solvable into stable optical antipodes at room temperature. We are actively investigating this possibility.

Stanley J. Brois
Esso Research and Engineering Company
Linden, New Jersey
Received October 27, 1967

Aziridines. XII. Isolation of a Stable Nitrogen Pyramid

Sir:

So far, all attempts to resolve substituted aziridines have been unsuccessful.[1] Moreover, Bottini and Roberts[1g] have concluded that "substituted aziridines with molecular asymmetry due to trivalent nitrogen are likely only to be resolvable into reasonably stable optical antipodes at temperatures below −50°."

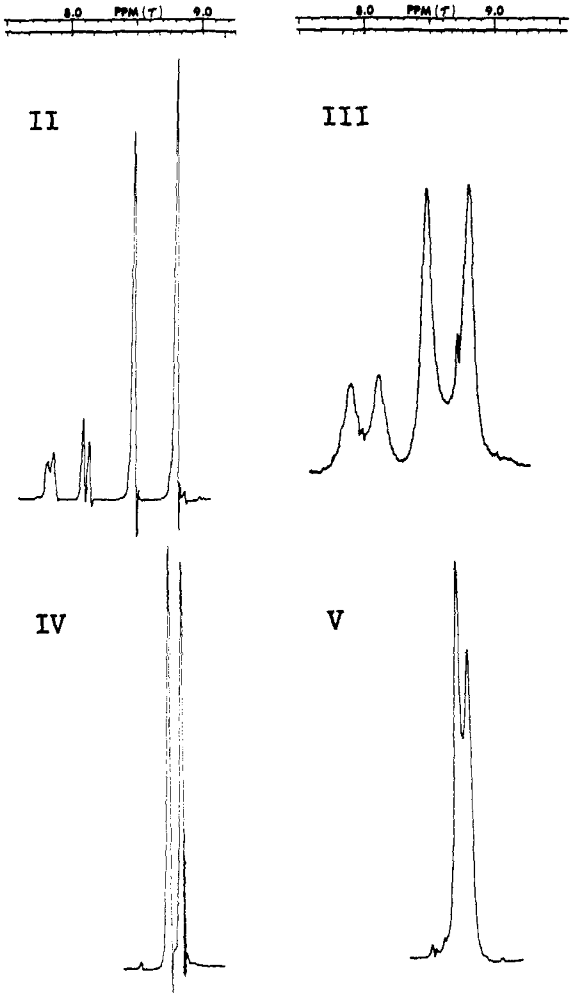
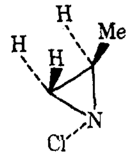


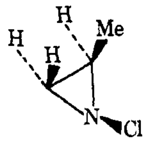
Figure 1. Proton spectra of N-haloaziridines as 25% (w/v) CCl_4 solutions at 25°.

However, we have recently uncovered nmr spectral evidence[2] which suggests that N-haloaziridines may indeed be resolvable at room temperature. The present study lends further substance to this proposal.

We wish to describe here the successful synthesis of *cis* (Ib) and *trans* (Ia) isomers of 1-chloro-2-methylaziridine (I). Ia and Ib represent the first isolable invertomers of trivalent nitrogen, and their isolation provides clinching evidence for the existence of a stable nitrogen pyramid in N-chloroaziridines.



Ia



Ib

The diastereogenic[3] aziridine I selected for study was prepared *via* the addition of 0.1 mole of propylenimine to 1 equiv of N-chlorosuccinimide in refluxing ether. Gas chromatographic analysis of the filtered reaction mixture on a 3-ft 10% silicone oil (mol wt 200) column at 25° showed two product peaks (Ia and Ib) in ~2:1 intensity ratio, respectively. Elemental analysis of the gc purified products revealed that Ia and Ib were identical in composition.[4] The alleged isomers gave positive halogen tests and liberated propylenimine on treatment with a secondary amine.

The 100-MHz nmr spectra of the *cis* and *trans* invertomers are shown in Figure 1 along with the first-order coupling constants obtained from the normal and decoupled (insert) spectra. The assignment of peaks is based on recent nmr data[5] for configurationally pure N-chlorostyrenimines. The magnitudes of the vicinal and geminal coupling constants for Ia and Ib are in consonance with our previously reported[5] J_{vic} and J_{gem} value for N-haloaziridines.

