disordered so that while only one set of ligand atoms can be resolved, there are two incompletely occupied sets of metal atom positions. An ORTEP diagram with the two different sets of Re atoms is shown in Figure 3. It is clear that each set of four Re atoms forms a plane, and these two planes are orthogonal to each other. The primary set, Re(3) and Re(4), is 97% occupied, and the secondary set, Re(3d) and Re(4d), is only 3% occupied.

The reactions of $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ with MeOH and H_2O are believed to be initiated by the attack of the Re^{3+} centers on the oxygen atom of methanol and/or water. The attack results in the breaking of the O–H bonds and subsequently the loss of chloride ligands from each rhenium metal center. The intermediate of low coordination number is unstable and condenses to form the tetramer, through the formation of two Re–Re single bonds that join two triple-bonded units together. The initiation is due to the high acidities of the Re^{3+} centers, which have been found to be able to rearrange the diop ligand by their coordination to the oxygen atoms of the diop ligands.[16]

Complexes **1** and **2** make an interesting comparison with $\text{Mo}_4(\mu\text{-OMe})_2(\mu\text{-OiPr})_2(\text{OiPr})_8$[17] (**3**). Complex **3** has two short (2.238 (1) Å) Mo–Mo bond distances and two long (3.344 (1) Å) Mo–Mo distances, corresponding to Mo–Mo triple-bond and nonbonding distances. Complexes **1** and **2** have two triple bonds and two single bonds. The metal centers of **1** and **2** are Re^{3+} and have d^4 electronic configurations, and those of **3** are Mo^{3+} and have d^3 electronic configurations. The addition of four more electrons leads to the formation of two single bonds in both **1** and **2**.

Acknowledgment. We thank the National Science Foundation for Support.

Supplementary Material Available: Complete tables of crystal data, positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, bond angles, and refinement results for **2** with different multiplicities for Re atoms (26 pages); two listings of observed and calculated structure factors (58 pages). Ordering information is given on any current masthead page.

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Novel Photodimerization of 2-Alkoxy-3-cyanopyridines Involving Unexpected Rearrangement

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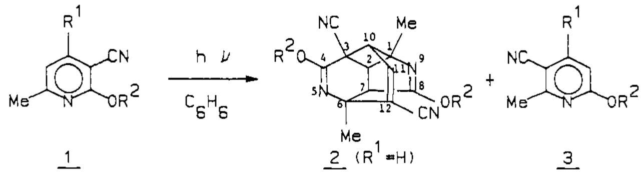
Received December 3, 1990
Revised Manuscript Received May 14, 1991

A great deal of attention has been paid to the photochemistry of aromatic compounds by photochemists. Benzene and its derivatives undergo a number of important photoreactions including isomerization and photoadditions with various unsaturated compounds.[1] Pyridine undergoes fewer photochemical reactions than does benzene. It forms an unstable para-bonded isomer,[2] and fluorinated pyridines gave azaprismanes.[3] The photoaddition of pyridines to alkenes is generally unsuccessful.[4] We now find that 2-alkoxy-3-cyano-6-methylpyridines undergo [2π + 2π] photodimerization followed by novel rearrangement. This reaction represents the first example of [2π + 2π] cyclodimerization in pyridine photochemistry.

All 2-alkoxy-3-cyanopyridines **1** in Table I were prepared by alkylation of the corresponding pyridones.[5] The structures of these compounds were determined on the basis of elemental analyses and the spectral data. The UV spectrum of the methoxy derivative **1a** in cyclohexane showed maxima at 231 (ε 10 100), 284 (8400), 289 (11 000), 294 (11 000), and 299 nm (9200).

Table I. Photolysis of 2-Alkoxy-3-cyanopyridines **1a–e**



1	R¹	R²	concn (mol/L)	conversn (%)	yield (%) 2	yield (%) 3
a	H	Me	0.02	52	36	44
a	H	Me	0.04	52	93	0
a	H	Me	0.20	45	93	0
b	H	Et	0.02	40	31	47
b	H	Et	0.20	40	89	0
c	H	*i*-Pr	0.02	44	80	trace
d	Me	Me	0.02	54	0	92
e	Me	Et	0.02	58	0	90

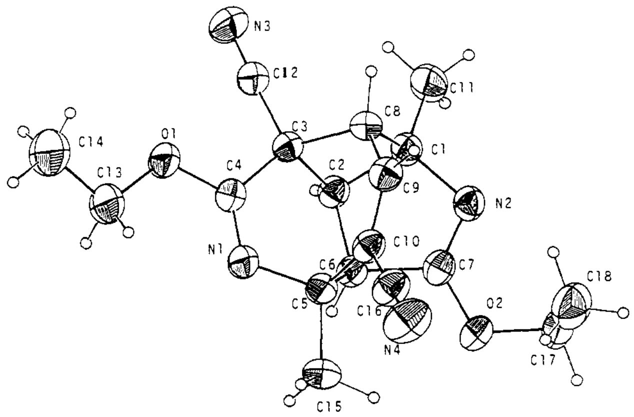


Figure 1. ORTEP diagram of dimer **2b**.

