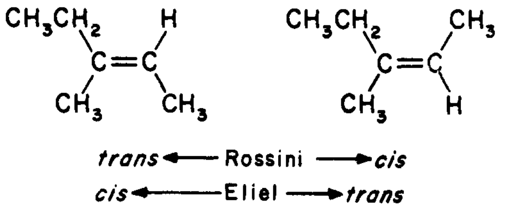

Figure 3. Comparison of descriptions of stereoisomeric 3-methyl-2-pentenes according to Rossini's[4] and Eliels'[8] definitions.

*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 $\alpha$, *syn*, or *cis* for that configuration in which the reference groups are on the same side of the reference plane, and $\beta$, *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.

**Acknowledgment.** Partial support of this work by National Science Foundation Contract C-414 is gratefully acknowledged. The authors also wish to express their appreciation to Drs. R. S. Cahn, E. L. Eliel, and P. G. Gassman for helpful discussions on various aspects of this work.

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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.

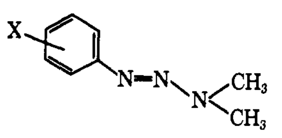
[2] C. E. Looney, W. D. Phillips, and E. L. Reilly, *ibid.*, **79**, 6136 (1957).

[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).

triazenes (**1**). These results establish that the rates of rotation around the N–N bond for these compounds are measurable by standard nmr methods and that the *exchange-averaging process obeys a linear free energy relationship.*



**1**

The proton spectra of **1** show a single methyl resonance at magnet temperature. Cooling the sample results first in a broadening of the methyl signal and then in formation of a widely separated doublet. The pertinent nmr and kinetic data are given in Table I.

**Table I.** Nmr Data[a,b] on the Rotation of **1**

| X | $T_c$, °C | $\Delta\nu_0$, cps | $k(T_c)$, sec$^{-1}$ | $\Delta F^{\ne}(T_c)$ | $k(0°)$, sec$^{-1}$ |
|---|---|---|---|---|---|
| $p$-CH$_3$ | −33.9 | 19.2 | 42.6 | 12.1 | 533 |
| H | −22.5 | 18.5 | 41.0 | 12.7 | 194 |
| $p$-Cl | −11.3 | 20.2 | 44.8 | 13.3 | 81.9 |
| $m$-CF$_3$ | 5.3 | 20.0 | 44.2 | 14.2 | 29.3 |
| $p$-NO$_2$ | 35.1 | 20.2 | 44.8 | 15.7 | 5.3 |

[a] Spectra were taken in chloroform solution at a concentration of 14% (w/w) except for the $p$-nitro compound which was 7% (w/w). [b] A Varian A-60 equipped with a Varian variable-temperature probe was used to observe the chemical shift as a function of temperature. Temperatures were measured with an accuracy of ±0.8°. A given temperature could be held constant to ±0.1°. Spectra were calibrated by the side-band method, using a frequency counter to measure the side-band frequency. The method described by J. A. Pople, W. S. Schneider, and H. J. Bernstein ("High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 224) was used to calculate $\tau$ values. At each temperature no less than six determinations were made, with 15 determinations being made at the point of maximum separation. Arrhenius plots were made using no less than seven temperatures. All slopes gave a correlation coefficient of better than 0.99 when treated by the method of least squares.

Inspection of Table I shows that the $\Delta\nu_0$ values for the series of triazenes are all very similar, and therefore the rates at the coalescence temperature ($T_c$) are all nearly the same. However, $T_c$ spans a range of almost 70°, progressively increasing in going from X = CH$_3$ to X = NO$_2$. It therefore would be expected that a comparison of rates at the same temperature for the series of triazenes would show a progressive rate decrease with increasing electron withdrawal by the substituent. This is also evident from a comparison of the $\Delta F^{\ne}$ values which progressively increase in going from $p$-CH$_3$ to $p$-NO$_2$.

In order to compare rates at the same temperature Arrhenius plots were determined for each compound, and from these data specific rate constants were calculated at both 25 and 0°. The values obtained at 0° are included in Table I. Figure 1 shows a Hammett plot of these data. An excellent linear relationship is observed at both 25 and 0° with a $\rho$ value of −2.01 and −2.03, respectively. This is a gratifying result since a number of previous attempts to systematically correlate the electronic effects of substituents in a variety of nmr exchange processes, such as the rotational rates of amides,[6,7] nitrogen inversion rates,[8,9] and isomerization of iminocarbonates,[10] have not been successful. Inversion or rotational rates and barriers can be markedly affected by steric as well as electronic effects. Nonbonded interactions can destabilize the ground state and thereby lower the barrier[11–14] or these interactions can destabilize the transition state and increase the barrier.[15,16] There should be, however, no significant difference in nonbonded interactions between ground and transition states for the series of triazenes being reported here, and therefore the change in rate should be a function only of the electronic effect of the substituent.

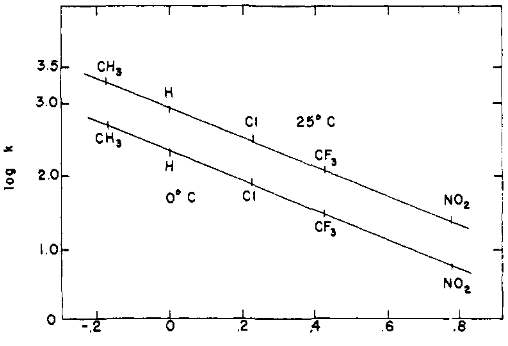


Figure 1. Plot of log $k$ for the rotational rate of 1-aryl-3,3-dimethyltriazenes *vs.* Hammett substituent constants.

The negative slope found for the Hammett plot requires that during the rotational process the electron density at the nitrogen atom bonded to the aryl group decreases in going from ground to transition state. In addition, the relatively large magnitude of $\rho$ suggests that there is a considerable difference in polarization of the ground state compared to the transition state. This is consistent with the view that restricted rotation is due to $\pi$ overlap between the amino and azo nitrogens in the ground state which is lost when the dimethylamino group is rotated 90° out of the ArN=N plane. The observed change in rate, then, is attributed to the extent by which the substituents influence the difference in $\pi$ delocalization energy between the ground and transition states,[14] and furthermore this energy difference is linearly related to the substituent.

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(9) F. A. L. Anet, R. Trepka, and D. J. Cram, *ibid.*, **89**, 357 (1967).

(10) N. P. Marullo and E. H. Wagener, *ibid.*, **88**, 5034 (1966).

(11) A. T. Bottini and J. D. Roberts, *ibid.*, 80, 5203 (1958).

(12) F. A. L. Anet and J. M. Osyany, *ibid.*, **89**, 352 (1967).

(13) S. J. Brois, *ibid.*, **89**, 4242 (1967).

(14) J. Sandstrom, *J. Phys. Chem.*, **71**, 2318 (1967).

(15) A. Mannschreck, *Tetrahedron Letters*, 1341 (1965).

(16) H. A. Staab and D. Lauer, *ibid.*, 4593 (1966).

(17) National Aeronautics and Space Administration Predoctoral Fellow.

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## The Case of the Ersatz Aryne. A New Mechanism of Cine-Substitution

*Sir:*

One of the most characteristic features of the elimination–addition (benzyne) mechanism[1] of nucleophilic

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(1) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *J. Am. Chem. Soc.*, **78**, 601 (1956).