Figure 1. The ir spectrum of F_2NPF_2 at 10 mm of pressure in a 8.5-cm cell (AgCl windows).

attached to nitrogen. These groups should compete for the lone pair of electrons on nitrogen and reduce the extent of $(p \rightarrow d)\pi$ bonding. This reduction should be reflected in an increased P–N bond length and a loss of planarity about nitrogen. In this communication we report the preparation of F_2NPF_2, which was prepared by allowing PF_2I and N_2F_4 to interact at 23°. The interaction of $(CF_3)_2PI$ and N_2F_4 under conditions similar to those employed for the preparation of F_2NPF_2 did not result in the formation of $F_2NP(CF_3)_2$.

Difluoroaminodifluorophosphine, F_2NPF_2, *is an exceedingly explosive and treacherous compound.* Samples of the compound have detonated in the gas, liquid, and solid phases, and at temperatures as low as $-196°$.

In a typical reaction a 4.4-mmol sample of PF_2I[5] was condensed at $-196°$ into a previously dried 1000-ml round-bottom flask equipped with a Teflon high-vacuum valve (Kontes). A 4.5-mmol sample of N_2F_4 (Air Products Co.) was condensed on top of the sample of PF_2I. The reaction mixture was allowed to warm to 23° for a period of 45 hr. After 15 min the formation of a purple vapor (I_2) indicated a reaction was occurring. The volatile products were separated by codistillation.[6] Only three volatile compounds were obtained from the reaction mixture. Two of these, N_2F_4 and PF_2I, were easily identified by their characteristic infrared spectra. Elemental iodine, identified by a starch test and mass spectral data, remained in the reaction flask. The boiling point of the third volatile compound, F_2NPF_2, lies between those of PF_2I and N_2F_4. No other products were obtained. In another reaction, in which N_2F_4 was removed by passing the volatile products through a trap held at $-140°$, the yield of F_2NPF_2 was 26% (based on the amount of PF_2I used).[7] Although we were unable to obtain detailed stoichiometric data, we suggest the reaction can be represented by

$$N_2F_4 + 2PF_2I \longrightarrow I_2 + 2NF_2PF_2 \qquad (1)$$
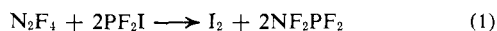
Difluoroaminodifluorophosphine was unequivocally characterized by spectral data. The ^{19}F nmr spectrum at $-60°$ consists of a broad low-field doublet (δ from $CFCl_3$ -2.0 ppm, $^2J_{FNP} = 120$ Hz) of area 1 which is assigned to the fluorines attached to nitrogen. The

(5) J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Syn.*, 10, 147 (1967).

(6) C. H. Cady and D. P. Siegwarth, *Anal. Chem.*, 31, 618 (1959).

(7) We believe higher yields can be obtained by careful photolysis; however, the reaction mixture exploded when we attempted irradiation with a sunlamp in a Pyrex vessel for longer than 1 hr.

broadening arises from the spin–lattice relaxation of the resonances by the quadrupole moment of the nitrogen. In addition to the low-field doublet there is also a high-field doublet (δ from $CFCl_3$ $+71.8$ ppm, $^1J_{PF} = 1336$ Hz) of area 1 which is assigned to the fluorines attached to phosphorus. Each member of the doublet is further split into a 1:2:1 triplet ($^3J_{FPNF} = 13.2$ Hz) by the fluorines attached to nitrogen. The ^{31}P nmr spectrum consists of a triplet (δ -127 ppm from H_3PO_4; $^1J_{PF} = 1345$ Hz), each member of which is split into a triplet ($^2J_{FNP} = 126$ Hz). Both the coupling constants and chemical shifts are consistent with the proposed formulation and are similar to values previously reported for alkylaminodifluorophosphines[8a] and difluoroamino derivatives.[8b]

