highly symmetrical cyclic polyether compound are observed for both independent ethers as a result of the ligand competition.

Crystals of **2** were obtained by cooling a hot solution of K_2Pc[6] in diglyme (DG). Crystal structure analysis was performed on a green prism (0.25 × 0.25 × 0.35 mm) mounted in a glass capillary.[13]

The structure of **2** mimics that of **1** with two DG molecules forming a quasi-macrocyclic oxygen-donor ligand and taking the place of one crown ether molecule. In contrast to **1**, however, **2** consists of infinite stacks of $KPcK(DG)_2$ units with the DG_2 quasi-macrocycles flanked by two potassium ions approximately 1.8 Å from the mean oxygen plane. While the distance between the mean nitrogen and oxygen planes is the same in **1** and **2**, the shorter N–K and O–K distances in **2** reflect less competition for coordination by the DG_2 ligand and its better adaptability to the K_2Pc template.

The most striking feature of **2** is the remarkable conformation of the dianion in which nearly planar isoindole rings tilt alternately up and down to give rise to the saddle-shaped phthalocyanine illustrated in Figure 2. The opposite isoindole rings make angles of 135.5 and 151.6° with respect to each other, while the dihedral angles between neighboring rings range from 25.3 to 27.1°. As in **1**, the nonplanar conformation is achieved by rotation of the isoindole rings about the C–N(aza) bonds. The maximum carbon atom displacements from the 4-N plane are ±1.68 Å while the four C–N(aza)C–N(iso) torsion angles (0° in planar systems) are −14.9, −15.0, 12.6, and 17.4°. As a result, the inner core geometry of the saddle configured dianion is a flattened disphenoid having isoindole N–N distances equal to those in **1**. The dianion in $K_2Pc(DG)_2$ exhibits the greatest distortion from planarity found in any phthalocyanine system.

Although the saddle-shaped conformation is known in other macrocyclic systems,[14] the present conformation bears a remarkable resemblance to the saddle-shaped core of the porphyrin diacids studied by Stone and Fleischer.[15] In those systems, however, steric and repulsive forces are the predominant influencing factors. Since steric factors are absent in **2**, the saddle-shaped conformation of the dianion is attributed predominantly to crystal packing effects. Inner core repulsive forces, if present, are weak as evidenced by the existence of the planar dianion in **1** and $K_2Pc(DMF)_4$.[16]

The variation in conformation of the dianion from nearly planar in **1** and $K_2Pc(DMF)_4$,[16] through the pleated to saddle-shaped conformation in **2**, demonstrates the heretofore unknown flexibility of the Pc system. While the degree of flexibility is novel, the mode is not, since the substantial nonplanar conformation of the metallophthalocyanines (SnPc,[17] VOPc,[18] and others) also occur principally through rotations about the C–N(aza) bonds. In these cases, however, metal coordination properties usually dominate the ring conformation. An important inference regarding the metallophthalocyanines is that the planarity of the MPc systems is not due to any inherent planar rigidity of the Pc macrocycle. This conclusion amplifies the criticality of "hole size" in determining the difference in degree of distortion from planarity between the metallophthalocyanines and their porphyrin analogues.

Complexes in this new series of compounds provide much needed sources of soluble phthalocyanine[4,5,16] and offer potential for use as starting materials in the synthesis of new and known derivatives.

The solution absorption spectra of **1** and **2** exhibit the single MPc-like Q band associated with a D_{4h} symmetry of the phthalocyanine ring and suggest that species similar to **1** and **2** exist in solution. The spectra resemble those of basic solutions of H_2Pc,[19] $(NH_4)_2Pc$ and Li_2Pc in Me_2SO[20] and *N*,*N*-dimethylacetamide,[21] respectively, and K_2Pc in DMF.[16]

Supplementary Material Available: Positional and thermal parameters and observed and calculated structure factors for **1** and **2** (22 pages). Ordering information is given on any current masthead page.

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(13) Space group *C*2/*c*; $a = 24.734$ (8), $b = 7.579$ (5), $c = 22.165$ (5) Å; $\beta = 112.15$ (2)°, $Z = 4$ (23 °C). A total of 2603 reflections were measured for $\theta < 45°$, of which 664 were considered to be observed. The final agreement factors are $R = 0.085$ and $R_w = 0.092$. The positions of the diglyme molecules are approximate due to disorder. Attempts to refine various disorder models were unsuccessful because of the limited number of observed data.

