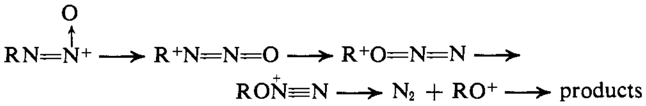
Ureas (I) and carbamates (IV) were used (in addition to the nitrosoamides (V)) because of the stabilities of these derivatives. The reactions shown in Chart I were compared.

A comparison of reactions 1,2 (and 4,6) shows that the formation of nitrous oxide rather than nitrogen has no pronounced effect on the reaction. If the gas molecules were effectively solvating the carbonium ions, nitrous oxide should be superior to nitrogen as indicated by the relative solubilities in water (N_2O, 58 m*M*; N_2, 1 m*M* at 0°)[7] and the boiling points (N_2O, $-89°$; N_2, $-196°$),[7] etc. No evidence was found for the following process ("A" reaction series)



$$\mathrm{RN{=}\overset{\overset{O}{\uparrow}}{N}{}^{+} \longrightarrow R^{+}N{=}N{=}O \longrightarrow R^{+}O{=}N{=}N \longrightarrow RO\overset{+}{N}{\equiv}N \longrightarrow N_2 + RO^{+} \longrightarrow products}$$

and the addition of a large excess of nitrous oxide to reaction 3 had no effect on the product distribution.[8] Thus, neither the size nor solvating ability of the gas molecule are important variables, and externally added nitrous oxide does not appear to enter into the reaction.

Reactions 4 and 5 show that the stereochemistry of the diazo species (VI *vs.* X) is not an important variable.[9] The yields for runs 4–6 were essentially the same (20–25%), and a similar yield was obtained for the acylation of the anti salt VII. These results suggest that VI and X react *via* a common intermediate, candidates being the anti form VI, the diazonium ion pair XI, and the carbonium ion pair XII.[10] In any event, the syn form is clearly not responsible for characteristic features of deamination such as overall retention of configuration and intramolecular ester (or alcohol) formation.[1,11]

The above results show that the gas molecule (N_2 or N_2O) is not involved detectably in the product forming steps, and they suggest strongly that the products are determined at the carbonium ion stage of the reaction.

$$\mathrm{VI \longrightarrow \underset{XI}{RN_2{}^{+}X^{-}} \longrightarrow \underset{XII}{R^{+}N_2X^{-}} \longrightarrow R^{+}N_2X^{-} \longrightarrow products} \quad (7)$$

The transient separation of carbonium ion and counterion by an inert molecule, XII, can, in principle, account for the counterion effect (runs 2 and 3) and for certain of the characteristic features of deamination, such as extensive hydride shifts and skeletal rearrangements (relative to solvolysis). However, an additional factor is required to account for: (1) the virtual identity of the product distribution, whether nitrogen or nitrous oxide is ejected, (2) the observation that in deaminations 1–3 the cation is captured preferentially by a relatively inert solvent molecule rather than by the negatively charged counterion, and (3) the fairly general observation in deamination of product RX formed with inversion of configuration by an *intramolecular* pathway.[1,12] The additional factor is probably the existence of disorder in the product-forming steps,[1] undoubtedly a result of the energetic formation of the nitrogen (or N_2O) molecule (recoil).[13,14]

Acknowledgment. We thank the National Science Foundation for its support of this work (GP-8993).

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(6) The anti salt *dl*-VII was prepared by the method of J. Thiele [*Justus Liebigs Ann. Chem.*, **376**, 239 (1910)]: mp 208° (dec); ir (Nujol mull) 1600, 1490, 1410, 1300, 1166, 1079, 1015, 760, 695, and 611 cm^{-1}; nmr (CD_3SOCD_3) δ 1.36 (d, 3.0, J = 6.8 Hz, $CHCH_3$), 3.59 (s, 0.7, H_2O), 4.79 (q, 1.0, J = 6.8 Hz, $CHCH_3$), 7.09–7.44 (broadened s, 4.9, C_6H_5). *Anal.* Calcd for $C_8H_9N_2OK \cdot 0.5H_2O$: C, 48.71; H, 5.11; N, 14.20. Found: C, 48.87; H, 4.70; N, 14.28. The syn salt IX was prepared by methods similar to those of A. Hantzsch and M. Lehmann [*Chem. Ber.*, **35**, 897 (1902)] and R. A. Moss [*J. Org. Chem.*, **31**, 1082 (1966)]: mp 153–154°; ir (Nujol mull) 1600, 1490, 1375, 1160, 1150, 1087, 758, and 697 cm^{-1}; nmr (CD_3SOCD_3) δ 1.19 (d, 3.0, J = 6.8 Hz, $CHCH_3$), 5.58 (q, 1.0, J = 6.8 Hz, $CHCH_3$), 7.05–7.43 (m, 5.2, C_6H_5). The corresponding methyl diazotates have been distinguished on the basis of their nmr spectra [H. Suhr, *Chem. Ber.*, **96**, 1720 (1963)], and the structure of the syn form has been determined by X-ray diffraction [E. Müller, W. Hoppe, H. Hagenmaier, H. Haiss, R. Huber, W. Rundel, and H. Suhr, *ibid.*, **96**, 1712 (1963)].

