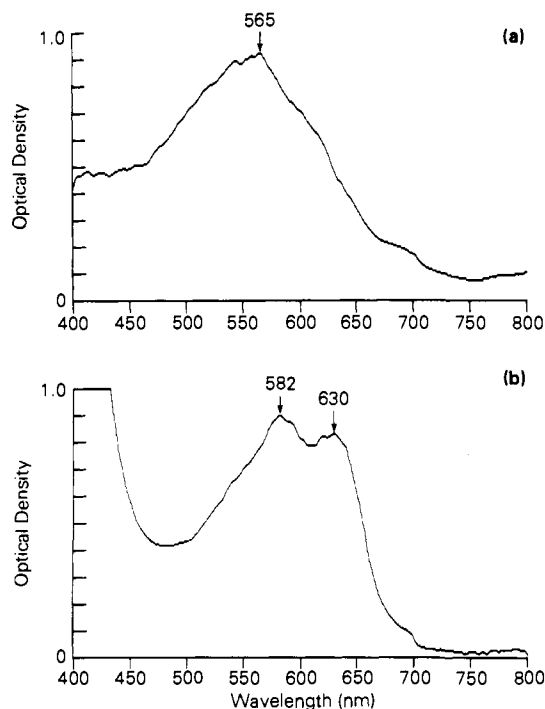


Figure 4. Solid-state optical absorption spectra of chlorodiane blue on aluminized polymer coated from (a) ethylenediamine and tetrahydrofuran co-solvent and (b) the sample in (a) overcoated with a charge transport layer. The absorption below 450 nm is attributed to the hole transport molecule *p*-(diethylamino)benzaldehyde diphenylhydrazone.

of the azo structure in CDB, Figure 3 is presented which shows a series of spectra for CDB in increasingly alkaline alcoholic solution. In basic solutions, CDB is deprotonated shifting its absorption maximum to 565 nm, considerably blue-shifted from the azo absorption maximum. Trace 1 in Figure 3a is the predominantly hydrazone form of chlorodiane blue, as investigated previously in Figure 2. With increasing alkalinity of the solvent, as shown in traces 2–7, the absorption band maximum of chlorodiane blue changes dramatically from 638 to 565 nm and exhibits an isosbestic point at 608 nm. On the basis of analogous data,²⁰ we assign the 565-nm absorption to the anion form of the azo dye. The hydrazone form of CDB may be recovered by increasing the acidity in the solvent (traces 8 and 9 in Figure 3b).

(b) Solid State. The solid-state optical absorption spectrum of the coated carrier generation layer (CDB on aluminized polymer substrate) and a completely coated organic layered photoconductor are shown in Figure 4. The solid-state optical absorption spectrum of a film of CDB, Figure 4a, coated from ethylenediamine/tetrahydrofuran co-solvent and dried (as described in the Experimental Section), shows an absorption maximum at 565 nm. This is considerably blue-shifted from the liquid phase (Figure 2b, 589 nm band maximum) and is tentatively attributed to solid-state effects.

In the organic photoconductor, after the carrier generation layer (on the aluminized polymer substrate) is prepared, a 20 μm thick charge transport layer is coated on top of the carrier generation layer. The composition of the charge transport layer is typically 40% by weight mixture of a hole transporting molecule like *p*-(diethylamino)benzaldehyde diphenylhydrazone and a polymer like bisphenol A polycarbonate.²³ Because the charge transport layer is coated from a solvent, in this case a mixture of tetrahydrofuran and toluene, the surface of the chlorodiane blue dye layer is in intimate contact until the solvent is evaporated. This contact of chlorodiane blue with the solvent introduces dramatic changes in the optical absorption spectrum of the dye. A comparison of the spectra in parts a and b of Figure 4 reveals that the coating process causes the absorption band maximum at 565

