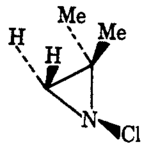
spectral studies on N-haloaziridines will be reported in a separate paper.

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 ~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.

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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 ~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).

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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***).**

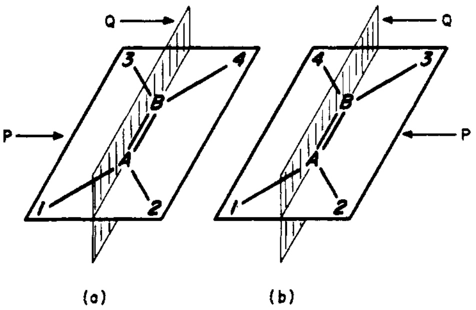

Figure 1. Geometry of a pair of doubly bound atoms, A and B, and their nearest neighbors.

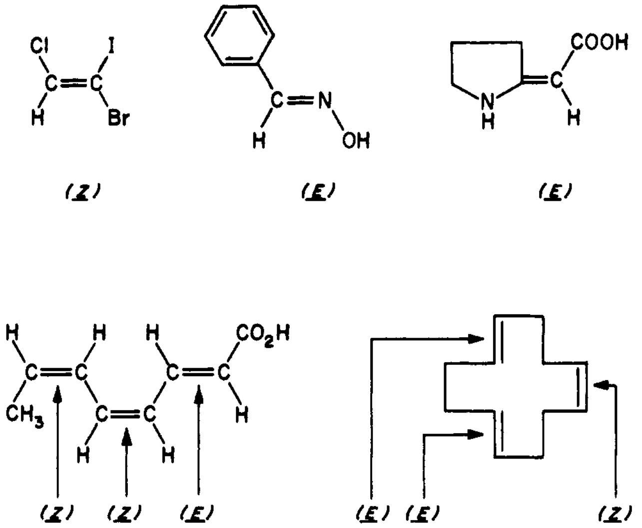

Figure 2. Examples illustrating application of the rules for assignment of *E* and *Z*.

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

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(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.

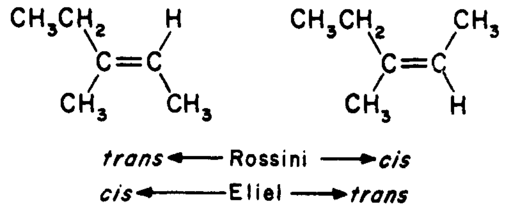

Figure 3. Comparison of descriptions of stereoisomeric 3-methyl-2-pentenes according to Rossini's[4] and Eliels'[8] definitions.

Chemical Abstracts names for the structures in Figure 2 are: 1-bromo-2-chloro-1-iodoethylene, (*Z*)-; benzaldehyde oxime, (*E*)-; $\Delta^{2,\alpha}$-pyrrolidineacetic acid, (*E*)-; 2,4,6-octatrienoic acid, (*E*,*Z*,*Z*)-; and 1,5,9-cyclododecatriene, (*E*,*E*,*Z*)-. The descriptors for the last two examples are listed in decreasing order of priority of the respective double bonds. This ordering principle will be described elsewhere.[3]

Previously reported methods for describing double bond stereoisomerism are of limited applicability or have not gained wide acceptance. Epstein and Rossini[4] have described a method for naming geometrical isomers of hydrocarbons in which one indicates whether the carbons of the fundamental chain[5] adjacent to the doubly bound carbons are on the same (*cis*) or opposite (*trans*) sides of the reference plane.[6] Stereoisomeric oximes have traditionally been named by using the descriptors α, *syn*, or *cis* for that configuration in which the reference groups are on the same side of the reference plane, and β, *anti*, or *trans* for that configuration in which these groups are on opposite sides of the reference plane.[7] Eliel's more generalized treatment[8] gives results which are sometimes opposite those of Rossini's (*cf.* Figure 3). According to Eliel, configurational differences for the constitutional type in which $1 = 3$, $2 = 4$, and $1 \neq 2$ (Figure 1) may be described by using the prefix *cis* for that configuration in which the equal groups are on the same side of the reference plane (Figure 1a) and *trans* for that configuration in which the equal groups are on opposite sides (Figure 1b). Configurational differences for the constitutional type in which $1 = 3$ and $1 \neq 2 \neq 4$ may be similarly described. However, as pointed out by Eliel and by Cahn, Ingold, and Prelog[1] there is no generally accepted method for describing configurational differences for the constitutional type in which $1 \neq 2 \neq 3 \neq 4$.

