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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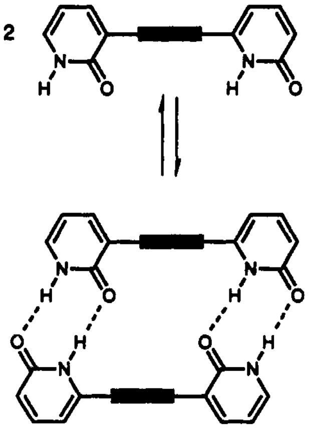
Summary: Flexible dipyridone 1, which incorporates an extensive, self-complementary pattern of hydrogen-bond donors and acceptors, exists largely as an antiparallel dimer at 0.0016 M in $CHCl_3$ at 25 °C. In the solid state, however, dipyridone 1 prefers a polymeric motif with an intramolecular hydrogen 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.

2



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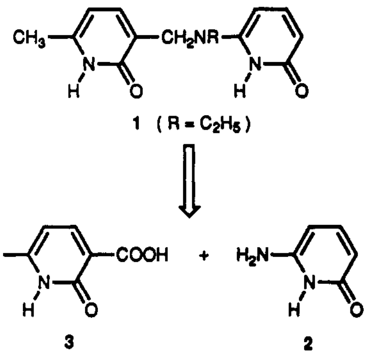
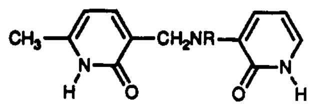


1 (R = C_2H_5)

3

2



4 (R = C_2H_5)

Self-complementary dipyridone 1[4] 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 reduction (BH_3·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 4[4] 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 C_6 of one pyridone ring and the hydrogen at C_3 of the remote pyridone ring. This can only arise in an antiparallel dimer that places the hydro-

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[3] Ducharme, Y.; Wuest, J. D. *J. Org. Chem.* **1988**, *53*, 5787–5789.

[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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[6] Showalter, H. D. H.; Domagala, J. M.; Sanchez, J. P. *J. Heterocycl. Chem.* **1981**, *18*, 1609–1612.

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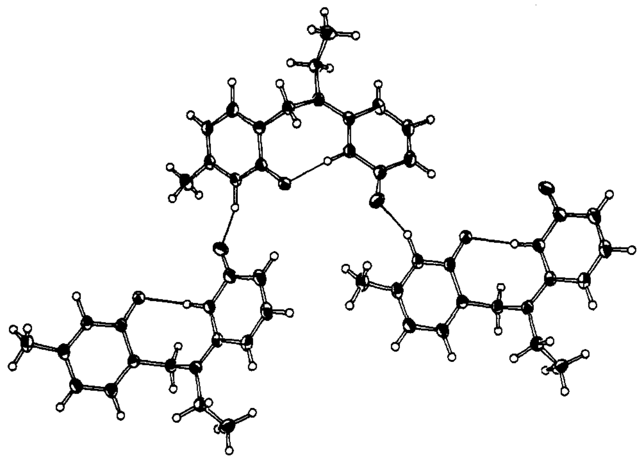
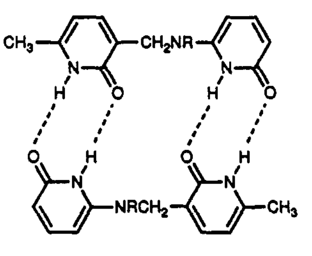


Figure 1. ORTEP drawing of dipyridone 1 showing the monomeric unit and part of the intermolecular network of hydrogen bonds. The non-hydrogen atoms are represented by ellipsoids corresponding to 40% probability, and hydrogen atoms are shown as spheres of arbitrary size. Hydrogen bonds are represented by narrow lines.

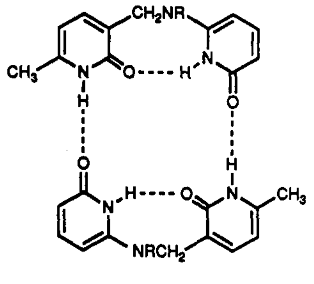
gens in close proximity.