The rather weak *cis* coupling in Ib may be ascribed to a stereospecific electronegativity effect[6] by chlorine on H_a and H_b in the *cis* invertomer. Owing to steric compression between the chlorine and the methyl group, the dihedral angle between the *trans* protons (H_a and H_b) and chlorine approaches 180°, the angle of maximum electronegativity effect and minimum J_{ab}.

Steric compression between the ring substituents in Ib is also reflected in the low-field shift of the methyl protons and the upfield shift of H_a relative to the corresponding protons in the *trans* invertomer. Apparently nonbonded interactions between chlorine and the methyl group in Ib shift the electron cloud away from the methyl hydrogens toward the region of H_a, thus accounting for the deshielding of the methyl protons and higher shielding of H_a.[9] The upfield shift of H_c in the *cis* isomer compared to H_c in Ia is attributable to the magnetic anisotropy of chlorine.[10] Details of the nmr

---

(1) (a) R. Adams and T. L. Cairns, *J. Am. Chem. Soc.*, **61**, 2464 (1939); (b) P. Maitland, *Ann. Rept. Chem. Soc. London*, **36**, 239 (1939); (c) J. Meisenheimer and L.-H. Chou, *Ann.*, **539**, 70 (1939); (d) J. D. C. Mole and E. E. Turner, *Chem. Ind.* (London), **17**, 582 (1939); (e) T. L. Cairns, *J. Am. Chem. Soc.*, **63**, 871 (1941); (f) H. M. Kissman and D. S. Tarbell, *ibid.*, **74**, 4317 (1952); (g) A. T. Bottini and J. D. Roberts, *ibid.*, **80**, 5203 (1958).

(2) S. J. Brois, *J. Am. Chem. Soc.*, **90**, 506 (1968).

(3) Capable of diastereoisomerism owing to the presence of asymmetric carbon and nitrogen atoms.

(4) *Anal.* Calcd for C_3H_6NCl: C, 39.36; H, 6.61. Found (Ia): C, 39.34; H, 6.89; (Ib): C, 39.37; H, 6.85.

(5) (a) S. J. Brois and G. P. Beardsley, *Tetrahedron Letters*, 5113 (1966); (b) S. J. Brois, manuscript in preparation.

(6) By analogy, variations in vicinal coupling constants due to the orientation of electronegative substituents in six-[7] and five-membered[8] rings have recently been reported.

(7) H. Booth, *Tetrahedron Letters*, 411 (1965).

(8) L. H. Zalkow and M. Ghosal, *Chem. Commun.*, 922 (1967).

(9) For a relevant discussion of dispersion-induced shielding and deshielding effects in aziridines, see S. J. Brois, *Tetrahedron*, in press.

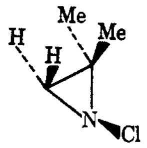
(10) A similar chemical shift trend has also been observed[11] in chlorooxiranes. Assuming *cis* coupling is stronger than *trans* coupling[5] we find that the proton *cis* to chlorine in 2-chlorooxirane resonates at higher field relative to the *trans* proton.[12]

(11) S. J. Brois and E. L. Stogryn, unpublished results.

(12) The chemical shift values previously assigned[13] to the protons

spectral studies on N-haloaziridines will be reported in a separate paper.

Most significantly, the isolation of stable invertomers of I logically implies that N-haloaziridines are resolvable into optical antipodes at room temperature. Accordingly, we have elected to initially study the resolution of 1-chloro-2,2-dimethylaziridine (II) in view of the remarkable configurational stability of this molecule even at $\sim$135°.[14]



II

The exceptional stability of Ia and Ib demonstrates, in another sense, the remarkable configuration-holding power of chlorine and clearly negates the concept of d-orbital resonance stabilization of pyramidal inversion in N-chloroaziridines.[15]

Variable temperature nmr studies on Ia and Ib are in progress.

---

cis and *trans* to chlorine in 2-chlorooxirane are incorrect and should be reversed.

(13) B. P. Dailey, A. Gawer, and W. C. Neikam, *Discussions Faraday Soc.*, **34**, 18 (1962); K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Am. Chem. Soc.*, **86**, 762 (1964).

(14) No change in the ambient temperature nmr spectrum[2] of II was evident even at $\sim$135°. The thermal lability of II has thus far precluded attempts to ascertain a coalescence temperature.

(15) V. F. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. U. Stepanyants, and O. A. Iuzhakova, *Opt. Spectry.* (USSR), **19**, 122 (1965).

