where $k_2[\text{pipH}^+] \gg k_3$

$$\frac{-d[E]}{dt} = \frac{k_1k_3[E][\text{pip}][H_2O]}{k_2[\text{pipH}^+]} = \frac{K_a'k_1k_3[E][OH^-][H_2O]}{k_2K_w}$$

Thus, $(K_a'k_1k_3[H_2O]/K_wk_2) = 1.02 \times 10^4\ M^{-1}\ \text{min}^{-1}$ and $(k_1k_3/k_2)[H_2O] = 193.6\ M^{-1}\ \text{min}^{-1}$. The similarity of the unsymmetrical mechanisms of 15 and 1 is obvious. We have previously asserted that for nucleophilic attack only addition to carbonyl is rate determining. Hence it is necessary here to postulate that the rate of addition of water to the ester is so enhanced by general base catalysis that it far exceeds the rate of breakdown of the intermediate (T) to products.

No deviation from third-order kinetics was found for the k_{gb} term for piperidine.

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Synthesis and Structures of the 2,3-Bis(N-fluorimino)butanes[1]

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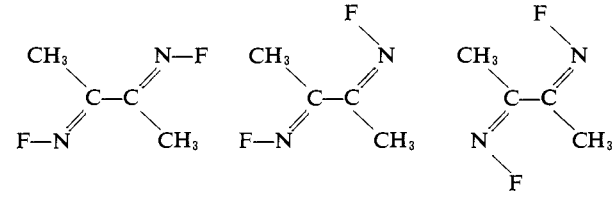
Abstract: The three 2,3-bis(N-fluorimino)butanes (*syn,syn; syn,anti; anti,anti*) have been prepared, isolated, and characterized. The configurations of these geometric isomers have been determined from combined nmr and mass spectral data. The planarity of the isomers is discussed.

There are relatively few unequivocal examples in which imines have been separated into all possible geometric isomers of known configuration.[2,3] Structural assignments generally have been based upon dipole moments, products from stereospecific reactions, and ultraviolet, infrared, and nmr spectral data. Nmr has been employed extensively in the structural determinations of imines, particularly of isomeric mixtures.[4] These structural assignments have been dependent on the coupling constants and chemical shifts of various groups adjacent to the imine function. Mass spectrometry has not been used to study the geometry of imines.

With the exception of the perfluoro analogs,[5] N-fluorimines have been prepared only recently.[6] Logothetis and Sausen[6b] have reported the only example in which a N-fluorimine (1-cyano-N-fluoroformimidoyl fluoride) has been separated into all geometric isomers. Using fluoroolefins as model compounds, the stereochemistry of these isomers has been assigned by nmr. In a similar manner, structures have also been assigned to isomeric mixtures of other N-fluorimines.[6b]

We now wish to report the preparation, isolation, and characterization of the three 2,3-bis(N-fluorimino)-butanes, I (*syn,syn; syn,anti; anti,anti;* the *syn* and *anti* assignments refer to the fluorine and methyl group on the carbon–nitrogen double bond). The configura-



syn,syn Ia *syn,anti* Ib *anti,anti* Ic

tions of these geometric isomers have been determined from combined nmr and mass spectral data. The symmetrical compounds (*syn,syn* and *anti,anti*) have been differentiated from the unsymmetrical compound (*syn,anti*) by means of their nmr spectra. Specific structures have then been assigned to the symmetrical isomers by means of their mass spectra.

Experimental Section

Elemental analyses were performed by the microanalytical laboratory, Stanford University. Ultraviolet spectra were determined with a Cary 14 recording spectrophotometer. Infrared spectra were recorded with a Perkin-Elmer 237-B grating spectrophotometer.

2,3-Bis(N,N-difluoramino)butane. This compound was prepared by the gas-phase addition of tetrafluorohydrazine to 2-butene.[7]

(1) This work was supported by the Office of Naval Research, Contract Nonr 3760(00).