The compound F_2NPF_2 exhibits gas-phase ir absorptions (Figure 1) at 980 (w), 890 (vs), 725 (m), 540 (w), 410 (?) cm^{-1}. We tentatively assign the broad absorption at 980 cm^{-1} to a N–F symmetric stretch. The frequencies of the asymmetric NF stretch and the symmetric and asymmetric PF stretches lie close together. We feel that these bands overlap and give rise to the rather intense bands centered at about 890 cm^{-1}. The band at 725 cm^{-1} is assigned to the NF_2P symmetric deformation. The band which appears at 410 cm^{-1} may be assigned to a symmetric FPF deformation.[9]

All attempts to obtain a large enough sample of pure F_2NPF_2 for molecular weight vapor density measurements failed because the sample detonated. The mass spectrum of a sample of F_2NPF_2 which contained N_2F_4 as an impurity consisted of peaks attributable to NF_2^+ and PF_2^+. As expected, no parent ion was observed.

(8) (a) R. Schmutzler, *Advan. Fluorine Chem.*, 5, 31 (1965); (b) W. H. Hale and S. M. Williamson, *Inorg. Chem.*, 4, 1342 (1965), and references therein.

(9) The cell employed in this study was fitted with AgCl windows which absorb strongly in this region. A spectrum obtained for an empty cell showed no shoulder at 410 cm^{-1}. The band at 410 cm^{-1} is real.

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Barrier to Inversion at Nitrogen in Imines. Configurational Studies on *O*-Methyl Imidates

Sir:

Inversion at nitrogen in compounds of the type $XYC{=}NZ$ is a problem of long-standing interest.[1a–v]

(1) (a) D. Y. Curtin, E. J. Grubbs, and C. G. McCarty, *J. Amer. Chem. Soc.*, 88, 2775 (1966); (b) H. A. Staab and F. Vögtle, *Chem. Ber.*, 98, 2681 (1965); (c) H. A. Staab and F. Vögtle, *ibid.*, 98, 2691, 2701 (1965); (d) H. A. Staab and F. Vögtle, *Tetrahedron Lett.*, 51 (1965); (e) G. Saucy and L. H. Sternbach, *Helv. Chim. Acta*, 45, 2226 (1962); (f) S. C. Bell, G. L. Conklin, and S. J. Childress, *J. Amer. Chem. Soc.*, 85, 2868 (1963); (g) G. Wettermark and L. Dogliotti, *J. Chem. Phys.*, 40, 1486 (1964); (h) D. G. Anderson and G. Wettermark, *J. Amer. Chem. Soc.*, 87, 1433 (1965); (i) E. Fisher and Y. Frei, *J. Chem. Phys.*, 27, 808 (1967); (j) A. Rieker and H. Kessler, *Tetrahedron*, 23, 3723 (1967); (k) H. Kessler, *Tetrahedron Lett.*, 2041 (1968); (l) H. Kessler and D. Liebfritz, *ibid.*, 427 (1969); (m) H. A. Staab and D. Lauer, *Chem. Ber.*, 101, 864 (1968); (n) A. Rieker and H. Kessler, *Tetrahedron*, 23, 3723 (1967); (o) E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, 51, 17 (1968); (p) V. I. Minkin, Yu. Zhdanov, E. A. Medyantzenz, and Yu A. Ostroumov, *Tetrahedron*, 23, 3651 (1967); (q) H. Saito and K. Nukado, *ibid.*, 22, 3313 (1966); (r) S. Andreades, *J. Org. Chem.*, 27, 4163 (1962); H. A. Staab, F. Vögtle, and A. Mannschreck, *Tetrahedron Lett.*, 697 (1967); (s) F. A. L. Anet, J. C. Jochim, and C. H. Bradley, *J. Amer. Chem. Soc.*, 92, 2557 (1970); (t) J-M. Lehn and B. Munsch,