(7) "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964, p B-199.

(8) Dr. M. J. Todd, unpublished results.

(9) The stereochemical results in the decomposition of nitrosoamides of 1-phenylethylamine are relatively independent of the solvent [ref 4 and E. H. White, *J. Amer. Chem. Soc.*, 77, 6014 (1955)].

(10) Formed either in a one- (M. C. Whiting, *Chem. Brit.*, **2**, 482 (1966)), or two-step process.

(11) It appears unlikely that the anti derivatives isomerize to the syn forms (*e.g.*, VI → X) before decomposition in view of the low activation energy estimated for the decomposition of alkyldiazonium ions [(3–5 kcal): A. Streitwieser, Jr., and W. D. Schaeffer, *J. Amer. Chem. Soc.*, **79**, 2888 (1957)]. The results of M. Wilhelm and D. Y. Curtin [*Helv. Chim. Acta*, **40**, 2129 (1957)] also suggest a low value. These authors have estimated that the activation energy for the decomposition of a bridgehead diazonium ion in ether is 21 kcal lower than the value for the solvolysis of the corresponding bromide in ethanol. The activation energy for the conversion of a series of *cis*-diazocyanides into the trans forms is about 23 kcal [R. J. W. LeFevre and J. Northcott, *J. Chem. Soc.*, 944 (1949)]. Similarly, both cis and trans forms of azobenzenes, oxime derivatives, hydrazenes, etc., can be isolated ($E_{act} > \sim 15$ kcal). The thermal equilibrium favors the trans forms by a large margin ($K \geq \sim 100$) and thus $\Delta G_{s \to t} \geq \sim 3$ kcal. Thus, it seems reasonable that the conversion of VI to X, *e.g.*, would require more than 3–5 kcal.

(12) R. A. Moss, D. W. Reger, and E. M. Emery, *J. Amer. Chem. Soc.*, **92**, 1366 (1970).

(13) This description is essentially the same as that presented previously.[1,2]

(14) Because there are striking similarities between the nitrous acid, nitrosoamide, nitroamide, and triazene methods of deaminations,[1,15] the views expressed above, we believe, can be generally applied to deamination type reactions leading to carbonium ions and a gas such as nitrogen ($RNH_2 \rightarrow RX + N_2(N_2O)$, etc.).

(15) E. H. White and D. W. Grisley, Jr., *J. Amer. Chem. Soc.*, **83**, 1191 (1961); H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 496 (1965).

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Stereochemical Consequences of Adjacent Electron Pairs. A Theoretical Study of Rotation–Inversion in Ethylene Dicarbanion

Sir:

The notion that there is stereochemistry, *i.e.*, nonspherical symmetry, associated with lone electron pairs is very widely held. It is seen, for example, in the valence shell electron pair repulsion theory,[1] in the rabbit-ear effect,[2] in discussions of the anomeric effect,[3] and in the continuing controversy over the size of the lone pair.[4] It also forms the conceptual basis of the recently postulated[5] "gauche effect," a term which describes in an

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(1) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); **47**, 18 (1970); R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970).

(2) R. O. Hutchins, L. D. Kopp, and E. L. Eliel, *J. Amer. Chem. Soc.*, **90**, 7174 (1968); E. L. Eliel, *Sv. Kem. Tidskr.*, **81**, 22 (1969).

(3) J. T. Edward, *Chem. Ind.*, 1102 (1955); C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4**, 39 (1969).

(4) R. A. Y. Jones, A. R. Katritzky, A. C. Richards, R. J. Wyatt, R. J. Bishop, and L. E. Sutton, *J. Chem. Soc. B*, 127 (1970); N. L. Allinger, J. A. Hirsch, and M. A. Miller, *Tetrahedron Lett.*, 3729 (1967).