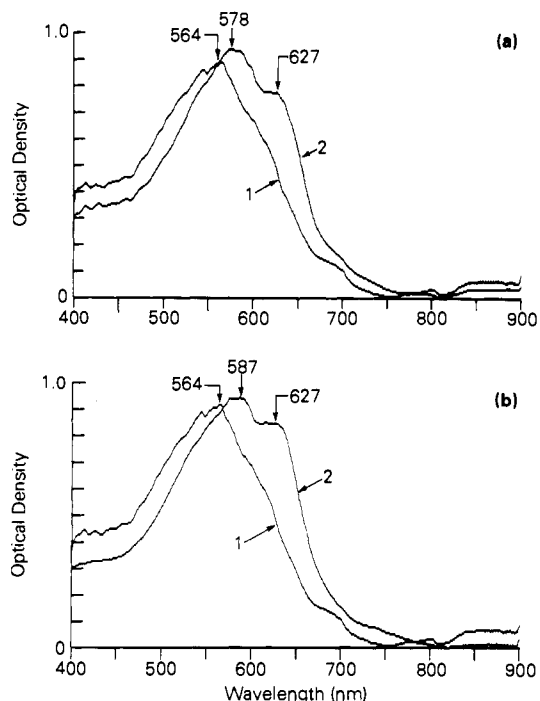
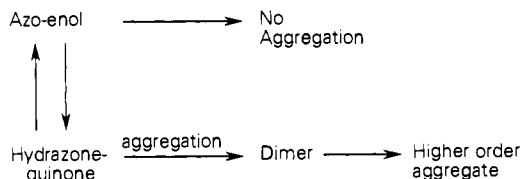


Figure 5. Solid-state optical absorption spectra of chlorodiane blue on aluminized polymer. In (a) trace 1 shows the spectrum of CDB coated from ethylenediamine/tetrahydrofuran co-solvent, and trace 2 shows the same sample after exposure to the vapor of glacial acetic acid and then drying. In (b) trace 1 shows the spectrum of CDB coated from ethylenediamine/tetrahydrofuran co-solvent, and trace 2 shows the sample after immersing the sample into tetrahydrofuran for several seconds and then drying.

nm (Figure 4a) to red-shift to 582 and 630 nm. The shape of the electronic absorption is quite reminiscent of the hydrazone form of the dye; compared to the liquid spectrum of CDB in glacial acetic acid, Figure 2a, the band maxima here are also blue-shifted by 10–20 nm in the solid state. Thus we observe in the solid state that by coating a charge transport layer atop the chlorodiane blue layer, the predominantly azo form of the dye initially coated now contains appreciable hydrazone in the finished photoconductor. Because chlorodiane blue has limited solubility in most organic solvents, the conversion to the predominantly hydrazone form of the CDB dye might have occurred primarily at or near the surface, which nevertheless is significant for photoconductor applications since carrier injection from the dye into the hole transport molecule is an interfacial process. The optical absorption spectrum of chlorodiane blue shown in Figure 4b is similar to the optical absorption spectrum of chlorodiane blue published by Khe et al.,⁵ which exhibited the best photoconductivity effect, i.e., gain. They reported a gain of ≈ 0.2 at 660 nm compared to 0.06 at 590 nm.⁵ On the basis of these data, we conclude that the hydrazone structure of chlorodiane blue exhibits the highest xerographic gain, and is in fact the desired molecular structure of chlorodiane blue to use in electrophotographic applications. To better understand these aspects, a sample of the carrier generation layer was exposed to the vapor of glacial acetic acid and the results are shown in Figure 5a. After exposure to the acid, we observe a shift of the solid-state spectrum from 564 to 587 and 627 nm, consistent with the hydrazone. When the solid CDB film (after coating from ethylenediamine) is immersed in tetrahydrofuran solvent, a similar red-shift is observed in Figure 5b. In both instances, the shifting of the band maximum from 564 to 627 nm increases significantly the optical absorption between 630 and 700 nm. The origin of the spectral red-shift may in part be attributed to the following: the solvent in intimate contact with CDB allows some conversion of azo to hydrazone form. Once the solvent evaporates, the hydrazone form of the dye is left which is then free to aggregate, thereby causing a red-shift of the optical absorption. It has been demonstrated using a variety of spectroscopic techniques²⁴ that

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only the hydrazone-quinone form of azo dyes participates in molecular aggregation. The azo-enol form is relatively inactive toward the formation of molecular aggregates. In conclusion,



regardless of whether or not molecular aggregation has actually occurred in the solid form of CDB, the most important fact is that conversion to the hydrazone-quinone form of the dye is responsible for the spectral red-shift. If molecular aggregation persists in the solid state of chlorodiane blue, it is only because of its conversion first to the hydrazone-quinone form, thus the latter is the important species involved and is the pertinent structure of the dye for photoconductors.