For X = Y = Z = alkyl a barrier of greater than 23 kcal/mol exists and stable configurational diastereomers occur.[1c,f,2a,b] For X = Y = OCH₃, Z = aryl a much lower barrier of around 13 kcal/mol was found.[3a,b] A class of previously uninvestigated compounds of key interest for a more complete knowledge in this area is the O-alkyl imidates, X = OR, Y = Z = alkyl or aryl. We report now upon the barrier to inversion and configurational stability for members of the series of cyclic O-methyl imidates from ring size five to sixteen as well as the four open-chain derivatives N-methyl-acetimidate (1), N-phenylacetimidate (2), N-ethylacet-imidate (3), and N-n-butylacetimidate (4).[4]

n = 2–8   n = 9–13

1, R = CH₃
2, R = C₆H₅
3, R = C₂H₅
4, R = n-C₄H₉
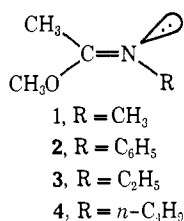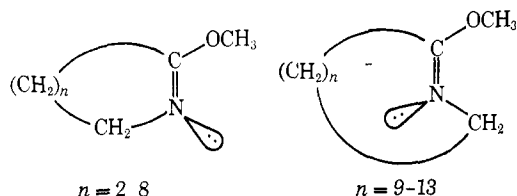
The five-, six-, and seven-membered rings must have the syn configuration for the imino group. For larger rings inspection of molecular models reveals the possibility of incorporating the anti imino group. The pertinent nmr spectral parameters for the series of cyclic compounds are collected in Table I. Reference to Table I reveals that while the singlet O-CH_3 and multiplet CH_2-C=N resonances are quite constant throughout the series, a transition occurs between ring size 11 and 12 for the CH_2—N=C absorption. It goes from a constant value of around 3.40 ppm in the 11- and smaller membered rings, to 3.28 ppm in the 12-, 3.25 ppm in the 13-, and 3.20 ppm in the 16-membered rings, respectively. Significantly, the CH_2—N=C resonance in the open-chain derivative N-ethyl-acetimidate (3) appears at 3.17 and 3.14 ppm in 4. Evidence is presented below to show that 3 and 4 possess the anti configuration as drawn. Therefore the above transition is taken to indicate an anti arrangement about the two methylene groups attached to the C=N group in the 12-, 13-, and 16-membered systems. Next we turned our attention to the determination of the barrier height for syn–anti interconversion in the 11-, 12-, 13-, and 16-membered rings. To this end we examined the temperature dependence of the nmr spectra of these compounds from −100 to +120°.[5] The

Theoret. Chim. Acta, **12**, 91 (1968); (u) M. S. Gordon and H. Fisher, *J. Amer. Chem. Soc.*, **90**, 2471 (1968); (v) H. Kessler, *Angew. Chem.*, **79**, 997 (1967).

(2) (a) F. Vögtle, A. Mannschreck, and H. A. Staab, *Justus Liebigs Ann. Chem.*, **708**, 36 (1967); (b) H. A. Staab, F. Vögtle, and A. Mannschreck, *Tetrahedron Lett.*, 697 (1966).

(3) (a) N. P. Marullo and E. H. Wagner, *J. Amer. Chem. Soc.*, **88**, 5034 (1966); (b) F. Vögtle, A. Mannschreck, and H. A. Staab, *Justus Liebigs Ann. Chem.*, **708**, 51 (1967).

(4) These compounds were prepared from the corresponding amides and lactams by methylation using trimethyloxonium fluoroborate. All compounds had correct microanalyses and consonant ms, ir, and nmr spectra.

(5) Studies were carried out at 100 MHz in CFCl₃-CDCl₃ for low-

Table I. Chemical Shifts for Proton Absorption in Cyclic and Open-Chain O-Methyl Imidates[a]

Ring size	δ, ppm, OCH₃	C=NCH₂	N=C—CH₂
4[b]	3.80		
5	3.72	3.57	
6	3.50	3.40	2.17
7	3.48	3.41	2.36
9	3.52	3.41	2.32
11	3.54	3.40	2.27
12	3.51	3.28	2.22
13	3.52	3.25	2.20
16	3.51	3.20	2.21

Compd	OCH₃	C=NCH₃	N=C—CH₃
1	3.50	2.92	1.78
2	3.73		1.76
3	3.50	3.17 (NCH₂)	1.77
4	3.50	3.14 (NCH₂)	1.76

[a] Spectra were determined at 100 MHz and shifts are relative to TMS in CCl₄ (15% w/w). [b] D. Bormann, *Justus Liebigs Ann. Chem.*, **725**, 124 (1969). Data from 60 MHz.