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Table I. Nmr Data for Ia, b, and c

Compd	Instr	Signal	Temp, °C	Chemical shift[a]	Multiplicity[b]	J, cps
Ia	HA-100	H^1	31[c]	τ 7.84	t	2.5
			−50 → 115[d]		t	2.5
		F^{19}	31[c]	φ −34.1	Broad s	
	A-60	H^1	30[c]	τ 7.91	t	2.5
Ib	HA-100	H^1	31[c]	τ 7.78	d of d	2.9, 4.6
				τ 7.86	d	3.75
			−50 → 115[d]		d of d	2.8, 4.6
					d	3.75
		F^{19}	31[c]	φ −38.6	Broad s	
				φ −33.4	Broad s	
	A-60	H^1	30[c]	τ 7.88	d of d	2.8, 4.6
				τ 7.94	d	3.6
Ic	HA-100	H^1	31[c]	τ 7.93	t	1.75
		F^{19}	31[c]	φ −41.5	Broad s	
	A-60	H^1	30[c]	τ 7.96	t	1.75

[a] φ = shift from reference, $CFCl_3$, in ppm. [b] Abbreviations used: s = singlet, d = doublet, t = triplet. [c] $CFCl_3$ solvent, TMS internal standard. [d] Pyridine solvent.

Since the liquid bis(difluoramino)butane has been known to explode, extreme care was taken in handling the neat material. The compound, however, is quite stable and safe as a 50% solution in methylene chloride. It was recovered by cautiously distilling off the excess solvent, and the residue was purified by preparative gas chromatography (15% didecyl phthalate column).

2,3-Bis(N-fluorimino)butane (I). The three isomers of I were conveniently prepared in pyridine and methylene chloride. In a typical preparation, a mixture of 2,3-bis(N,N-difluoramino)butane (3.0 ml), pyridine (17 ml, 10 molar excess), and methylene chloride (65 ml) was heated under reflux for approximately 24 hr. The reaction mixture was then extracted repeatedly with 5% hydrochloric acid to remove all pyridine. The organic phase was dried over sodium sulfate, and the excess solvent was distilled off. The isomeric products were separated from this residue by gas chromatography (15% didecyl phthalate on 80–100 AW Chromosorb P DMCS, 10 ft × 3/8 in. Al, 105°, 125 cc He/min) in an over-all yield of approximately 34%. The compounds were eluted off the column in the order, Ia (16 min), Ib (23 min), Ic (29.5 min), in the approximate ratio of 69:28:3, respectively.

The three volatile, liquid products all had molecular weights of 120, as determined by mass spectrometry. The compounds all exhibited absorption of varying intensities in the carbon–nitrogen double bond region of the infrared (Ia, 1600 cm^{-1}, s; Ib, 1640 cm^{-1}, m, 1620 cm^{-1}, m, sh; Ic, 1630 cm^{-1}, w) and all absorbed in the same region of the ultraviolet [$\lambda_{max}^{mixed\ hexanes}$: Ia, 212 mμ (ε 1810); Ib, 212 mμ (ε 1750); Ic, 209 mμ (ε 507)]. The proton nmr spectra of these compounds only showed the presence of methyl groups (Table I).

Anal. Calcd for $C_4H_6N_2F_2$: C, 40.00; H, 5.04; N, 23.32. Found for Ia: C, 40.01; H, 5.30; N, 23.19. Found for Ib: C, 40.00; H, 5.12; N, 23.24. Found for Ic: C, 40.06; H, 5.05.

Photoisomerization of I. At an initial concentration of 5 × 10^{-2} *M* Ia or b in mixed hexanes, photolysis with an unfiltered, immersion, quartz mercury lamp (Pen-Ray lamp, Ultraviolet Products, Model 11-SC-1, ~10-w) at 0° resulted in production of the remaining two isomers after only a few hours of irradiation. The photolysis, carried out in a nitrogen atmosphere, was followed by gas chromatography and the identity of the isomers was established by peak enhancement upon addition of known material to the samples. In all cases, prolonged irradiation led to polymeric material.