Optical Absorption and ab Initio Studies on CDB. One of the important results of the theoretical studies on chlorodiane blue, apart from elucidation of the optimized chemical structure, is characterization of the electronic structure. This is decidedly pertinent to the optical absorption studies discussed above, and molecular orbital pictures for the HF/3-21G half CDBs are shown in Figure 6. The computed energy levels reveal that the highest occupied molecular orbitals (HOMO) for HCDBA and HCDBH are -8.00 and -8.03 eV, respectively, and the lowest unoccupied molecular orbitals (LUMO) for HCDBA and HCDBH are 0.60 and 0.30 eV, respectively. Thus ab initio predicts a smaller band gap for the HOMO \rightarrow LUMO transition for HCDBH, 8.3 eV, compared to HCDBA, 8.6 eV, as might be expected on the basis of experimental data. While the values obtained from the gas-phase calculations are not directly comparable to the experimental data due to a lack of accounting for solid-state effects, the relative trends are definitive. Additionally, from Koopmans' theorem, the calculated gas-phase ionization potentials are essentially identical for both HCDBA and HCDBH at 8.0 eV.

The ab initio molecular orbital plots, shown in Figure 6, are relatively similar for HCDBH and HCDBA. In HCDBA, the HOMO wave function is localized primarily on the phenylamido group while for HCDBH the HOMO wave function does include the hydrazone amine N9 (refer to Figure 1) and the carbonyl O19, albeit weakly. Thus the HOMO for HCDBA consists primarily of the lone pair of electrons that reside on the p orbitals of the oxygen and nitrogen atoms and the π p orbitals in the phenylamido group. In HCDBH, there is an additional although weak contribution to the HOMO wave function from the lone pair of electrons on the hydrazone amine nitrogen atom (N9 in Figure 1) and the carbonyl oxygen atom O19. For both molecules, the HOMO and the second highest occupied molecular orbital (2HOMO) differ by ≈ 0.3 eV. The LUMOs for both HCDBA and HCDBH are qualitatively very similar, delocalized over the phenylazaphthol and phenylazonaphthoquinone, respectively. The LUMOs in both cases are antibonding with respect to the $-N=N-$ and $-NH-N=$ bonds. An electronic excitation from the HOMO to the LUMO may be viewed in both HCDBH and HCDBA as primarily an excitation where charge is moved from the phenylamido to regions between the $-N=N-$ and naphthol bonds.

XPS Data on CDB. Samples of chlorodiane blue films, all spin coated from ethylenediamine and some immersed in tetrahydrofuran thereafter, were interrogated in the solid state via optical absorption studies prior to sampling by the X-ray photoelectron spectrometer. The optical absorption spectra are shown in Figure 7. As in the previous studies, the solid films coated from ethylenediamine (EDA) have an optical absorption maximum at 560 nm and hence are primarily the azo form of the dye. The CDB films after treatment in tetrahydrofuran (THF) have maxima at 590 and 630 nm, corresponding to predominantly the

Table I. XPS Elemental Composition for CDB, $C_{46}N_6O_4Cl_2$

element	formula	XPS data	
		CDB-AA	CDB-HH
C	0.793	0.775	0.795
N	0.103	0.103	0.085
O	0.069	0.067	0.061
Cl	0.034	0.060	0.055

Table II. C_{1s} Binding Energies for CDB-AA and CDB-HH

bond	CDB-AA			CDB-HH		
	E_b (eV)	formula	expt	E_b (eV)	formula	expt
CC	284.6	0.59	0.67	284.6	0.59	0.70
CN	286.2	0.14	0.20	286.2	0.14	0.16
CO	288.0	0.07	0.09	287.7	0.07	0.08
CCl	291.7 ^a	0.03	0.05	291.1 ^a	0.03	0.06

^aOverlap with CC aromatic $\pi \rightarrow \pi^*$ shake-up transition.