O-methyl resonance appeared as a sharp singlet throughout the entire range with no evidence of broadening at either temperature extremum. This behavior agrees with either a low or high barrier although the latter appeared more probable. A clue to solve this fundamental uncertainty was provided by studies on the two open-chain derivatives 1 and 2. The three methyl resonances of 1 appear as sharp singlet peaks (Table I). One sees a downfield of 0.23 ppm for the O-CH_3 resonance in 2 relative to 1, while the position of the C-CH_3 resonance is shifted by only 0.02 ppm (Table I). This shift results from the diamagnetic shielding due to the anisotropy of the phenyl group in the configuration as drawn in 2. The spectra were invariant with temperature over the range −100 to +120°. This could indicate either a high barrier (>23 kcal/mol) and, corollarily, configurationally stable anti diastereomers for compounds 1–4, or a low barrier with a large thermodynamic preference for the anti form.

The most convincing evidence in favor of a high barrier in this series came from a study of their conjugate acids. At room temperature in 100% sulfuric acid 1 is converted completely to the protonated form; J_{NHCH_3} = 5 Hz. Heating at 80° caused a gradual doubling of the OCH_3, C-CH_3, and each of the spin-coupled NHCH_3 resonances. After 90 hr at 80°, equi-


librium was established with the interesting result that the stabilities of the anti and syn forms reverse. While the anti diastereomer is the exclusive form for 1, the ratio of 5:6 at equilibrium is 1:2. Similarly for 2 the ratio of the conjugate acids is anti:syn, 1:3.
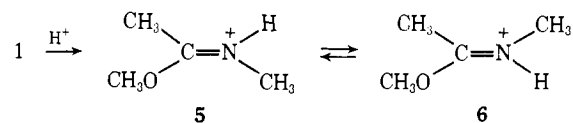
Now returning to the cyclic compounds, for the five- to nine-membered rings no equilibration was observed upon heating the protonated forms at 80° for

temperature work and o-dichlorobenzene for the high-temperature determinations.

90 hr. This, of course, agrees with a syn form for both the imidate and conjugate acid. Neither form can accommodate an anti imino group. However, the 11-, 13-, and 16-membered systems did undergo equilibration. The ratios found were: 11, anti:syn, 1:1; 13, 1:2; 16, 1:1.5. These results indicate an anti configuration for the free imidate for the 13 and 16 rings which upon protonation goes to a mixture of the predominant syn conjugate acids. The 11-membered ring is of syn configuration in the unprotonated form; the protonated forms in this system are of about equal energy.

We interpret the high barrier to inversion at nitrogen in the O-methyl imidates as resulting from interorbital electron repulsion between the nonbonding electrons on oxygen and the electrons localized in a p orbital on nitrogen in the transition state for the sp^2 $\rightleftarrows$ sp $\rightleftarrows$ sp^2 inversion process.
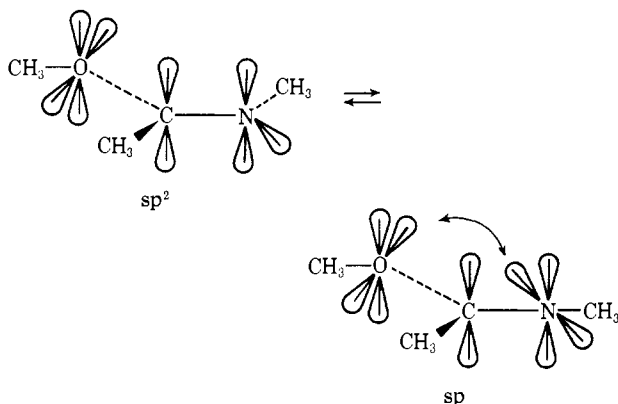
The same destabilizing interaction, likewise, may account for the configurational instability of the syn isomer. Protonation relieves this interaction and rotational equilibration of the conjugate acid yields isomers in which relative stabilities are chiefly dependent upon steric interactions.

