drogen atoms was evolved upon treatment of the nitrogen complex with deuterium in benzene for 24 hr at 25°. In a similar experiment at 65° for 2 days, oxidation of the exchange product with hydrogen peroxide gave triphenylphosphine oxide in which proton nmr revealed 82% *ortho* deuteration.[11]

(11) Acknowledgment is made to G. W. Parshall for the deuterium-exchange experiments.

W. H. Knoth
Contribution No. 1461, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Co.
Wilmington, Delaware 19898

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A New Synthesis of Diazenes. The Preparation and Properties of *trans*-Methyldiazene

Sir:

Diazene, HN=NH, has been proposed as an intermediate in the reaction of hydroxylamine-O-sulfonic acid (I) with hydroxylamine in alkaline solution. Evidence for diazene in this system is the hydrogenation of multiple bonds when olefins and azo compounds are present.[1] We have investigated the kinetics of the reaction of I with hydroxylamine in aqueous solution and have found the rate law to be rate = $k[OH^-][H_2NOH][H_2NOSO_3^-]$. Since similar studies with hydrazine and I revealed no hydroxide ion concentration dependence, we were led to investigate the reaction of I with N- and O-substituted hydroxylamines to clarify the role of the hydroxide ion. We have found that the reaction of I with N-methylhydroxylamine (II) in aqueous sodium hydroxide solution produces *trans*-methyldiazene (III), which is surprisingly stable.

$$\underset{\text{I}}{H_2NOSO_3^-} + \underset{\text{II}}{CH_3NHOH} + OH^- \longrightarrow \underset{\text{III}}{CH_3N{=}NH} + SO_4^{2-} + H_2O \qquad (1)$$

To a solution of II in aqueous sodium hydroxide was added a solution of I. Final concentrations of each reactant and the hydroxide ion were about 0.1 *M*. Gas evolution began immediately, and a nitrogen dioxide like odor was detectable. An ultraviolet spectrum of the solution revealed the growth of a peak with λ_{max} at 350 mμ. This peak reached maximum intensity in 2–3 min and then disappeared over a period of hours. The stoichiometry was consistent with eq 1 and with III subsequently decomposing as in eq 2 and 3.

$$CH_3N{=}NH \longrightarrow CH_4 + N_2 \qquad (2)$$

$$CH_3N{=}NH \longrightarrow CH_2{=}NNH_2 \xrightarrow{H_2O} H_2CO + H_2NNH_2 \qquad (3)$$

The formation and *trans* configuration of III was confirmed by its ultraviolet spectrum λ_{max} 350 mμ (ε 24)[2] and its gas-phase infrared spectrum.

Table I. Observed Infrared Bands of *trans*-Methyldiazene and *trans*-Methyldiazene-N-d_1[a–c]

	trans-Methyldiazene			*trans*-Methyldiazene-N-d_1		
Symmetry	Freq, cm^{-1}	I	Shape	Freq, cm^{-1}	I	Shape
a′	3130	m	A			
	2900–3000[b]	m		2920[b]	m	A
				~2870[b]	m	
				2320	m	A
	1575	w	A	1550	w	A
	1410[b]	m	B	1405[b]	m	B
	1125	m		1060	m	A
				890	m	A
	550	m	B	535	m	A
a′′				2985	m	C
	1470[b]	m	C	1450[b]	m	C
	1140	m	C			
	844	m	C	662	m	C
a′	920	w	A	2110	w	A?

[a] Bands given are believed to be fundamentals except for the last entry for each molecule. Ten a′ and five a′′ fundamentals are expected. [b] Absorption by methane or methane-d_1 in the 2900–3100- and 1150–1450-cm^{-1} regions may have prevented observation of some bands, while those observed in these regions may have been subject to an error of more than ±5 cm^{-1} generally assigned to all bands. [c] The a′′ fundamentals fit the product rule satisfactorily (0.745 calcd, 0.775 found); failure to identify all of the fundamentals that should shift appreciably precludes such a calculation for the a′ modes.