(5) (a) S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972); (b) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971). (c) In ref 5b this statement is presented as Rule 2 of the gauche effect.

empirical way the tendency of species containing adjacent electron pairs and/or polar bonds to exist preferentially in that conformation which has the maximum number of gauche interactions between these electron pairs or polar bonds.[5c] Although the gauche effect can be invoked to account for a variety of stereochemical observations,[6] and thus seems to be a useful concept, it is difficult to understand why the phenomenon exists, because of our intuitive feeling that lone-pair–lone-pair repulsion ought rather to have *de*stabilized gauche conformations.

It is now generally accepted[7] that nonempirical molecular orbital calculations are helpful in providing insight into the physical bases of rotation–inversion phenomena, because such calculations generate not only the total energy but also the components[8] of the total energy of a system as a function of molecular geometry. With these in hand, it becomes possible to justify, in a more rigorous way, a conclusion that a given stereochemical phenomenon is governed, for example, by attractive effects or repulsive effects, by kinetic energy changes or potential energy changes, and to achieve a more complete structural description than is possible with electron–electron repulsion considerations[1] alone.

In this communication we describe the results of a study[9] of ethane (**1**; $E = E(\theta)$), methyl carbanion (**2**; $E = E(\phi)$), ethyl carbanion (**3**; $E = E(\theta,\phi)$), and ethylene dicarbanion ($^-CH_2CH_2^-$; **4**; $E = E(r,\theta,\phi)$). The principal objectives of the work were to determine (a) whether a gauche effect is predicted[10–15] for **4** and how this varies with internuclear distance; (b) the physical interpretation of the results, based on the component analyses; (c) the changes that occur in both rotation and inversion as lone pairs replace bond pairs. The SCF–MO calculations were performed on an IBM 360/65 computer using a modified version of IBMOL-IV[16] and, in each case, the double ζ contracted Gaussian basis set of Huzinaga.[17] The results are summarized in the two figures.

Two features of the results are immediately clear: a gauche effect is found for the dicarbanion ($\theta_{\min} = 79°$ for the optimized C–C bond length and pyramidal angle); and the effect is *more pronounced* at the shorter bond length ($E_{\mathrm{trans}} - E_{\mathrm{gauche}} = 10.7$ kcal mol^{-1} *vs.* 2.5 kcal mol^{-1} at the optimized bond length). The interpretation suggested by these findings is that *the lone-pair–lone-pair interactions behave as though they are invariant with dihedral angle, i.e.*, as concluded in our earlier study of the Edward–Lemieux effect:[5b] "*the nonbonding electron pairs create a quasispherical potential field in which the true ligands* (*or bonding pairs*) *move.*" This concept is supported by the results of the component analyses for **1**, **3**, and **4** (Figure 1). Three maxima and three minima are seen in all cases for E_T and for the individual components of E_T except for the V_{nn} term of the dicarbanion. In a 360° rotation this term (V_{nn}) is a maximum at $\theta = 0°$ and a minimum at $\theta = 180°$, the barrier being 58.1 kcal mol^{-1}. The shape of this potential curve does not seem unreasonable, because nuclear–nuclear repulsion is expected to decrease progressively in the direction 2 eclipsing ($\theta = 0°$) > 3 gauche (60°) > 1 eclipsing (120°) > 2 gauche (180°); and, in terms of V_{nn}, the 60° structure of **4** has three, and the 180° structure has four fewer gauche interactions than the 60 or 180° (staggered) structures of **1** since the lone pairs (whatever their shape) do not contribute to this energy term.

A directed lone-pair model[20] of **4** would presumably predict electron–electron repulsion (V_{ee}) to be greatest for the 0°, and least for the 180° conformations. Neither of these predictions is correct; V_{ee} is a maximum at $\theta = 120°$ and a minimum at $\theta = 50°$. Similarly the directed lone-pair model predicts attraction to be greatest (*i.e.*, lowest value of V_{ne}) in the 120° conformation because of the two hydrogen–lone-pair eclipsing interactions, and least (*i.e.*, maximum value of V_{ne}) in

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(6) (a) J. D. Aubort and R. F. Hudson, *Chem. Commun.*, 937 (1970); (b) H. Booth and R. U. Lemieux, *Can. J. Chem.*, **49**, 777 (1971); (c) G. Wood, J. M. McIntosh, and M. H. Miskow, *ibid.*, **49**, 1202 (1971); (d) T. Durst, *J. Amer. Chem. Soc.*, **91**, 1034 (1969); (e) G. Barbarella, A. Garbesi, and A. Fava, *Helv. Chim. Acta*, **54**, 341 (1971); (f) A. A. Hartmann and E. L. Eliel, *J. Amer. Chem. Soc.*, **93**, 2572 (1971); (g) J. N. Roitman and D. J. Cram, *ibid.*, **93**, 2225 (1971).