Nuclear Magnetic Resonance Measurements. H^1 and F^{19} nmr spectra were obtained using a Varian HA-100 instrument at 31° in $CFCl_3$ solution (~15% by volume) with an internal TMS standard, using the same sample for both spectra. In addition, H^1 spectra were obtained using these same samples on a Varian A-60 instrument at 30°. Two of the isomers, Ia and b, were examined on the HA-100 instrument in pyridine solution at temperatures ranging from −50 to +115°. In all cases, only methyl or >C=NF absorption was observed. The nmr data are summarized in Table I.

Mass Spectral Measurements. Mass spectra were obtained with a Consolidated Electrodynamics Corp. mass spectrometer, Type 21-103C, with the ionization chamber at room temperature to prevent thermal decomposition prior to ionization. Figure 1 shows the mass spectral fragmentation patterns of Ia, b, and c, expressed in per cent total ionization, Σ_{12} (the absolute intensity of any peak, *m/e*, relative to the sum of the absolute intensities of all peaks with $m/e \geq 12$) obtained with this instrument. The mass spectrum of Ic was also obtained with a Consolidated Electrodynamics Corp. 110B high-resolution mass spectrometer with the ionization chamber at 70° and the inlet system at room temperature. Under these conditions, the mass peak of 79 actually becomes the base peak.

Results and Discussion

The three geometric isomers of 2,3-bis(N-fluorimino)butane (I) were prepared by the pyridine-catalyzed dehydrofluorination of 2,3-bis(N,N-difluoramino)butane in methylene chloride. The three products were purified and separated by preparative vapor phase chromatography (Ia, b, and c by retention time). The three compounds were shown to be isomers of the same molecular structure by elemental composition, molecular weight, infrared, ultraviolet, and nmr spectral data. Finally, the three products were unequivocally demonstrated to be geometric isomers of the same compound by light-induced interconversion. From nmr (Table I) and mass spectral data (Figure 1), configurational assignments have been made for the three geometric isomers.

The proton and fluorine nmr spectra for the three isomers showed only methyl and >C=NF absorption, respectively. Proton nmr measurements at 60 and 100 Mc/sec demonstrated that the methyl absorption patterns for Ia and c were due to field-independent, spin–spin coupling and not due to overlap of different resonance absorption signals (field-dependent). The methyl absorption pattern for each of these two isomers was a single triplet. Although they did not integrate exactly for 1:2:1 (both 1:1.7:1), the triplet patterns and coupling constants remained unchanged at both field frequencies. The proton spectrum of Ib was more complex, consisting of a doublet of doublets (equal intensity) overlapped with another doublet. These two groups of multiplets converged on going from 100 to 60 Mc/sec, although the spin–spin splittings of each group remained unchanged.

The fluorine nmr spectra for both Ia and c had only single broad F^{19} resonance signals, whereas the Ib spectrum had two such signals. The F^{19} signals must necessarily show splitting corresponding to that in the

proton spectra. However, the nitrogen quadrupole relaxation had apparently collapsed the multiplets to such an extent that fine structure could not be resolved.

From these nmr data, symmetrical and unsymmetrical structures can be assigned to the three isomers. In the Ib isomer, neither the methyl groups nor the fluorine atoms are equivalent. One methyl group is split by two nonequivalent fluorines producing a doublet of doublets. The remaining methyl group is split by only one fluorine, giving rise to the remaining doublet. Isomer Ib corresponds to the unsymmetrical *syn,anti* configuration.

Since isomers Ia and c have magnetically equivalent methyl groups and fluorine atoms (only one signal each in H^1 and F^{19} spectra), they have been assigned the symmetrical structures (*syn,syn* and *anti,anti*). The fine structure of the proton spectra of Ia and c can be rationalized in terms of these symmetrical structures. From symmetry considerations alone, the two methyl groups and two fluorine atoms should be equivalent. An $AA'X_3X_3'$ spin system then describes either symmetrical isomer. If it is assumed that the two methyl groups are not coupled, the spin system reduces to $AA'X_3$ which is a special case of an ABX_3 system.[8] The observed proton spectra of Ia and c are consistent with that predicted for an $AA'X_3$ system. The X part of this spectrum consists of a field-independent doublet with a central line in the middle. The relative intensities of this apparent triplet are a function of the various resonance frequencies and coupling constants. These nmr data do not permit further assignment of specific symmetrical structures to isomers Ia and c.