The infrared spectrum of the gas evolved in reaction 1 displayed the bands presented in the left half of Table I. The intensity of these bands decreased with time, and ultimately a spectrum of methane[3] was obtained. When reaction 1 was carried out in deuterium oxide, the infrared spectrum contained the bands presented in the right half of Table I; the spectrum was ultimately that of methane-d_1.[3] In the gas phase III decomposed faster than the N-deuterio isomer IV. Consequently we did not obtain as intense a spectrum of III as of IV, and have placed correspondingly greater confidence in the latter. Confident assignments were made to the N—H stretch at 3130 (2320 in IV), the N=N stretch at 1575 (1550), and the N—H out-of-plane bend at 844 cm^{-1} (662). The N—H stretch agrees with that found for *trans*-diazene.[4]

In addition to survey infrared spectra, high-resolution scans were made of the 844- and 662-cm^{-1} bands on a Perkin-Elmer 621 spectrometer. In analyzing the well-developed rotational structure, the following structural parameters were assumed for methyldiazene: $r_{N-H} = 1.014$,[5a] $r_{C-H} = 1.093$,[5a] $r_{C-N} = 1.470$,[5a,b] and $r_{N=N} = 1.240$ Å[5b]; ∠NNH = 110,[4] ∠HCH = ∠HCN = 109.5,[5a] and ∠CNN = 110°.[5b,6]

Moments of inertia and rotational constants were calculated for the *cis* and *trans* configurations of III and IV. The two isomers are near-prolate ($\kappa \sim -0.95$), and calculations for rotamers gave identical results. On the symmetric top approximation the rotational spacings of the near-perpendicular, type-C bands were predicted to be 2.65 (*cis*-III), 2.26 (*cis*-IV), 3.28 (*trans*-III), and 3.32 cm^{-1} (*trans*-IV). Examination of the 844-cm^{-1} band of III and the 662-cm^{-1} band of IV gave average spacings of 3.25 and 3.21 cm^{-1}, respectively. Both the magnitude of the spacing and the small change upon deuteration strongly supported the *trans* configuration. Variation of the NNH angle (±10°) did not appreciably affect these calculations,

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(1) E. Schmitz, R. Ohme, and G. Kozakiewcz, *Z. Anorg. Allgem. Chem.*, **339**, 44 (1965).

(2) For azomethane the *trans* isomer has λ_{max} 343 mμ (ε 25), and the *cis* isomer has λ_{max} 353 mμ (ε 240): R. F. Hutton and C. Steel, *J. Am. Chem. Soc.*, **86**, 745 (1964).

(3) J. K. Wilmshurst and H. J. Bernstein, *Can. J. Chem.*, **35**, 226 (1957).

(4) A. Trombetti, *Can. J. Phys.*, **46**, 1005 (1968).

(5) "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958: (a) methylamine, p M115; (b) *trans*-azomethane, p M137.

(6) J. H. Bryden, *Acta Cryst.*, **14**, 61 (1961).

and variation of the CNN angle (±5°) changed the magnitude but not the expected difference upon deuteration.

The properties of *trans*-methyldiazene were found to differ markedly from the other known monosubstituted diazenes.[7] Its bimolecular decomposition rate showed no pH dependence over the range 6.5–13.5 with $k_2 \sim 0.02\ M^{-1}\ \text{sec}^{-1}$. III was isolated and kept as a yellow solid at −196°; upon warming decomposition to methane and nitrogen began. We were unable to establish a simple kinetic order for the gas-phase decomposition of III. The half-life decreased as the partial pressure of III was decreased, *e.g.*, $t_{1/2} \sim 2$ min at 82 mm which increased to ~8 min at 10 mm at a total pressure of ~400 mm. IV had an appreciably longer half-life.

Diazene itself decomposes so rapidly that it has only recently been observed in some detail.[4] As the simplest substituted diazene of reasonable stability yet reported, methyldiazene is of considerable chemical interest. We have made the extension of the preparative method to obtain ethyldiazene by substituting N-ethylhydroxylamine in reaction 1.

Acknowledgment. We are grateful to Professor Norman C. Craig for numerous helpful discussions and for the use of his computer programs and to David D. Sherertz for carrying out some of the calculations. Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(7) Compare the phenyl- and *t*-butyldiazenes: P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2367 (1968); **89**, 3911 (1967).

(8) National Science Foundation undergraduate research participant, summer 1967.

Martin N. Ackermann, James L. Ellenson, David H. Robison[8]
Department of Chemistry, Oberlin College
Oberlin, Ohio 44074

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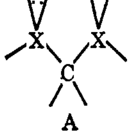
Repulsion of *syn*-Axial Electron Pairs. The "Rabbit-Ear Effect"

Sir:

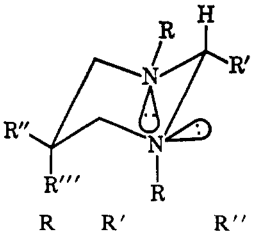
We wish to draw attention to a widespread effect in structural chemistry which leads to a disfavoring of conformations in which unshared electron pairs on nonadjacent atoms are parallel or *syn*-axial[1] (A). For obvious reasons, we propose to call this phenomenon the "rabbit-ear effect." It is probably due to a repulsion of the electric dipoles engendered by the pairs.



