

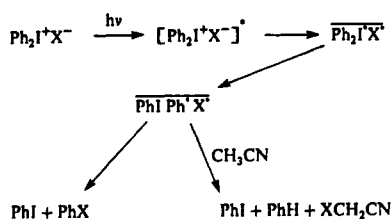
Figure 1. UV absorption spectra of diphenyliodonium chloride at 5×10^{-5} M in 0, 1, 5, and 25% aqueous acetonitrile (a-d) and at 5×10^{-4} M in 0 and 25% aqueous acetonitrile (e, f).

aqueous acetonitrile. These dramatic changes in product distribution and yield from photolysis of diphenyliodonium halides in acetonitrile and aqueous acetonitrile clearly demonstrates the difference in reactivity of a tight ion pair and solvent-separated ion pair. The diphenyliodonium halides are not very soluble in acetonitrile, likely due to the solvent being incapable of separating the ion pair. In contrast diphenyliodonium triflate and hexafluorophosphate are readily solubilized by acetonitrile. UV absorption spectra were measured for the aqueous and nonaqueous solutions. For the iodonium halides, the nonaqueous solutions exhibited UV absorption bands which were red-shifted from those observed in the aqueous solutions (e.g. Figure 1). This red shift may be due to a charge transfer absorption.¹⁰ Indeed the UV absorption spectra of the 25% aqueous solutions of iodonium halides were similar to the spectra of other iodonium salts in anhydrous solvent. If the charge-transfer absorption is responsible for the photochemistry observed in the nonaqueous solutions, then the initial products would be diphenyliodonium radical and halogen radical, which would decompose to the triad of iodobenzene, phenyl radical, and halogen radical. This differs from other iodonium salt photolyses where reactivity from both heterolytic and homolytic cleavage reactions are observed.⁷ In addition to our results, recent picosecond flash photolysis experiments and conductance measurements on 1- PF_6 and 1-Cl in dichloromethane also show different reactivities from solvent separated and tight ion pairs.¹¹

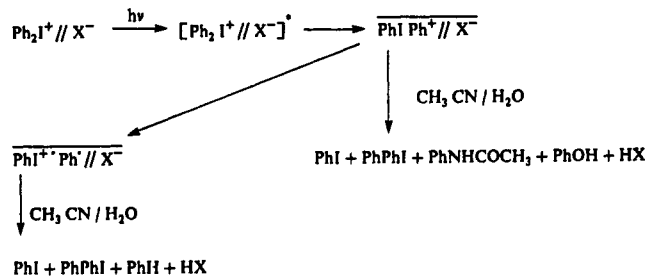
(10) (a) Irving, H.; Turner, G. P. A.; Reid, R. W. *J. Chem. Soc.* 1960, 2082 and see ref 4a. (b) For an example of charge transfer absorption in triphenylsulfonium salts see: Nickol, S. L.; Kampmeier, J. A. *J. Am. Chem. Soc.* 1973, 95, 1908.

Scheme II. Mechanism for Product Formation from Photolysis of Diphenyliodonium Halides in Acetonitrile and Aqueous Acetonitrile

NON-AQUEOUS SOLVENT



AQUEOUS SOLVENT



X = Cl, Br or I

// represents solvent separation of ions

The mechanism for product formation from diphenyliodonium halides in acetonitrile and aqueous acetonitrile is shown in Scheme II. In acetonitrile the tight ion pair of diphenyliodonium halide gives a charge-transfer excited state which decomposes via the diphenyliodonium radical and halogen radical pair to give an in-cage triad of iodobenzene, phenyl radical, and halogen radical. The latter two intermediates can combine in the solvent cage to give halobenzene, whereas reaction with the solvent gives benzene and cyanomethyl radical which combines with halogen radical to yield haloacetonitrile. Abstraction of hydrogen from solvent by the halogen radical to generate cyanomethyl radical or dimerization of cyanomethyl radical does not occur, as benzyliodonium and succinonitrile are not detected among the photoproducts. In aqueous solutions, the diphenyliodonium halides are solvent separated and charge transfer is less favored. Thus photodecomposition occurs via initial heterolysis of the excited state as previously reported for other iodonium salts.