It is possible, however, to assign specific configurations to these symmetrical isomers by mass spectrometry. Figure 1 shows the mass spectral fragmentation patterns of Ia, b, and c. Although the over-all fragmentation patterns appear quite similar for the three isomers, there are important intensity and peak differences which permit the structural assignments to be made.

Reasonable structures can be assigned and fragmentation pathways can be written for all of the intense peaks in the three mass spectra. Acetonitrile, which is produced in many ways, accounts for the cluster of intense peaks around *m/e* 41.[9] On the basis of metastable peaks, two important one-step decomposition pathways can be assumed.[10] These metastable peaks appear at *m/e* 85 and 36. They are quite intense in the Ia spectrum, of intermediate intensity for Ib, and essentially nonexistent in the Ic spectrum. The molecular ion, *m/e* 120, loses a fluorine atom to produce the 101 peak (eq 1), as indicated by the metastable peak at *m/e* 85. The 101 peak, in turn, fragments to neutral acetonitrile and the 60 peak, giving rise to the metastable peak at 36.

The metastable peaks, the molecular ion (*m/e* 120), and the 101 peak are extremely weak for the Ic isomer (the 60 peak can arise by other fragmentation processes),

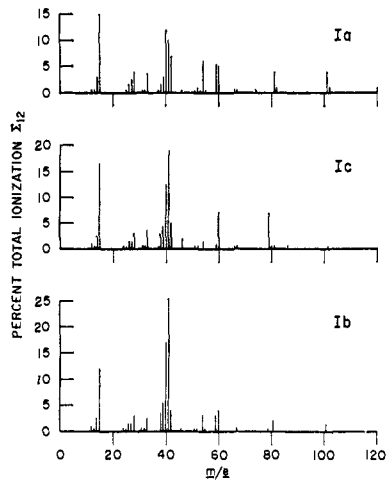
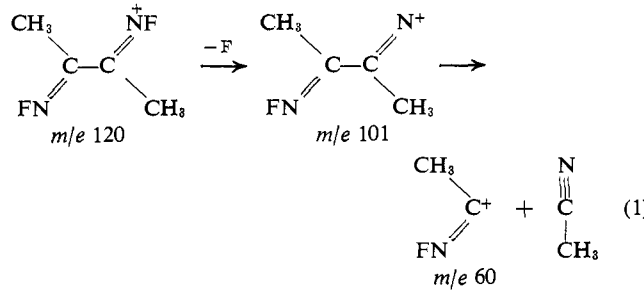
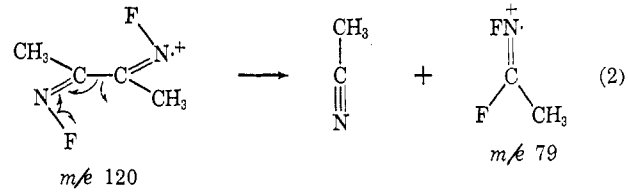


Figure 1. Mass spectral fragmentation patterns of Ia, b, and c.

indicating that other important fragmentation pathways are available to this isomer. In fact, the mass spectrum of this symmetrical isomer exhibits a major peak at *m/e* 79 which is essentially nonexistent in the other two spectra. Since this 79 peak is very intense in mass spectra of Ic at very low temperatures at which this isomer is known to be stable, the peak does result from an ionized fragmentation process and not from a thermal decomposition. The molecular weight of this fragment, measured under high resolution, is 79.0230. Of all possible fragments, this molecular weight is consistent only with that calculated for the species, $C_2H_3NF_2$ (79.0234). This species is the key to the final structural assignment.