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Wavelength and Solvent Effects on Ionic Photodissociation of Charge-Transfer Complexes. The Hexamethyl(Dewar benzene) System

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Photoisomerization reactions driven by irradiation of charge-transfer complexes have been only recently reported.[1] Our study of the rearrangement of hexamethyl(Dewar benzene) (HMDB) exciplexes[2] has been extended to the investigation of photochemistry of ground-state (CT) complexes of HMDB. We have observed again the unusual adiabatic photoisomerization[2,3] of HMDB in nonpolar solvents. For rearrangement in more polar media we have obtained another novel result, a dependence of photoisomerization quantum yield on excitation wavelength. A recent review[4] shows that such wavelength effects remain relatively rare in solution photochemistry. In the present case we ascribe the quantum yield dependence to photoionization from upper vibrational levels of the first excited CT state.[5]

Red-shifted absorption bands were obtained on combination of HMDB or hexamethylbenzene (HMB) with electron acceptors, fumaronitrile (FUM) and diethyl-1,2-dicyanofumarate (DDF),[6] as shown in Figure 1. The new structureless bands (λ_{max}, Table I) were assigned to CT transitions[8] involving complexes of the HMDB and HMB electron donors.[9,11] Irradiation of the complex

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Table I. Quantum Efficiencies for Photoisomerization (HMDB → HMB) of CT Complexes of HMDB[a]

acceptor[b]	solvent	λ_{max} (CT), nm	excitation wavelength, nm[c] 436	405	366	334	313
FUM	acetonitrile	310			1.1	2.3	5.5
	acetonitrile[d]	310			0.38	0.72	2.1
	dichloromethane	300			0.22	0.41	0.87
	isopropyl ether	300			0.063	0.064	0.041
DDF	acetonitrile	380	1.9	3.6	17		
	dichloromethane	380	0.66	1.4	11		

[a] Nitrogen purged samples, 0.25 M in HMDB and 0.1 M in acceptor (except where noted), 25 °C, 1.0 ± 0.5% conversion. [b] FUM = fumaronitrile (*trans*-1,2-dicyanoethylene), DDF = diethyl 1,2-dicyanofumarate. [c] Monochromator bandpass = 9.6 nm. [d] Inverse complex [HMDB] = 0.06, [acceptor] = 0.73 M.

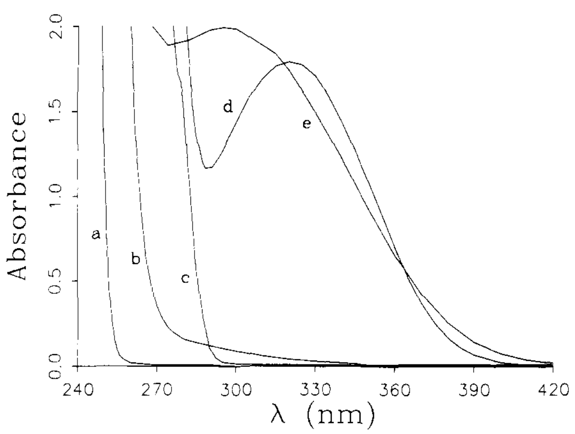
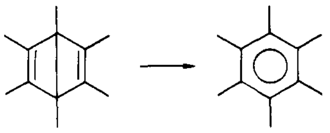


Figure 1. Digitized spectra for CT complexes and their uncomplexed components in dichloromethane: (a) fumaronitrile (FUM), (b) hexamethyl(Dewar benzene) (HMDB), (c) hexamethylbenzene (HMB), (d) 0.50 M FUM + 0.01 M HMB, and (e) 0.50 M FUM + 0.05 M HMDB.

of HMDB and FUM in isopropyl ether (ϵ 3.9) resulted in isomerization, HMDB → HMB, with low quantum efficiency (Table I). Fluorimeter excitation (λ_{exc} = 334 nm) of FUM/HMDB at



HMDB HMB

room temperature in isopropyl ether gave rise to an emission which was identical with the fluorescence observed on irradiation of the FUM complex of HMB. Comparison of the FUM/HMDB and FUM/HMB emission yields showed that the quantum yield of excited FUM/HMB product originating from FUM/HMDB (the adiabatic[14] isomerization yield) is 0.7.[15]

Photoisomerization of complexes of HMDB in relatively polar media was generally efficient but showed a complex dependence on the solvent and other system parameters. Quantum yields in excess of unity were observed (Table I), consistent with radical-ion formation and chain reaction (Scheme I), as shown by Evans[10] for isomerization via exciplexes or electrochemical oxidation. A dependence of isomerization yield on extent of reaction was observed, due in part to the better complexing ability of HMB over HMDB.[11] The behavior of FUM/HMDB in acetonitrile is shown in Figure 2. A similar dependence was found for DDF/HMDB (e.g., for photolysis at 405 nm, ϕ = 3.6 at 1.1% conversion and 15 at 3.1% conversion; ϕ = 2.6, extrapolated to zero irradiation time).