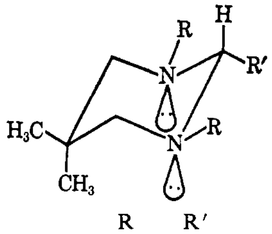
A

Although the existence of the effect has been pointed out before,[2,3] its implications in both acyclic and cyclic structures containing heteroatoms do not seem to have been generally recognized. Its consequences are seen, for example, in the preferred conformation of dimethylformal[2] and polyoxymethylene,[4] in the anomeric effect,[4] in the crystal structure of sugars and glycosides,[4] and in the conformation of certain heterocyclic rings.[5,6]

We have now found a particularly striking indication of the effect through an nmr study of variously substituted 1,3-diazanes (I–IX) synthesized from appropriately substituted trimethylenediamines and aldehydes.[7] The important data bear on the chemical shift of H-2 and are summarized in Table I (shifts measured at 60 Mcps).



	R	R′	R″	R‴
I	H	CH_3	H	H
II	H	CH_3	CH_3	CH_3
III	CH_3	CH_3	H	H
III-*d*	CH_3	CD_3	H	H
V	H	C_2H_5	H	H
VI	H	C_2H_5	CH_3	CH_3
VII	CH_3	C_2H_5	H	H
VII-*d*	CH_3	CD_2CH_3	H	H
IX	CH_3	C_2H_5	CH_3	H
IX-*d*	CH_3	CD_2CH_3	CH_3	H



	R	R′
IV	CH_3	CH_3
IV-*d*	CH_3	CD_3
VIII	CH_3	C_2H_5
VIII-*d*	CH_3	CD_2CH_3

Table I

Compound	I	II	III	III-*d*	IV	IV-*d*
$\nu_{H\text{-}2}$, cps	213.7	211.4	172.4	168.9	*Ca.* 129	132.7
Compound	V	VI	VII	VII-*d*	VIII	VIII-*d*
$\nu_{H\text{-}2}$, cps	202.9	196.8	158.4	157.1	*Ca.* 119	121.6
Compound	IX	IX-*d*				
$\nu_{H\text{-}2}$, cps	*Ca.* 150.5	148.5				

Introduction of methyl groups at position 5 of 2-methyl- and 2-ethyl-1,3-diazanes (II *vs.* I and VI *vs.* V) causes little change in the H-2 signal position. This is as predicted, since only long-range anisotropy effects come into play.[8] The situation is totally different when 5-methyl groups are introduced into 2-alkyl-N,N-dimethyl-1,3-diazanes. Although the introduction of one (equatorial) methyl group has little effect (*cf.* IX *vs.* VII), the second (axial) methyl group at C-5 produces a large upfield shift of the H-2 signal (III-*d vs.* IV-*d*, 36.2 cps; VII-*d vs.* VIII-*d*, 35.5 cps). (The reported shifts refer to the compounds deuterated in the C-2 methyl substituent or the methylene group of the C-2 ethyl substituent. Shifts in undeuterated IV and VIII were difficult to measure, since the H-2 signal is a multiplet and partially overlapped with signals of the protons at C-4,6 and the N-methyl protons. However, the identity of the H-2 protons was confirmed in the

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(1) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Division, John Wiley & Sons, Inc., New York, N. Y., 1965, p 43.

(2) R. U. Lemieux in "Molecular Rearrangements," P. De Mayo, Ed., Interscience Publishers, New York, N. Y., 1964, p 739.

(3) *Cf.* also M. Kabayama and D. Patterson, *Can. J. Chem.*, **36**, 563 (1958).

(4) E. L. Eliel and C. A. Giza, *J. Org. Chem.*, **33**, 3754 (1968), especially footnote 16 therein.

(5) J. E. Anderson and J. D. Roberts, *J. Amer. Chem. Soc.*, **90**, 4186 (1968).

(6) Y. Allingham, R. C. Cookson, T. A. Crabb, and S. Vary, *Tetrahedron*, **24**, 4625 (1968).

(7) The C and H analyses of all diazanes in Table I were within 0.35% of the calculated value.

(8) *Cf.* H. Booth, *Tetrahedron*, **22**, 615 (1966).