A most energetically favorable process can be formulated for production of the 79 fragment, $C_2H_3NF_2$, involving fluorine migration and carbon–carbon bond fission in the molecular ion (eq 2). Fluorine migration from nitrogen to carbon is a highly exothermic process (by some 36 kcal/mole) and in the present example (eq 2),



the simultaneous carbon–carbon bond fission results in a stable neutral molecule and a highly stabilized radical cation. The proposed rearrangement appears to be the only attractive, energetically favorable process leading to the mass peak at 79. Although mass spectral fragmentations involving halogen migration from

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carbon to carbon are well documented,[11] the present case of fluorine migration appears to be the first substantiated example of a fragmentation process involving intramolecular fluorine migration from nitrogen to carbon.[12]

It is proposed that the *anti,anti* isomer of 2,3-bis(N-fluorimino)butane corresponds to Ic. This structural assignment is dependent upon the assumption that fragmentation involving the postulated fluorine migration accounts for the mass peak at 79. In the *anti,anti* configuration, the position of the fluorine atoms is especially favorable for fluorine migration to carbon, resulting in an intense mass peak at 79. Inspection of molecular models reveals that in this configuration the fluorine atom lies over the carbon atom in question. If the fluorine is in the *syn* position, overlap with the carbon is not possible and migration cannot occur.

The configurational assignment for the three isomers is now complete. The *syn,anti* configuration was assigned to Ib by nmr; the *anti,anti* configuration has now been assigned to Ic by mass spectrometry. Consequently, the *syn,syn* configuration must correspond to Ia.

The rearrangement peak, *m/e* 79, for the unsymmetrical *syn,anti* isomer (Ib) is extremely weak. Although fluorine migration presumably can occur in this isomer, it is predominantly cleavage that takes place in the mass spectrometer. Clearly, this is more than just a statistical difference; the cleavage process must be energetically more favorable in order to compete so successfully with migration. This fragmentation behavior presumably reflects the steric requirements in the molecules.

Examination of molecular models and the various spectral data suggests that the three geometric isomers of 2,3-bis(N-fluorimino)butane are sterically hindered, and probably each exists in predominantly one rotational conformation. Rotation about the central carbon–carbon single bond is sterically hindered by methyl–methyl interactions and by methyl–fluorine interactions when the fluorine is in the *anti* position. The nonbonding pair of electrons on the nitrogen also interacts with the various groups. Over a temperature range of -50 to $+115°$, the proton nmr splitting patterns and coupling constants for the Ia and Ib isomers remain unchanged. For no change to occur, the isomers probably either exist in one very favorable conformation or are rotating very rapidly.[13] The latter alternative is unlikely from considerations of steric hindrance and planarity necessary for possible conjugation. The most sterically favorable single conformation in each isomer places the two methyl groups approximately 180° apart. In this conformation, the *syn,syn* isomer can be planar, while the *anti,anti* isomer is probably somewhat twisted from this plane. The *syn,anti* isomer assumes some intermediate geometry. Clearly, the more planar the molecule, the better the orbital overlap permitting conjugation between the two carbon–nitrogen double bonds. Such conformations would also result in the smallest possible dipole moments.

Unless conjugated, the >C=N— chromophore does not normally absorb above 200 mμ in the ultraviolet.[3a,14] The measurable absorption around 210 mμ for each of the isomers indicates a reasonable degree of conjugation between the two imine chromophores. Although small, the bathochromic shift on going from the *anti,anti* isomer (Ic) to the *syn,anti* (Ib) or the *syn,syn* (Ia) isomer reflects the increasing degree of planarity, and conjugation, in the molecules.

The mass spectral data also provide evidence that the isomers each exist in only one rotational conformation. It has been proposed that the *anti,anti* isomer (Ic) initially fragments to a large extent by a fluorine migration process. Although fluorine migration presumably could occur in the *syn,anti* isomer (Ib), cleavage is the primary fragmentation process. If the *anti,anti* isomer (Ic) is twisted from the plane, the fluorine can be directly over the carbon atom to which it migrates with little interference from the methyl group on that carbon. Since the *syn,anti* isomer is probably more planar than the *anti,anti* isomer, it is possible that the methyl group hinders the fluorine migration, making other fragmentation processes more favorable. Apparently, the *syn,anti* isomer does not rotate into a conformation more favorable for migration. It seems reasonable to assume that each of the geometric isomers exists in only one conformation in which the two methyl groups are approximately 180° apart.

Acknowledgment. The authors are indebted to Mr. Derek Tegg for assistance in the handling and isolation of the compounds and to Professor John I. Brauman for many helpful discussions.

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