Studies are underway to support this interpretation with appropriate model compounds, as well as to examine chemical consequences of the higher energy of the syn isomers in small and medium rings.

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Photoreaction of Michler's Ketone with Benzophenone. A Triplet Exciplex

Sir:

We have discovered that Michler's ketone (4,4'-bis-(dimethylamino)benzophenone) (MK) undergoes a photoreaction with benzophenone, yielding the coupling product I. Because this photoreaction proceeds from the triplet state of MK, yet has its closest analogies in the reactions of triplet benzophenone, we visualize that the photoreaction proceeds through a triplet "exciplex."

Irradiation of 1.0×10^{-3} M MK plus 1.0×10^{-3} M benzophenone in 2-propanol in a 366-nm merry-go-round apparatus[1] leads to formation of photoproduct I with a quantum efficiency of 0.079 ± 0.010.

I
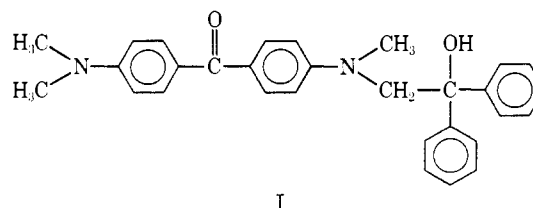
The following properties were observed for I: mp 173–175°; mass spectrum[2] m/e 450 (M$^+$); ir (Nujol) 1600 (strong), 3400 cm^{-1} (broad); uv (CH$_2$Cl$_2$) 245 (ϵ 1.9×10^4), 356 nm (ϵ 3.5×10^4).

By flash photolysis studies,[3] the presence of two photointermediates was demonstrated. One photointermediate was benzophenone ketyl radical (II), identified by its characteristic absorption spectrum (λ_{max} 546 nm)[4] and second-order decay kinetics ($k = 3.1 \times 10^7$ M^{-1} sec^{-1} in 2-propanol).[5] The second photointermediate shows a broad absorption with λ_{max} 500 nm, and we believe this to be either the radical cation of MK or the corresponding deprotonated species (III). At present, we cannot differentiate between radical or radical-ion intermediates.

II   III
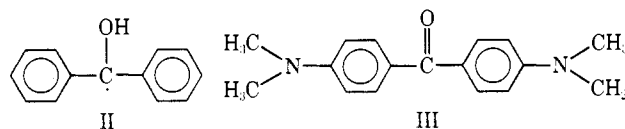
The disappearance of III was monitored at 600 nm, where II does not absorb, and found to follow second-order decay kinetics ($k/\epsilon = 5.3 \times 10^5$ cm sec^{-1}). These kinetics were unaffected by variation in the concentration of benzophenone and by the addition of the triplet quencher 1,3-cyclohexadiene (CHD). These kinetics were taken to represent the coupling of the free radicals II and III to give the final photoproduct I. The kinetics will be second order if II and III are formed in equal amounts and maintain themselves in approximately equal concentrations. This was shown to be essentially true, although there must be some concentration imbalance since the decay of residual II can be observed (*vide supra*) after III is undetectable.

The addition of CHD did diminish the initial concentration of II and III and correspondingly quenched the quantum yield of photoproduct formation. This was the expected consequence of the triplet state of MK.

(1) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).
(2) Taken by Dr. Alan Duffield with the Stanford University MS-9 low-resolution mass spectrometer.
(3) Using the apparatus and techniques described by W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, 88, 4769 (1966).
(4) G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, 57, 1686 (1961).
(5) Using ϵ_{II} (546 nm) 5100 M^{-1} cm^{-1}: A. Beckett and G. Porter, *Trans. Faraday Soc.*, 59, 2038 (1963).