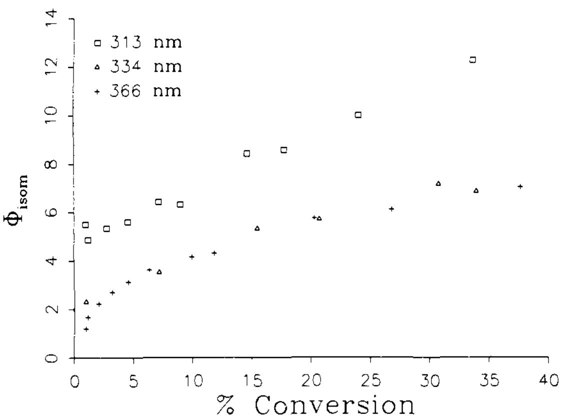


Figure 2. Dependence of quantum yield of valence isomerization of HMDB in acetonitrile on wavelength and the extent of conversion to HMB.

Scheme I

$$HMDB^{+\cdot} \rightarrow HMB^{+\cdot}$$

$$HMB^{+\cdot} + HMDB \rightarrow HMDB^{+\cdot} + HMB$$

Quantum efficiencies for HMDB isomerization at various wavelengths and very low conversion (1.0 ± 0.5%) (Table I) were examined in greater detail by using a modification of the monochromator/light pipe/quantum counter apparatus previously described.[16,17] Data provided in Table I also include measurements made for the "inverse" complex of FUM-HMDB for which the lowest practical concentrations of HMDB were employed and the radical-ion chain reaction held to a minimum.

The response of HMDB photoisomerization quantum efficiencies to the identity of the acceptor, solvent, and excitation wavelength is consistent with a mechanism involving photoionization. Radical-ion propagation serves as an amplifier of the trends for primary ion yield. The wavelength effects are not likely the result of competitive absorption by different complexes or population of upper electronic states.[18]

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(11) Association constants were obtained by an iterative weighted curve fitting of a general concentration-absorption relationship.[12] The data include K = 0.47 and ϵ 2683 for DDF-HMB-CH_2Cl_2 and K = 0.33 and ϵ 140000 for FUM-HMB-$(C_3H_7)_2O$. Measured K's were uniformly low and (along with the ϵ's) subject to significant error.[13] The HMDB complexes were clearly weaker, and K's (<0.05) could not be reliably determined.

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(18) Multiple absorption bands, such as those observed for HMB and 1,2,4,5-tetracyanobenzene and ascribed to excitation to different unoccupied acceptor orbitals,[19] were not observed. CT bands for HMDB could involve excitation from two high lying occupied HMDB orbitals and the wavelength effect on isomerization yield associated with the nature of the depopulated orbital. However, the orbital separation for a_1 (HOMO) and b_2 orbitals of HMDB is 0.5 eV[20] (a value which is not readily associated with photoexcitation energy differences); oscillator strengths for CT transitions involving these orbitals of different symmetry should not be similar.

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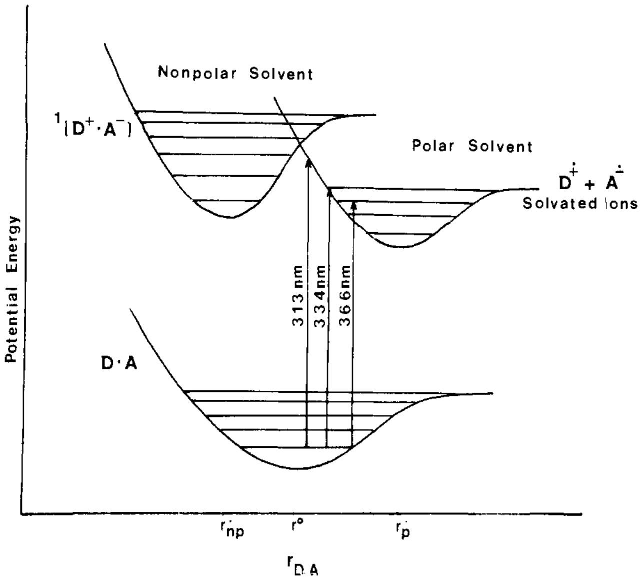

Figure 3. Potential-energy surfaces for ground- and excited-state charge-transfer complexes. The reaction coordinate is the distance of separation for electron donor (D) (e.g., HMDB or HMB) and electron acceptor (A) (e.g., FUM or DDF) species. The model is only approximate with regard to the energy scale.