(11) Hilinski, E. F., manuscript in preparation. The authors thank Professor Hilinski for personal communication of his results.

4-Piperidinylimino: A Nearly Linear Head-to-Tail Linking Group for Dipolar Chromophores

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Summary: Linkage of the *p*-aminobenzaldimine and *p*-nitroaniline chromophores through a piperidine ring gives

a compound whose dipole moment is almost exactly the sum of the moments of the constituent chromophores.

Oligomers consisting of head-to-tail-linked, dipolar, π -conjugated monomers are of interest as electrically

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soluble elements in polymeric second-order nonlinear optical materials.¹ If these oligomers could be made rigid and linear, they should be orientable by electric fields to give materials with larger polar order parameters than similar materials containing corresponding monomers, because the oligomer dipole moment would be the sum of all the constituent monomer moments, leading to an enhanced orientational polarizability. The resulting orientation should be more stable than for small or nonrigid dipoles because of the large volume of matrix material that would have to move during orientational randomization.² A second motivation for studying these oligomers is the possibility of observing interesting aggregation phenomena in a polar rigid rod. The contemplated aggregation is preceded in poly(benzthiazole),³ poly(1-benzyl glutamate),⁴ and compounds with self-segregating segments.^{5,6}

We have reported semirigid polar oligomers based on piperazinamide linkers,⁷ in which each segment may sweep out a 110° cone angle with respect to its neighbor. Although the angle is rigorously defined, the dipolar additivity between segments is much less than it would be if the angle were closer to 180°, and the rotational freedom around the cone leads to multiple conformations in oligomers larger than dimer. Here, we propose the 4-piperidinylimino group, which combines a parallel divalent imine acceptor with a 1,4-disubstituted six-membered ring donor, as a novel link between dipolar segments, with the ultimate aim of incorporating this linker in a polymer such as 1. Presently, we demonstrate via bis chromophore 2 that the dipoles on either side of this link are almost perfectly additive, i.e. the bonds to the internal donor and acceptor supplied by the link, as well as the principal moments of the segments, are virtually parallel.

The dimer and its synthesis are shown in Figure 1. Reaction of 4-fluoronitrobenzene with 4-piperidinone monohydrate hydrochloride in refluxing acetonitrile containing triethylamine provided the ketone 3. Our original intention was to proceed directly from 3 to the amine 5 by reductive amination; however, in spite of the ample precedent which exists for this reaction in various other contexts,⁸ we were unable to effect the desired transformation using combinations of ammonium salts and cyanoborohydride. We therefore resorted to a two-step sequence, where reaction of 3 with methoxylamine hydrochloride⁹ gave *O*-methyloxime 4, which was in turn reduced¹⁰ with borane-THF to provide 5. Although the

