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.

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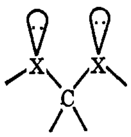
Repulsion of *syn*-Axial Electron Pairs. The "Rabbit-Ear Effect"

Sir:

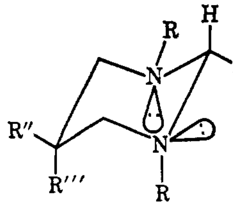
We wish to draw attention to a widespread effect in structural chemistry which leads to a disfavoring of conformations in which unshared electron pairs on nonadjacent atoms are parallel or *syn*-axial[1] (A). For obvious reasons, we propose to call this phenomenon the "rabbit-ear effect." It is probably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



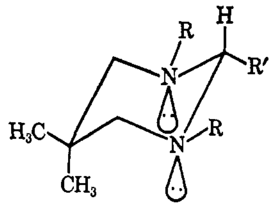
A

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).

undeuterated compounds IV and VIII by decoupling the methyl or methylene group at C-2.)

Since the large upfield shift of H-2 in N,N,2-trimethyl-1,3-diazane (III) and N,N-dimethyl-2-ethyl-1,3-diazane (VII) upon introduction of geminal methyl groups at C-5 is not a direct effect (*vide supra*), it can only be explained as an indirect effect on the N-methyl groups. The only reasonable interpretation we can think of is to assume that, in the N,N-dimethyl-5,5-di-H compounds, one methyl group on nitrogen is axial, but that, in the 5,5-dimethyl compounds, both methyl groups must be equatorial in order to avoid a serious *syn*-axial methyl–methyl interaction. It is known[9] that the signal of an axial hydrogen on carbon next to amino nitrogen undergoes an appreciable upfield shift when the nitrogen bears an axial electron pair and equatorial methyl group as compared to the case where the electron pair is equatorial and the methyl group axial or absent. It is still controversial whether that shift is caused by the axial pair[9a,10] or by the equatorial N-methyl group,[9b,11] or both. For the present purpose, however, the origin of the shift is immaterial; it suffices to record that it occurs in going from III to IV or from VII to VIII and that therefore IV and VIII are likely to have axial pairs and equatorial N-methyl groups where III and VII have one equatorial pair and axial N-methyl. (The second N-methyl group is assumed to be equatorial.)

The conclusion that N,N-dimethyldiazane[12] contains an axial N-methyl group is in agreement with recent findings that N,N′,N′′,N′′′-tetramethyl-1,2,4,5-tetrazane contains two axial N-methyl groups[5] and that certain N-methyl-, N-ethyl-, and N-*n*-propyl-1,3-oxazanes (but not the corresponding N-isopropyl or N-*t*-butyl compounds) bear axial alkyl groups.[6] Since the conformational strain in an axial N-methyl-1,3-diazane (one *syn*-axial methyl–H plus one *syn*-axial methyl–pair interaction) is probably close to 1 kcal/mol[13] and, since some of the oxazanes previously investigated[6] appear to have *syn*-axial methyl and nitro groups, the magnitude of the rabbit ear effect appears to be substantial.

Acknowledgment. This work was supported under Air Force Grant AF-AFOSR-772 and National Institutes of Health Grant GM-13515. We acknowledge an exchange of information with Dr. G. Riddell, Stirling University, Stirling, Scotland, who has obtained independent evidence for the presence of axial methyl groups in N-methyl-1,3-diazanes. We are indebted to Mr. Donald Schifferl for the decoupling experiments.

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[9] *E.g.*, (a) J. B. Lambert, F. G. Keske, R. E. Carhart, and A. P. Jovanovitch, *J. Amer. Chem. Soc.*, **89**, 3761 (1967); (b) M. J. T. Robinson, *Tetrahedron Letters*, 1153 (1968).

[10] F. Bohlmann, D. Schumann, and C. Arndt, *ibid.*, 2705 (1965).

[11] H. Booth and J. Little, *Tetrahedron*, **23**, 291 (1967).

[12] The nmr spectra of the N-unsubstituted diazanes show H-2 at lower field than those of the N-methyl homologs, presumably because the former contain no equatorial N-methyl group whereas the latter have at least one such group. The insensitivity of the H-2 shift toward introduction of geminal methyl groups at C-5 (*cf.* I *vs.* II, V *vs.* VI) means either that the H-2 shift is insensitive toward the axial or equatorial nature of the unshared pairs on nitrogen or (much more likely) that both series (5,5-di-H and 5,5-di-Me) have one of the N–H hydrogens axial in order to avoid a rabbit-ear effect.