Table III. N_{1s} , O_{1s} , and Cl_{2p} Binding Energies for CDB-AA and CDB-HH

atom	bond	CDB-AA		CDB-HH	
		E_b (eV)	expt	E_b (eV)	expt
N_{1s}	$-N=N-$	400.2	1.0	400.1	1.0
	$>N-$				
	$=N-N<$				
O_{1s}	$>C=O$	533.2	0.20	533.4	0.53
	$>C_6H_5-OH$	531.2	0.8		
	$-NH-CO-$	531.2		531.1	0.47
Cl_{2p}	$2p_{3/2}$	200.8	0.67	200.7	0.60
	$2p_{1/2}$	202.5	0.33	202.3	0.40

hydrazone form. We designate the former as CDB/EDA and the latter as CDB/THF to distinguish the two forms of the dye.

The XPS data for both CDB/EDA and CDB/THF are summarized in Tables I and II. For both CDB-AA and CDB-HH, the experimentally determined elemental ratios are in excellent agreement with the calculated stoichiometry.

The detailed XPS core ionization spectra for C_{1s} , N_{1s} , O_{1s} , and Cl_{2p} for both CDB/EDA and CDB/THF are summarized in Figure 8 and Table II. For CDB/EDA the C_{1s} main line occurs at 284.6 eV, with additional peak centers fit at 286.2 , 288.0 , and 291.7 eV. The fractional areas from peak fitting and those expected from the chemical formula are summarized in Table II and are in good agreement. The main line at 284.6 eV corresponds to the aromatic CC bonds while the CN bonds occur at 286.3 eV. The additional peaks at higher energies may correspond to CO or CCl but aromatic π to π^* shake-up transitions undoubtedly overlap, and thus no attempt is made to obtain quantitative elemental ratios from these peaks. For CDB/THF the C_{1s} main line occurs at 284.6 eV, with additional peak centers at 286.2 , 287.7 , and 291.1 eV. As with CDB/EDA, the fractional areas from peak fitting of CDB/THF and those expected from the chemical structure are reasonably matched (Table II). The binding energies for the N_{1s} , O_{1s} , and Cl_{2p} for CDB/EDA and CDB/THF are summarized in Table III. The N_{1s} main line occurs at 400.1 – 400.2 eV for both materials. The Cl_{2p} lines occur at ≈ 200 and 202 eV in the expected two-to-one ratio and in both cases exhibit the normal 1.6 eV spin-orbit splitting.

The O_{1s} core ionization peaks for CDB/EDA and CDB/THF (Figure 8 and Table III) are significantly different and will be considered in greater detail. While both samples have their binding energy peaks at approximately 531 and 533 eV, the relative intensities are significantly different. For CDB/EDA, the O_{1s} shows a main line at 531.2 eV and a satellite at 533.2 eV in the peak area ratio of 0.8 to 0.2 , respectively. For CDB/THF, the two O_{1s} lines at 531.1 and 533.4 eV have peak area ratios of 0.47 to 0.53 , respectively. CDB-HH, the purely hydrazone structure of the chlorodiane blue dye, has two types of oxygen atoms distinguished by their oxygen chemical environment, one being a $>C=O$ in the $-CONH-$ amido group and the other a ketone $>C=O$ located in the naphthalene ring. The former oxygen atom