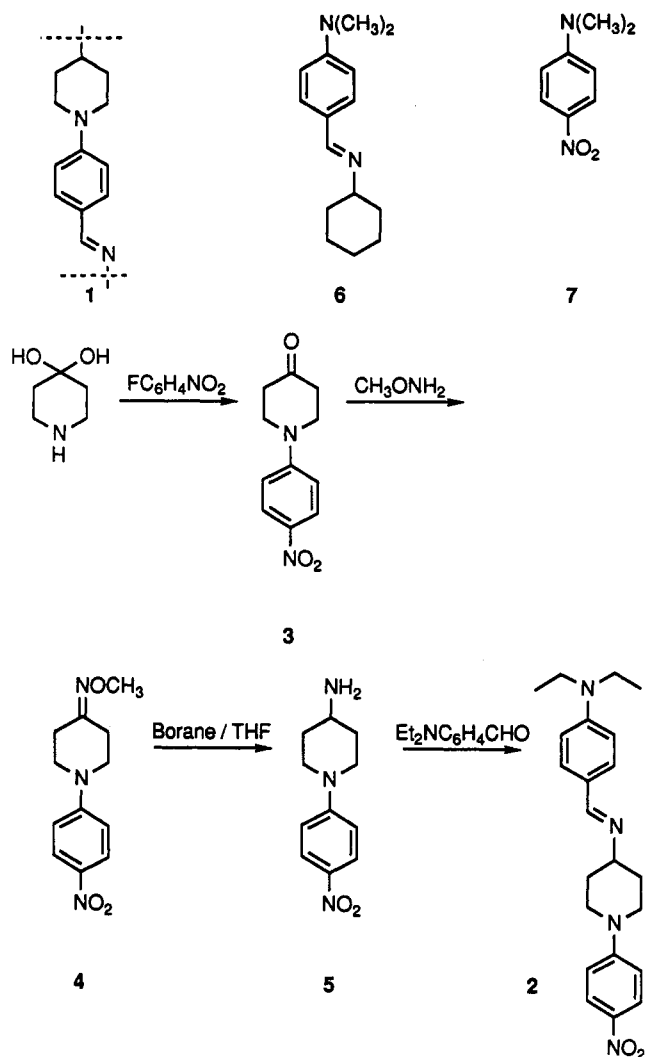


Figure 1. Structures of compounds discussed in the text.

amine could not be completely purified, it was suitable for use in the subsequent condensation step, whereby reaction with (diethylamino)benzaldehyde and removal of water using molecular sieves¹¹ resulted in imine 2. The dimethyl analogue of 2 was also prepared from 5 using (*N,N*-dimethylamino)benzaldehyde, but was not fully characterized due to its limited solubility. Compound 6 was synthesized analogously from (*N,N*-dimethylamino)benzaldehyde and cyclohexylamine in toluene.

The dipole moments of 2, 6, and 7 determined in dioxane solution from plots of dielectric constant vs weight fraction of solute⁷ (linear correlation coefficients of 0.9998) are 9.2, 2.7, and 6.8^{7a} D \pm 3%, respectively. A determination on the *N,N*-dimethylamino derivative of 2 gave a value of 9.4 D (correlation coefficient 0.987). Clearly, the dipole moments for models of the segments of 2 add up to a value (9.5 D) that nearly equals the dipole moment of 2 and is within experimental error of that moment. Molecular modeling¹² predicts a phenylene-phenylene angle for 2 of 150–180°, which is consistent with the observed additivity of the moments. The apparent additivity could have been diminished slightly because the axis of the benzaldimine chromophore moment is not entirely coincident with the 1,4-axis of the phenylene unit, and small contributions

(11) Bonnett, R.; Emerson, T. R. *J. Chem. Soc.* 1965, 4508–4511.

(12) Force-field optimization followed by MOPAC version 3 from QCPE, MNDO Hamilton. The 150–180° spread is due to imprecise definition of the relative puckering at atoms 1 and 4 of the piperidine ring.

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(6) Self-segregation of end groups leads to ordered aggregates in fluorocarbon-hydrocarbon diblocks. Pugh, C.; Höpken, J.; Möller, M. *Polym. Prepr.* 1988, 29, 460–461. Höpken, J.; Pugh, C.; Richtering, W.; Möller, M. *Makromol. Chem.* 1988, 189, 911–925.

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(8) (a) Borch, R. F.; Bernstein, M. D.; Durst, H. D. *J. Am. Chem. Soc.* 1971, 93, 2897–2904. (b) Borch, R. F.; Durst, H. D. *J. Am. Chem. Soc.* 1969, 91, 3996–3997.

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(10) Feuer, H.; Braunstein, D. M. *J. Org. Chem.* 1969, 34, 1817–1821.

from C-N single bonds may slightly influence the moments as well.

We expect polymers with structures like 1 to be highly dipolar rigid rods, by virtue of the significant dipole moment contributed by each segment and the nearly perfect projection of the moments along the rigid rod axis assured by the imino connector. More extended π -electron systems, such as stilbenediyl or azodiphenyl, could in principle

be substituted for the phenylene units in 1, possibly giving rise to enhanced dipolar or optical effects. Efforts to synthesize these polymers and apply them as described in the introduction are currently in progress.

Supplementary Material Available: Preparation and characterization of 2-6 (3 pages). Ordering information is given on any current masthead page.