We adopt the following model for CT photoisomerization of HMDB. In nonpolar solvents the excited CT singlet is essentially a very "tight" ion pair with Coulomb or dative binding which is enhanced vis-a-vis the ground state[21] (note displacement and depth of wells in Figure 3). Nonradiative decay requires only back-transfer of an electron and is very rapid.[22] Ring opening, which requires substantial nuclear motion, competes poorly with the annihilation of charge, and low quantum yields result.[23]

In polar media excited complexes are displaced to a longer distance of separation for the paired ions due to solvation. Dative bonding for the ion pair is reduced, corresponding to a shallow potential well for the r_{DA} ionic bond stretch (the reaction coordinate for photoionization, Figure 2). The CT transition is strongly coupled with this low frequency intermolecular vibration. The vibronic level reached with long excitation wavelengths near the 0-0 band corresponds to only modest excursion along r_{DA}. Irradiation at shorter wavelengths populates a continuum of vibrational levels above the dissociative limit, giving rise to large D-A separation and the opportunity for solvent intrusion (dielectric relaxation).

It will be important to determine the generality of ionic photodissociation of Franck-Condon states of CT complexes in fluid solution. The interpretation has been applied in another instance to the behavior of the complex of 1,2,4,5-tetracyanobenzene and benzene in dichloroethane on laser flash photolysis.[24] Another feature of our data is the continuation of the wavelength dependence of isomerization quantum yield at moderate conversion of HMDB (>10%, see Figure 2), under circumstances where the principal absorbing species are complexes of HMB.[25] A higher efficiency of isomerization (an apparently higher yield of chain carrying HMB cations) is clearly maintained for excitation of FUM complexes at the shortest wavelength (313 nm). The wavelength effect on ionic photodissociation of HMB complexes is thus reserved for the highest excitation energy, consistent with a larger barrier for separation of HMB ion pairs. The latter may be associated with a higher frequency ionic bond stretch for the HMB excited CT state (which parallels a larger formation constant for the CT ground state[11]).

A number of recent findings are relevant to our observations. Wavelength effects on the fluorescence yield of exciplexes in the gas phase have been observed, and the enhancement of nonradiative decay at shorter wavelengths ascribed to excitation of a low frequency intermolecular vibration.[26] Irradiation of tetramethyl-*p*-phenylenediamine at short wavelengths results in an increase in photoionization efficiency (a higher escape probability for solvated electrons).[26] In addition, picosecond flash photolysis studies of a moderately complex molecule (stilbene) in fluid solution show a time scale (tens of ps) for vibrational decay which is long with respect to solute-solvent relaxation.[28]

Acknowledgment. We thank Professor Maitland Jones for supplying samples of HMDB and Professor Colin Steel for helpful discussions. This work was supported by the U. S. Department of Energy, Division of Basic Energy Sciences.

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Production of Acrylonitrile and Other Unsaturated Nitriles from Hydrocarbons Using a Plasma

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The utility of gaseous plasmas formed from atoms is well established and will be self-evident if the reader is using a fluorescent lamp. The utility of plasmas formed from complex molecules[1] is only now being developed. In a similar fashion, understanding of molecular plasmas has lagged behind knowledge of the simpler atomic plasmas. There are, therefore, definite benefits accruing to the study of molecular plasmas. In the investigation reported here, we have attempted to extend the knowledge of plasma chemistry and develop a new and potentially useful preparative technique. We report a unique method for the production of unsaturated nitriles from inexpensive alkenes and alkynes. These nitriles are articles of commerce. The observed reactions are also unique and are of mechanistic interest. These results significantly enlarge the repertoire of plasma synthesis since previous studies on simple aliphatic compounds produced primarily fragmentation or polymerization.[1]

The plasma apparatus consisted of a glass tube reactor (25 cm long, 2.5-cm i.d.), around which was wrapped a copper coil (10 turns, $^1/_4$-in. i.d.). The coil was connected to a rf generator (13.6 MHz) through a "match box" which allowed the reflected power to be minimized. Reactants were weighed into separate reservoirs and then simultaneously distilled through the reactor. The flow

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