Stanley J. Brois
Esso Research and Engineering Company
Linden, New Jersey

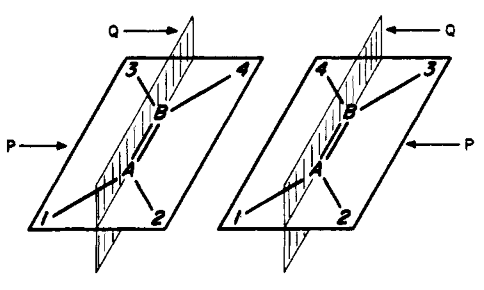
Received November 4, 1967

Unambiguous Specification of Stereoisomerism about a Double Bond

Sir:

Although the configurational descriptors *cis* and *trans* and *syn* and *anti* are widely employed in nomenclature to describe double-bond stereoisomerism, the resulting names are often ambiguous because these configurational descriptors have not been defined according to any generally accepted universally applicable rules. Described herein is a set of rules, based on the sequence rules of Cahn, Ingold, and Prelog,[1] which permit unambiguous description of double-bond stereoisomerism in all cases.[2] A new set of descriptors, *E* and *Z*, is also introduced, since redefinition of existing descriptors would add to the ambiguities already present in the literature. These descriptors will be used in *Chemical Abstracts* Indexes beginning with Volume 66.

The type of stereoisomerism under consideration, and the general method of specifying the configurational differences, may be described in terms of the completely general situation represented by a pair of doubly bound atoms, A and B, and their nearest neighbors, 1, 2 and 3, 4, respectively (Figure 1). Since the molecular configuration of this system is such that all of the atoms lie in the same plane, *P*, the necessary and sufficient condition for stereoisomerism is that the atoms or groups attached to A (1 and 2) and B (3 and 4), respectively, be unequal. Thus the two possible configurations shown in Figure 1 can be differentiated by indicating that groups 1 and 3 are on the same side of the reference plane, *Q* (Figure 1a), or on opposite sides of the reference plane (Figure 1b). The rules for specifying these configurational differences are: **(I) for each double bond to be described configurationally, determine which of the two groups attached to each of the doubly bound atoms has the higher priority according to the sequence rules of Cahn, Ingold, and Prelog;**[1b] **(II) that configuration in which the two groups of higher priority are on the** *same* **side of the reference plane (Figure 1) is assigned the stereochemical descriptor *Z* (from the German** *zusammen***); that configuration in which these groups are on** *opposite* **sides is assigned the descriptor *E* (from the German** *entgegen***).**



(a) (b)

Figure 1. Geometry of a pair of doubly bound atoms, A and B, and their nearest neighbors.

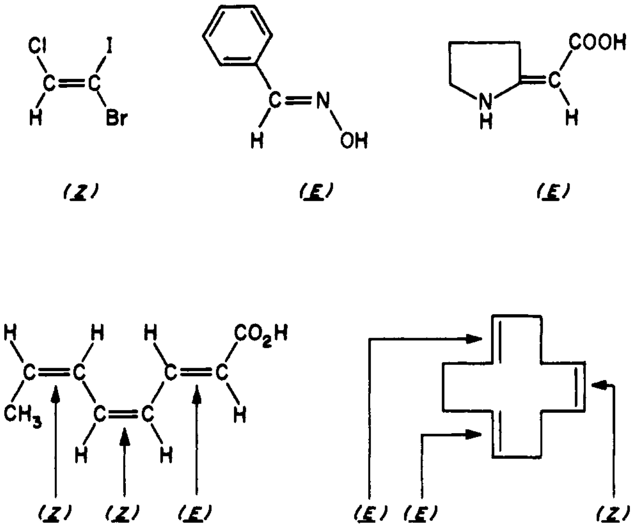


Figure 2. Examples illustrating application of the rules for assignment of *E* and *Z*.

The application of these rules is illustrated in Figure 2.

It is emphasized that the rules for assignment of the configurational descriptors *E* and *Z* are based entirely on the structure of the molecule and are independent of any vagaries of the nomenclature with which they may be used. Details concerning the use of these descriptors in *Chemical Abstracts* nomenclature will be published elsewhere.[3] By way of illustration, however, the

---

(1) (a) R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956); (b) R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966).

(2) Although both chiral and achiral elements may be associated with double bonds in some instances (*e.g.*, cyclooctene), our treatment pertains only to the achiral elements of double-bond stereoisomerism.

(3) J. E. Blackwood, C. L. Gladys, A. E. Petrarca, W. H. Powell, and J. E. Rush, *J. Chem. Soc.*, in press.