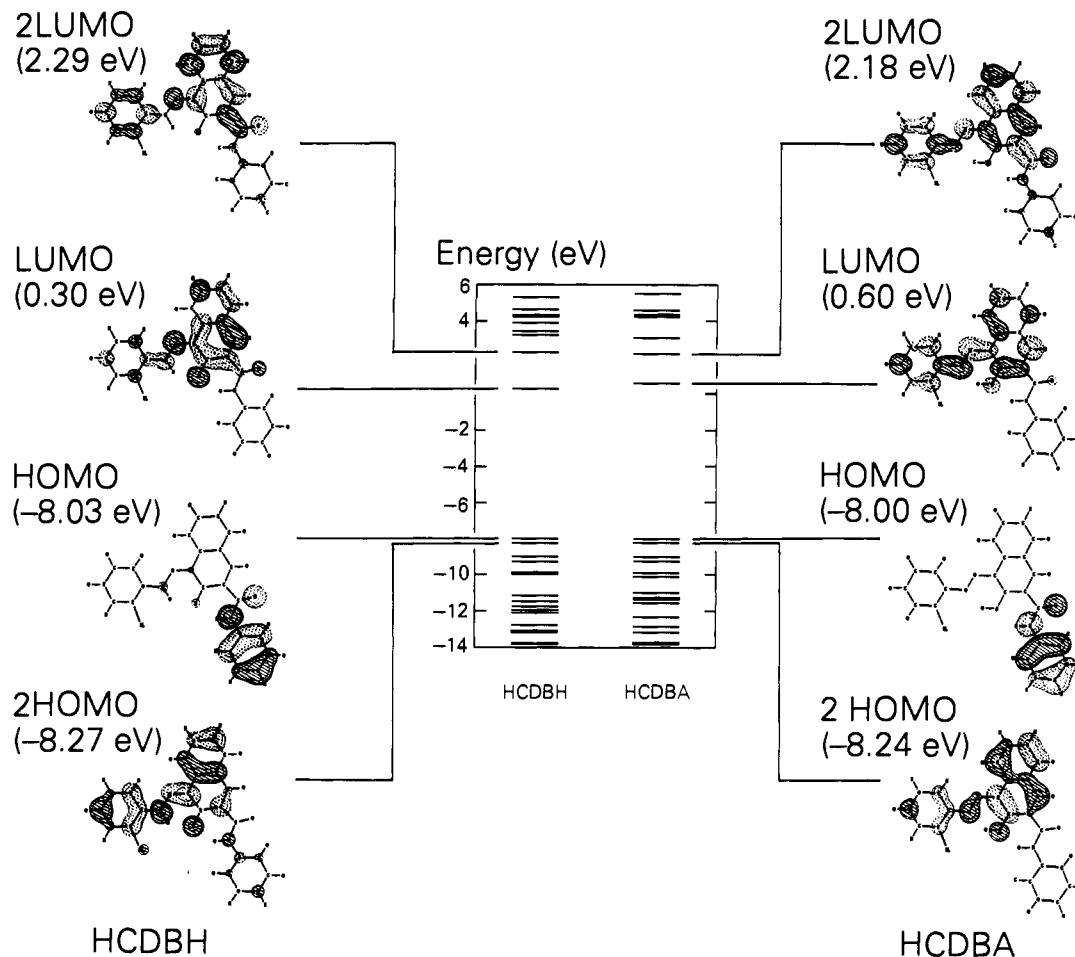


Figure 6. Ab initio (HF/3-21G) molecular orbital energies and molecular orbital plots for HCDBA and HCDBA.

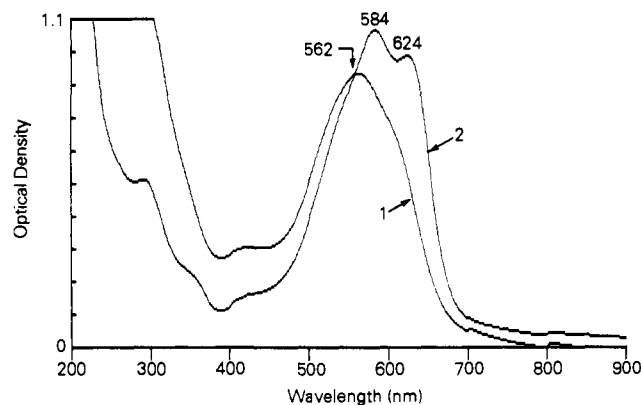


Figure 7. Solid-state optical absorption spectra of CDB used in the XPS studies. Trace 1 shows the spectrum of CDB coated from ethylenediamine while trace 2 shows the spectrum of an identical sample after immersion in tetrahydrofuran for several seconds.

is designated the amido oxygen while the latter is referred to as the naphthyl oxygen. Both are formally ketones or carbonyl bonds but have significantly different neighboring atoms and, therefore, chemical environments. Clark et al.²⁶ have shown that aliphatic alcohols and ketones have their O_{1s} core level binding energies at 533.6 eV. The O_{1s} binding energy of the amido oxygen atom, by virtue of the adjacent nitrogen atom to the carbonyl, shifts the O_{1s} binding energy lower by several eV compared to aliphatic carbonyl oxygen,²⁵⁻²⁷ thus for CDB/THF, the O_{1s} core ionization