Unexpectedly, an X-ray crystallographic study established that dipyridone 1 does not form discrete dimers in the crystal, but prefers a linear polymeric motif instead (Figure 1).[8] Noteworthy features of this structure include an intramolecular hydrogen bond[9] and a relatively long N–H distance (1.061 (9) Å), short O···H distance (1.716 (10) Å), and short O–N separation (2.736 (2) Å) in the intermolecular hydrogen bonds, which suggests that proton transfer is extensive.[3,10] In addition, sp^2 hybridization of the exocyclic nitrogen and systematic deviations in the bond distances within the aminopyridone ring provide evidence for extensive conjugation and an unusually basic carbonyl oxygen.

These observations suggest that the dimer formed in solution has structures 5 or 6. Intramolecular hydrogen bonding in dimer 6 reduces the number of intermolecular contacts but may make each one stronger, since one pyridone in each subunit is rendered more acidic by partial intramolecular protonation and the other is simultaneously made more basic by partial intramolecular deprotonation.[11]



5 ($R = C_2H_5$)



6 ($R = C_2H_5$)

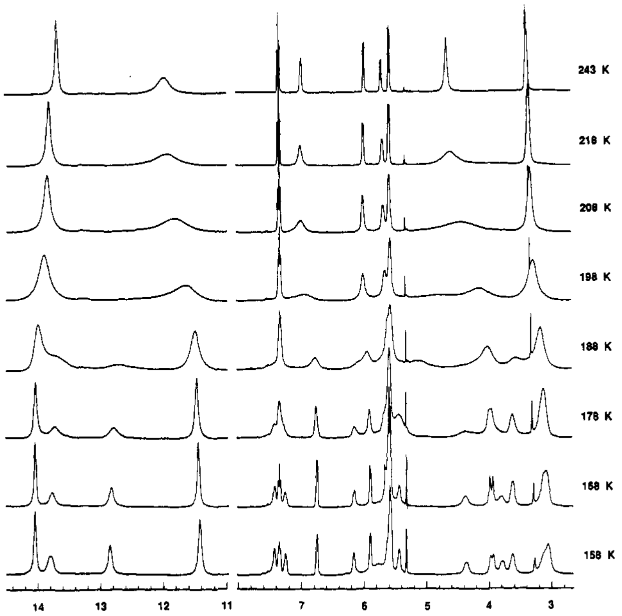


Figure 2. Variable-temperature ^1H NMR spectra of a nominally 0.0097 M solution of dipyridone 1 in CD_2Cl_2.

Neither dimer is ideal, since constraints imposed by the spacer or the intramolecular hydrogen bonds disfavor conformations that accommodate linear intermolecular hydrogen bonds.[10] This may help explain why low-temperature ^1H NMR spectra of dipyridone 1 in CD_2Cl_2 (Figure 2) show individual signals for a dimer as well as a higher aggregate, possibly a cyclic trimer with more nearly linear hydrogen bonds. Peaks at δ 11.4 and 14.1 can be assigned to the NH hydrogens of the dimer because they increase in intensity as the concentration decreases. Integration gives $K = 33 \pm 3$ L/mol at −115 °C in CD_2Cl_2 for formation of the putative trimer from the dimer, and standard analysis shows that $\Delta G^{\ddagger}$ for conversion of the dimer into the trimer is approximately 7.3 ± 0.2 kcal/mol at the temperature of coalescence, −80 °C.[12] The small equilibrium constant and the slow rate of interconversion[7] confirm that the dimer of dipyridone 1 is robust even

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[8] (a) Bélanger-Gariépy, F.; Gallant, M.; Hoogsteen, K.; Simard, M.; Wuest, J. D., unpublished results. (b) Dipyridone 1 was recrystallized from CH_3OH. The crystals belong to the orthorhombic space group $P2_12_12_1$ with $a = 8.818$ (2) Å, $b = 11.528$ (4) Å, $c = 12.752$ (4) Å, $V = 1296.3$ Å^3, and $Z = 4$. An Enraf-Nonius CAD-4 diffractometer was used to collect a set of intensity data at 180 K ($2\theta \leq 140.0°$, Cu Kα). The structure was solved using direct methods (SHELXS 86). Full-matrix least-squares refinement gave $R = 0.034$ and $R_w = 0.042$ for 1357 reflections with $I \geq 1.96\sigma(I)$. Tables of atomic coordinates, bond distances and angles, and anisotropic temperature factors are provided as supplementary material.