[13] Adding one *syn*-axial Me–H interaction (0.85 kcal/mol[1]) and one *syn*-axial Me–pair interaction [0.4 kcal/mol: E. L. Eliel and M. Knoeber, *J. Amer. Chem. Soc.*, **90**, 3444 (1968)] and offsetting the entropy of mixing of the *dl*-ea form would give 0.85 kcal/mol at 25°. See, however, R. J. Bishop, L. E. Sutton, D. Dineen, R. A. Jones, A. R. Katritzky, and R. J. Wyatt, *J. Chem. Soc.*, *B*, 493 (1967), who report a *syn* axial Me–H interaction in N-methylpiperidine (axial Me) of only 0.2 kcal/mol.

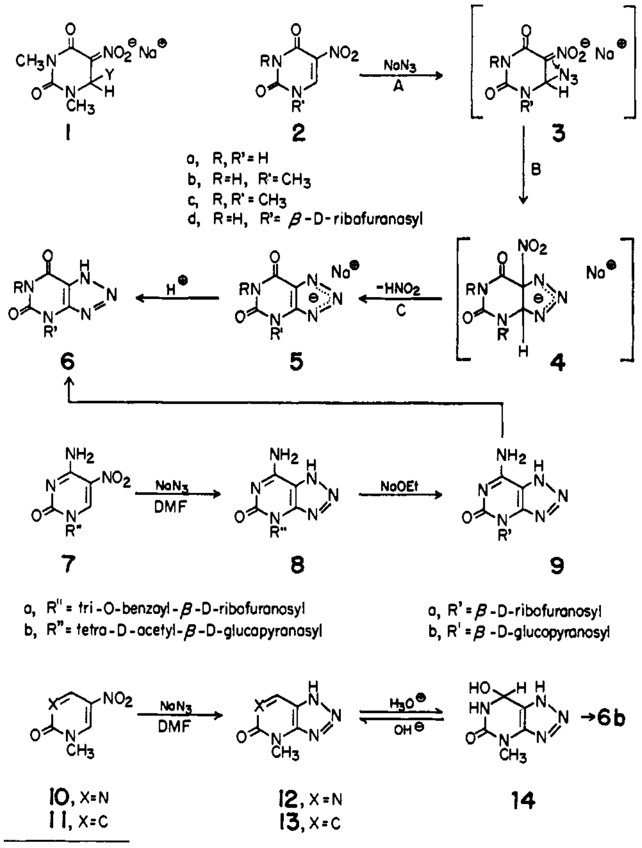
Pyrimidines. VII. A Simple Conversion of 2-Oxo-5-nitro Heterocycles to *v*-Triazolo Derivatives by Sodium Azide[1]

Sir:

In the course of our attempts to synthesize the sodium salt of 6-azido-1,3-dimethyl-5,6-dihydro-5-nitrouracil (**1**, Y = N_3) we found that treatment of certain 5-nitropyrimidines with sodium azide in various solvents leads to a novel, one-step synthesis of 2-oxo-8-azapurines. For example, reaction of the readily available 5-nitrouracil (**2a**) or its mono- and dimethylated derivatives (**2b, 2c**) with sodium azide in DMF or refluxing alcohol followed by acidification afforded the known[2] 8-azaxanthines (**6**)[3] in 70–90% yields.[4]

To our best knowledge, this type of reaction has not been previously described. We propose the following plausible mechanism for this unexpected cyclization (see Scheme I). The first step is the nucleophilic attack

Scheme I



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[1] This investigation was supported in part by funds from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA 08748).

[2] G. Nübel and W. Pfleiderer, *Chem. Ber.*, **98**, 1060 (1965), and leading references therein.

[3] The trivial nomenclature (*e.g.*, "8-azaxanthines") is used throughout this paper in order to emphasize analogy with the biologically important purines. Such heterocycles should be listed as derivatives of *v*-triazolo[4,5-*d*]pyrimidines.

[4] In the case of **2a** it was necessary to add ammonium chloride to the reaction in order to prevent ionization at N-1.