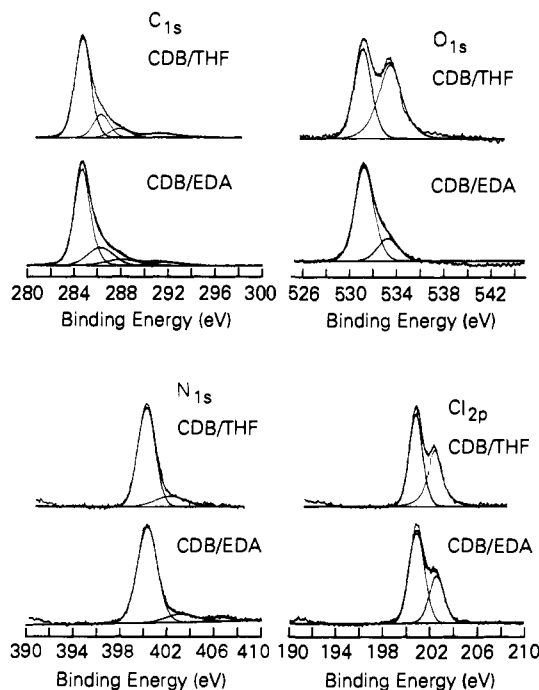


Figure 8. Various XPS core ionization spectra for CDB/THF and CDB/EDA.

peak due to the naphthyl oxygen atom is assigned a binding energy of 533.4 while the $-\text{CONH}-$ amido O_{1s} is assigned a binding

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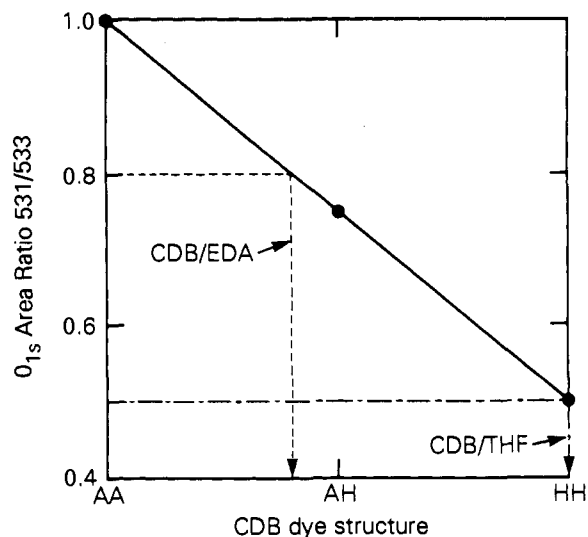


Figure 9. The O_{1s} 531/533-eV peak area ratios as a function of chlorodiane blue structure (AA = 100% azo; AH = 50% azo, 50% hydrazone; HH = 100% hydrazone).

energy of 531.1 eV. The relative ratio of the two peaks is very nearly 1:1, as would be expected for CDB-HH, and thus we conclude that CDB/THF is predominantly, if not completely, the hydrazone form of the dye.

CDB-AA, which is purely the azo structure of chlorodiane blue, has the same two types of oxygen chemical environment as observed in CDB/THF, the amido oxygen atom in the $-\text{CONH}-$ group and the naphthyl oxygen atom. However, in the azo form of chlorodiane blue, the naphthyl oxygen is formally bonded to a hydrogen atom, making it a naphthyl oxygen atom rather than a ketone. From Figure 8, we observe that the O_{1s} core ionization spectrum from CDB/EDA has a main line at 531.2 eV with a small shoulder at 533.2 eV; the relative ratios of the peak areas are 0.8:0.2, respectively. From the discussion above on CDB/THF, the O_{1s} core ionization peak for the amido oxygen atom was assigned the binding energy of 531.2 eV. The O_{1s} binding energy for the naphthyl oxygen atom is also assigned a binding energy of 531.2 eV based upon XPS studies of the structurally analogous phenol molecule by Folkesson et al.²⁹ The 533.2-eV O_{1s} line for CDB/EDA, at 20% relative concentration, is then attributed to the presence of some hydrazone in CDB/EDA and correspondingly to the naphthyl oxygen atom $>\text{C}=\text{O}$ as observed previously for CDB/THF. These considerations are summarized in Figure 9, which shows the peak area ratio of the two O_{1s} lines against the three structural forms possible for the chlorodiane blue dye, CDB-AA, CDB-AH, and CDB-HH. If the amido oxygen atom $>\text{C}=\text{O}$ and naphthyl-OH O_{1s} core ionization peaks occur at 531 eV while the naphthyl oxygen O_{1s} occurs at 533 eV, then the three solid points in Figure 9 are the expected O_{1s} peak area ratio based upon chemical formula, as a function of azo or hydrazone content in chlorodiane blue. From the experimental O_{1s} 531/533-eV peak area ratios, the figure reveals that the chemical structure of CDB/EDA is best described as a mixture of CDB-AA and CDB-AH, while CDB/THF is virtually all hydrazone, CDB-HH, at least near the surface where it was in intimate contact with