McCasland[9] and others[10] have devised methods of handling the completely general situation, but these methods have not been widely used in nomenclature.[11] Cahn, Ingold, and Prelog used their priority rules to determine the reference groups which are to be related by the descriptors *cis* and *trans*[1a] (or *seqcis* and *seqtrans*[1b]) in their system of chirality specification. However, since these geometrical labels do not appear in the final descriptions of the various chiral centers, Cahn, *et al.*[1] pointed out that the treatment is only a working tool for application of their rules. Nevertheless, they noted that the principles involved could also be applied to nomenclature.

The increasing amount of stereochemical information reported in the literature emphasizes the need for unambiguous communication of such information. The need is even greater now that techniques are available for translating unambiguous systematic names into computer structural representations[14] which may include stereochemical information at various levels of sophistication.[15,16] We believe that the rules described herein provide a simple means for unambiguous specification of double-bond stereoisomerism.

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(4) M. B. Epstein and F. D. Rossini, *Chem. Eng. News*, **26**, 2959 (1948).

(5) The fundamental chain is that carbon chain which includes, first, the maximum number of double bonds and, second, the maximum number of triple bonds.

(6) These rules were subsequently adopted by IUPAC (Comptes Rendus de la Seizième Conférence, New York, N. Y., and Washington, D. C., 1951) and were published in *Compt. Rend.*, 102 (1959).

(7) G. Wettermark, *Svensk Kem. Tidskr.*, 79, 249 (1967).

(8) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 318–319.

(9) G. E. McCasland, "A New General System for the Naming of Stereoisomers," proposal distributed by the Nomenclature Committee, Division of Organic Chemistry, American Chemical Society, 1953 (copies are available from Chemical Abstracts Service, Columbus, Ohio).

(10) A. P. Terentiev, A. N. Kost, A. M. Zuckermann, and V. M. Potapov, "Nomenclature of Organic Compounds," Akad. Nauk SSSR, Moscow, 1955. The stereochemistry portion of this report was submitted as a proposal to the IUPAC, 1966.

(11) However, IUPAC notation rules[12] for describing stereoisomerism about a double bond are based on the same principles as McCasland's rules for nomenclature. Beilstein[13] has recently adopted a similar system.

(12) "Rules for IUPAC Notation for Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1961.

(13) "Beilstein's Handbuch der Organishen Chemie," Vierte Auflage, Drittes Ergaenzungswerk, Band VI, Erster Teil, Springer-Verlag, Berlin, 1965, p v.

(14) G. G. Vander Stouw, I. Naznitsky, and J. E. Rush, *J. Chem. Soc.*, 7, 165 (1967).

(15) D. P. Leiter, Jr., H. L. Morgan, and R. E. Stobaugh, *ibid.*, **5**, 238 (1965).

(16) A. E. Petrarca, M. F. Lynch, and J. E. Rush, *ibid.*, 7, 154 (1967).

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Restricted Rotation about the N–N Single Bond. Linear Correlation of Rate with Substituent

Sir:

Restricted rotation about the C–N single bond as determined by the nmr technique has been the subject of many investigations.[1] Of equal theoretical interest is rotation about the N–N single bond; however there are few examples[2–4] of the determination of rotational rates and barriers for this process. The apparent reason for this is that previous studies have shown that the rates of the rotation about the N–N bond of most nitrosamines are too slow[2,5] whereas those of hydrazones[4] are too fast to observe exchange broadening.

We now wish to report results on the temperature-dependent nmr spectra of a series of 1-aryl-3,3-dimethyl-

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(1) H. S. Gutowsky, J. Jonas, and T. H. Siddall, *J. Am. Chem. Soc.*, **89**, 4300 (1967), and references cited therein.

(2) C. E. Looney, W. D. Phillips, and E. L. Reilly, *ibid.*, **79**, 6136 (1957).

(3) S. Andreades, *J. Org. Chem.*, **27**, 4163 (1962).

(4) A. Mannschreck and U. Koelle, *Tetrahedron Letters*, **10**, 863 (1967).

(5) G. J. Karabatsos and R. A. Tallen, *J. Am. Chem. Soc.*, **86**, 4373 (1964).