Use of Hydrogen Bonds To Control Molecular Aggregation. Association of Dipyridones Joined by Flexible Spacers

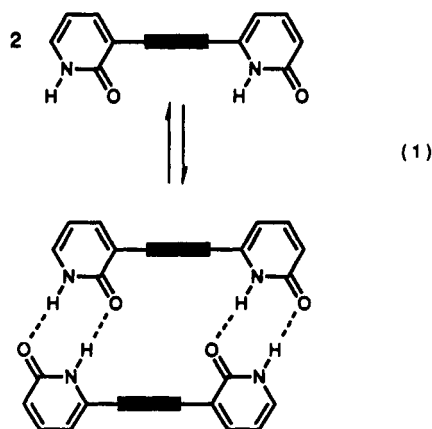
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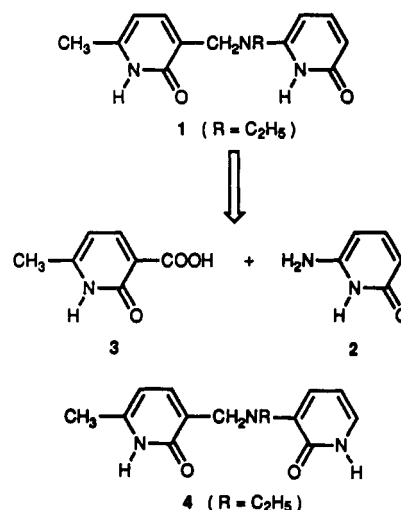
Summary: Flexible dipyridone 1, which incorporates an extensive, self-complementary pattern of hydrogen-bond donors and acceptors, exists largely as an antiparallel dimer at 0.0016 M in CHCl_3 at 25 °C. In the solid state, however, dipyridone 1 prefers a polymeric motif with an intramolecular hydrogen bond. We propose that the structure formed in solution is dimer 5 joined by four intermolecular hydrogen bonds or dimer 6 held together by two intermolecular hydrogen bonds strengthened by the cooperative effect of two intramolecular hydrogen bonds.

We have suggested that the elements of a molecular construction set can be made by linking 2-pyridones with rigid spacers to create compounds that form predictable, strongly hydrogen-bonded duplexes (eq 1).³ In this paper we describe the aggregation of similar dipyridones linked by flexible spacers.



Self-complementary dipyridone 1⁴ could be prepared in 36% overall yield by coupling 6-amino-2-pyridone (2)⁵ with the acid chloride derived from acid 3,⁶ followed by re-

duction ($\text{BH}_3 \cdot \text{THF}$), acetylation (pyridine, DMAP), and further reduction. Its IR spectrum (CHCl_3 , 0.0011 M) shows a broad band centered at 1647 cm^{-1} , and its UV spectrum (CHCl_3 , 0.0010 M) consists of an absorption at 332 nm, so the compound is primarily a dipyridone in solution, not a hydroxypyridine tautomer.⁷ Vapor-pressure osmometric studies at 25 °C in CHCl_3 indicate that its average molecular weight in saturated solutions does not exceed that of the dimer, and it is approximately 64% dimeric even at concentrations as low as 0.0016 M. In



contrast, 6-(diethylamino)-2-pyridone is only 17% dimeric under similar conditions, and non-self-complementary dipyridone 4⁴ has an average molecular weight of 706 at 0.0042 M. These observations demonstrate that dipyridone 1 forms strong dimers in solution, whereas isomer 4 is forced to form linear oligomers. In ¹H NMR spectra of dipyridone 1 (CDCl_3 , 0.059 M, 25 °C), a nuclear Overhauser effect of 1.1% could be observed between the hydrogens of the methyl group at C₆ of one pyridone ring and the hydrogen at C₃ of the remote pyridone ring. This can only arise in an antiparallel dimer that places the hydro-

(1) Fellow of the Natural Sciences and Engineering Research Council of Canada, 1984-1988.

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(4) The structure assigned to this new compound is consistent with its elemental analysis and its IR, NMR, and mass spectra. These data are included in the supplementary material.

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(7) For references and further discussion, see: Gallant, M.; Phan Viet, M. T.; Wuest, J. D. *J. Am. Chem. Soc.* 1991, 113, 721-723.