Table IV. RHF/3-21G Total Atomic Charges for HCDBA and HCDBH

atom	HCDBA	HCDBH	atom	HCDBA	HCDBH
C1	-0.223	-0.246	C24	-0.214	-0.214
C2	-0.194	-0.178	C25	-0.250	-0.244
C3	-0.242	-0.225	H26	0.269	0.274
C4	0.350	0.473	H27	0.257	0.261
C5	-0.320	-0.349	H28	0.250	0.255
C6	-0.201	-0.237	H29	0.250	0.254
H7	0.285	0.282	H30	0.496	0.465
H8	0.262	0.257	N31	-1.131	-1.128
N9	-0.512	-0.775	O32	-0.667	-0.670
C10	0.129	0.112	H33	0.435	0.425
H11	0.290	0.285	C34	0.384	0.383
N12	-0.363	-0.368	C35	-0.270	-0.270
C13	0.250	0.320	C36	-0.265	-0.265
C14	0.515	0.591	C37	-0.257	-0.256
C15	-0.046	-0.049	C38	-0.228	-0.228
C16	-0.093	-0.064	C39	-0.225	-0.225
C17	-0.129	-0.136	H40	0.237	0.241
C18	-0.282	-0.320	H41	0.308	0.307
O19	-0.826	-0.696	H42	0.234	0.234
C20	-0.202	-0.199	H43	0.240	0.240
C21	1.055	1.046	H44	0.238	0.239
C22	-0.175	-0.182	H45	0.264	0.257
H23	0.316	0.323			

tetrahydrofuran. In organic photoconductor applications, the CDB dye surface is, of course, in intimate contact with the charge transport layer and thus the hydrazone form is important for carrier generation.

The total atomic charges predicted by the ab initio calculations for HCDB are summarized in Table IV and assist in the interpretation of the XPS data. As observed in HCDB-A and HCDB-B-H, the oxygen and nitrogen atoms (see Figure 1) have excess negative charges of 0.7–0.8e and 0.4–1.1e, respectively, depending upon the atom environment. The carbon atoms bonded to these atoms are excessively positive, 0.3–1.1e depending upon location. On a relative basis, we observe that O19 (see Figure 1) becomes more positive in going from the azo structure to the hydrazone structure for HCDB, and this is consistent with the chemical shifts in the XPS data where the naphthyl oxygen $>\text{C}=\text{O}$ exhibited a higher O_{1s} binding energy than the naphthyl-OH oxygen atom.

Conclusions

A knowledge of the solid-state structure of the carrier generation molecule chlorodiane blue is of wide-spread importance in electrophotography. In particular, in photoconductor applications, the xerographic gain is extremely sensitive to structure and morphology. Consequently we have characterized the solid-state structure of chlorodiane blue utilizing optical absorption and X-ray photoelectron spectroscopy and have interpreted the experimental results based upon an ab initio quantum mechanical model. These results indicate that chlorodiane blue exists as azo-enol and/or hydrazone-quinone structures, but it is the hydrazone-quinone form of the dye that exhibits the highest xerographic gain and therefore is the desired chemical structure for use in electrophotographic applications. Using quantum mechanical molecular models, molecular properties for both the azo-enol and hydrazone-quinone forms of chlorodiane blue were calculated and were found to be consistent with the experimental results.

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