[9] For recent studies of intramolecular hydrogen bonding in diamides, see: Dado, G. P.; Desper, J. M.; Gellman, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 8630–8632.

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[11] For a discussion of cooperative effects in hydrogen bonding, see: Steiner, T.; Mason, S. A.; Saenger, W. *J. Am. Chem. Soc.* **1990**, *112*, 6184–6190. Ceccarelli, C.; Jeffrey, G. A.; Taylor, R. *J. Mol. Struct.* **1981**, *70*, 255–271. Jeffrey, G. A.; Takagi, S. *Acc. Chem. Res.* **1978**, *11*, 264–270. Jeffrey, G. A.; Lewis, L. *Carbohydr. Res.* **1978**, *60*, 179–182.

[12] Low-temperature ^1H NMR spectra were recorded at 400 MHz, and probe temperatures were calibrated by using the chemical shifts of methanol. Although pure CD_2Cl_2 freezes at −97 °C, solutions could be cooled to −115 °C. For the calculation of concentrations, the density of CD_2Cl_2 was assumed to vary linearly with temperature.[13] Appropriate pulse delays were used to ensure accurate integrations. Coalescence of the peaks that appear at δ 11.4 and 12.9 in limiting low-temperature spectra of nearly equimolar mixtures of dimeric and trimeric dipyridone 1 allowed $\Delta G^{\ddagger}$ (kcal/mol) at the coalescence temperature to be estimated by using the equation

$$\Delta G^{\ddagger} = aT_c\left[10.319 + \log\left(\frac{T_c[1_2]^{1/2}}{k}\right)\right]$$

where T_c is the coalescence temperature (K), $a = 4.575 \times 10^{-3}$, and k is the pseudo-first-order rate constant given by

$$k = \frac{\pi\delta\upsilon}{\sqrt{2}}$$

where $\delta\upsilon$ is the shift difference.[14] We assume that the ratio of dimer and trimer at T_c is similar to that measured at 158 K.

[13] Griffing, V.; Cargyle, M. A.; Corvese, L.; Eby, D. *J. Phys. Chem.* **1954**, *58*, 1054–1056.

[14] Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982, p 96.

though its hydrogen bonds cannot be ideal.

Acknowledgment. This work was financially supported by the Natural Sciences and Engineering Research Council of Canada and by the Ministère de l'Éducation du Québec. We thank Mike Evans and Christine Johnson for recording our mass spectra, we are grateful to Dr. Nga Hoduc for helping us with osmometric measurements, and we are indebted to Dr. Karst Hoogsteen for helping us solve the crystal structure of compound 1. In addition, we thank Prof. S. C. Zimmerman for helpful discussions and various reviewers for perceptive comments.

Supplementary Material Available: Spectroscopic and analytical data for compounds 1 and 4 and tables of atomic coordinates, bond distances and angles, and anisotropic temperature factors (6 pages). Ordering information is given on any current masthead page.

Direct Observation of α-Oxo Ketenes Formed from 1,3-Dioxin-4-ones and the Enols of β-Keto Esters

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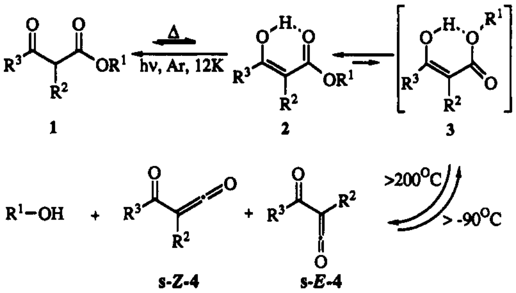
Received November 20, 1990

Summary: The enol forms of β-keto esters thermolyze to alcohols and α-oxo ketenes, which are characterized by low-temperature IR spectroscopy and on warming regenerate the β-hydroxy-α,β-unsaturated esters. The matrix isolated s-*Z* and s-*E* forms of α-oxo ketenes are characterized and photochemically converted into other conformers or sites. Matrix photolysis of 2,2,6-trimethyl-1,3-dioxin-4-one gives the s-*Z* acetylketene initially. α-Oxo ketenes polymerize in the cold and dimerize only at elevated temperatures.