Scheme I

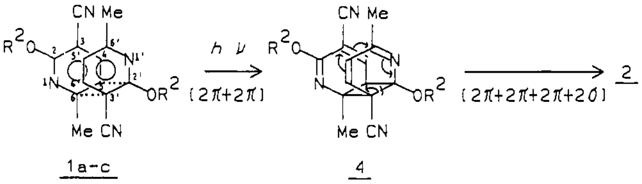


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Table II. Quantum Yields for Dimerization of **1a** in Various Conditions

solvent	concn (mol/L)	$\Phi_{\text{dim.}}$ ($\times 10^{-2}$)
C_6H_6	0.005	0.3
C_6H_6	0.01	0.6
C_6H_6	0.02	1.3
C_6H_6	0.03	1.4
C_6H_6	0.04	1.5
C_6H_6	0.10	1.5
Et_2O	0.02	1.0
CH_3CN	0.02	0.7

Irradiation of a benzene solution of **1a** (0.02 M) with a high-pressure mercury lamp through a Pyrex filter under argon gave two photoproducts. They were isolated by flash column chromatography and identified as the dimer, 3,12-dicyano-4,8-dimethoxy-1,6-dimethyl-5,9-diazatetracyclo[4.3.3.$0^{2,7}$.$0^{3,10}$]dodeca-4,8-diene (**2a**), and the transpositional isomer **3a**. Photolysis of other pyridines (**1b** and **1c**) gave the results shown in Table I. The structure of **2b** was confirmed by X-ray structural analysis (Figure 1).

When **1a** and **1b** were irradiated at a concentration above 0.04 M, the corresponding dimers (**2a** and **2b**) were obtained as sole photoproducts. In contrast to the photoreactions of the monomethylated pyridines (**1a**–**1c**), those of 3-cyano-4,6-dimethyl-2-methoxy- and -2-ethoxypyridine (**1d** and **1e**) did not give the dimers but formed the transpositional isomers (**3d** and **3e**) almost quantitatively. When **1d** and **1e** were irradiated at a higher concentration (0.1 M), the corresponding dimers were not detected. The difference in reactivity might be attributed to the steric effect of a methyl group at 4-position.

For the formation of the dimer (**2**), a mechanism is postulated that involves [$2\pi + 2\pi$] photodimerization between C5–C6 and C2′–C3′ bonds followed by [$2\pi + 2\pi + 2\pi + 2\sigma$] rearrangement (Scheme I). The rearrangement probably results from the weakened character of the carbon–carbon bond of the cyclobutane ring caused by donor–acceptor conjugation. The trapping of cyclobutane-type intermediate **4** with dienophiles was unsuccessful. The formation of the transpositional isomer **3** is reasonably explainable in terms of a 1,3-shift via Dewar pyridine.[6]

The photocycloadditions of many aromatic compounds proceed via exciplex or excimer. At a concentration of about 10^{-4} M or less, the fluorscence of **1a** was concentration-independent and was composed of pure pyridine monomer fluorescence. As the pyridine concentration increased, the monomer emission decreased in intensity; however, a new fluorescence emission due to the pyridine excimer was not observed. There was no change caused by pyridine concentration in the absorption spectra. The dimerizations were not sensitized by 3-methoxyacetophenone (E_T 72.4 kcal/mol).[7] Quenching of the dimerizations by 2,5-dimethylhexa-2,4-diene (E_T 58.7 kcal/mol)[7] or *trans*-stilbene (E_T 50 kcal/mol)[7] was quite inefficient. These results indicate that the photodimerizations proceed from the singlet excited states. The quantum yields were dependent upon the pyridine concentration, and the maximum was 1.5×10^{-2} at concentrations above 0.04 M[8] (Table II). Furthermore, it seems that a nonpolar solvent is preferred for the dimerization.

Whereas 2-pyridones[9] and 2-aminopyridinium ions[10] form well-known [$4\pi + 4\pi$] dimers on irradiation, pyridines, quinolines, and isoquinolines are generally unreactive toward addition reactions.[11] Although both inter- and intramolecular [$4\pi + 4\pi$] cycloadditions of naphthalenes[12] and anthracenes[13] have been studied extensively, there is no example of [$2\pi + 2\pi$] dimerization of six-membered monocyclic aromatic compounds, to our knowledge. The photoreaction of 3-cyano-2-methoxy-6-methylpyridines provides an unprecedented cyclodimerization in pyridine photochemistry. We are continuing to explore the scope and limitations of the photodimerization of heteroaromatics.

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An Algorithm for the Systematic Solvation of Proteins Based on the Directionality of Hydrogen Bonds

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Received February 21, 1991

We present the development of an algorithm for the systematic solvation of proteins based on the directionality of H bonds.[1-4] By analysis of the distribution and environment of H-bond donors and acceptors of a protein, positions for both internal and surface water molecules are identified. The algorithm was incorporated into the program AUTO-SOL, which is part of the molecular mechanics software "Yeti". In detail, the algorithm includes the following steps:

1. Linearity of H bonds is represented by H-extension vectors (HEVs), H-bond directionality by lone-pair vectors (LPVs). HEVs originate at H-bond donors, LPVs at H-bond acceptors. The end point of a HEV marks the ideal position for a H-bond acceptor atom relative to the H-bond donor fragment. The end point of a LPV marks the ideal position for a H-bond donor atom relative to the H-bond acceptor fragment. Length and orientation of HEVs and LPVs were derived from analyses of H-bond geometries in small-molecule crystal structures.[1-4]

To identify free HEVs and LPVs, able to engage in H bonds with additional water molecules, it is necessary to delete those vectors associated with already existing hydrogen bonds. Ideally, the HEV and LPV of a particular H bond would overlap entirely, but this is rarely observed in protein structures.[5] LPVs and HEVs

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