There has been considerable recent interest in α-oxo ketene (acylketene) chemistry.[1-3] In connection with our studies of the keto ketene–keto ketene[3a] and related rearrangements,[3c] we needed ready access to spectroscopically observable α-oxo ketenes as a prelude to ^{13}C labeling experiments. Here we report direct evidence that (i) it is the enol forms of β-keto esters which on flash vacuum pyrolysis (FVP) decompose to α-oxo ketenes and alcohols;[4] (ii) the ketenes react again with alcohols to regenerate the enols; (iii) in the absence of nucleophiles, the α-oxo ketenes do not dimerize in the cold, but polymerize; (iv) open-chain α-oxo ketenes can exist in s-*Z* and s-*E* forms, which are resolved and characterized by Ar matrix IR spectroscopy; (v) photolysis of the matrix isolated α-oxo ketenes produces new conformers or sites, a process which is partially reversed on warming.

Scheme I



The keto (1) and enol (2) forms of β-keto esters[5] are readily distinguishable by IR spectroscopy, the C=O groups of the former appearing at the higher frequencies[6] (e.g. **1b** (Ar, 12 K), 1748, 1683, 1157 cm^{-1}; **2b** (Ar, 12 K), 1655, 1643, 1246 cm^{-1}).

FVP of the esters 1 at temperatures above 200 °C (10^{-4} mbar) with Ar matrix isolation of the products at 12–18 K gave the ketenes 4 (Table I) together with mixtures of the unreacted keto and enol forms (1 and 2). Similar results were obtained on neat deposition of the products at 77 K, except that the bands due to the individual s-*Z* and s-*E* isomers of the ketenes (Table I) were not resolved due to the inherently broader bands obtained under such conditions (e.g. for **4a**: 2137 (s) cm^{-1}). It was particularly noticeable that those esters that do not readily enolize react very sluggishly; the reaction product containing the ketene is rich in the keto form 1 and depleted of enol 2. The keto forms are unreactive, and hence the reaction will not go

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(4) This confirms earlier suggestions made by Campbell, D. S.; Lawrie, C. W. *J. Chem. Soc., Chem. Commun.* **1971**, 355. Berkowitz (footnote 30 in ref 2d), and Leyendecker, F.; Bloch, R.; Conia, J. M. *Tetrahedron Lett.* **1972**, 3703.

(5) Materials: the esters **1a**, **1b**, **1e**, **1g**, **1i**, and **1j** were obtained from Aldrich Chemical Co., purified by fractional vacuum distillation, and checked by ^1H NMR. **1c** was prepared from **1b** (1.7 mmol) by exchange with D_2O (99.7%; 110 mmol) for 1 h at room temperature, extraction with ether, drying over Na_2SO_4 and vacuum distillation; 64% deuteration by ^1H NMR. **1d** was prepared according to Vlassa, M.; Barabas, A. *J. Prakt. Chem.* **1980**, *322*, 821. **1f** and **1l** according to Levine, R.; Houser, C. R. *J. Am. Chem. Soc.* **1944**, *66*, 1768. **1h** according to Savage, G. P. Ph.D Thesis, The University of Queensland, 1988; cf. Ito, Y., Nakatsuka, M.; Kise, N., Saegusa, T. *Tetrahedron Lett.* **1980**, *21*, 2873; and **1k** according to ref 6. **5** was obtained from Tokyo Kasei Kogyo Co. Ltd. and purified by distillation at 64–65 °C (3 Torr). **6** was prepared according to Arndt, F. *Org. Synth.* **1940**, *20*, 27.

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