(7) (a) J.-M. Lehn, "Proceedings of the International Symposium on Conformational Analysis, Brussels, 8–12 September, 1969," Academic Press, in press; (b) J.-M. Lehn, *Top. Curr. Chem.*, **15**, 311 (1970); (c) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970).

(8) L. C. Allen, *Chem. Phys. Lett.*, **2**, 597 (1968). The total energy of a system, E_T, is a sum of four terms: V_{ne}, the nuclear–electron attraction; V_{nn}, the nuclear–nuclear repulsion; V_{ee}, the electron–electron repulsion; and T, the kinetic energy of the electrons. The attractive component of E_T is $V_{\mathrm{attrac}} = V_{ne}$; and the repulsve component is $V_{\mathrm{rep}} = V_{nn} + V_{ee} + T$. The potential energy term is $V_{\mathrm{pot}} = V_{nn} + V_{ne} + V_{ee}$.

(9) In what follows, $E = E(\theta)$ refers to a cross section of an energy surface in which the total energy (E_T) is studied as a function of the dihedral angle (θ); $E = E(\phi)$ refers to a cross section in which E_T is studied as a function of the pyramidal angle(s) at an atom(s) undergoing pyramidal inversion; $E = E(\theta,\phi)$ corresponds to a rotation–inversion surface, *i.e.*, a study of the variation in E_T as a function of both θ and ϕ; $E = E(r,\theta,\phi)$ refers to a conformational hypersurface, *i.e.*, a study of the variation in E_T as a function of θ, ϕ, and C–C bond length (r).

(10) Experimentally, dihedral angles ranging from 72 to 123° have been observed[5a] for a variety of combinations of heteroatoms containing different numbers of adjacent electron pairs, and the gauche effect seems to be strengthened rather than weakened with a decrease in the internuclear distance.[5a,11] Nonempirical molecular orbital calculations of the type reported here have reproduced the gauche effect observed for H_2O_2,[12] H_2S_2,[13] H_4N_2,[14] H_4P_2,[15] and the Edward–Lemieux effect.[5b]

Experimental studies of *aryl*ethylene dicarbanions suggest a hydrazine-like twisted structure. See J. F. Garst, J. G. Pacifici, and E. R. Zabolotny, *J. Amer. Chem. Soc.*, **88**, 3872 (1966); D. H. Eargle, Jr., *ibid.*, **93**, 3859 (1971); K. Takahashi, Y. Inoue, and R. Asami, *Org. Magn. Resonance*, **3**, 349 (1971); J. F. Garst, *J. Amer. Chem. Soc.*, **93**, 6312 (1971).

(11) M. J. Cardillo and S. H. Bauer, *Inorg. Chem.*, **8**, 2086 (1969); R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Amer. Chem. Soc.*, **88**, 3729 (1966).

(12) A. Veillard, *Chem. Phys. Lett.*, **4**, 51 (1969).

(13) A. Veillard and J. Demuynck, *ibid.*, **4**, 476 (1970).

(14) A. Veillard, *Theor. Chim. Acta.*, **5**, 413 (1966); W. H. Fink, D. C. Pan, and L. C. Allen, *J. Chem. Phys.*, **47**, 895 (1967); E. L. Wagner, *Theor. Chim. Acta*, **23**, 115 (1971).

(15) J.-B. Robert, H. Marsman, and J. R. Van Wazer, *Chem. Commun.*, 356 (1970); E. L. Wagner, *Theor. Chim. Acta*, **23**, 127 (1971).

(16) A. Veillard, IBMOL: Computation of Wave Functions for Molecules of General Geometry, Version **4**, IBM Research Laboratory, San Jose, Calif., 1968.

(17) (a) Previous work[18] has indicated that, if one aims to reproduce an experimental inversion barrier to within less than 1 kcal, such large basis sets are required that any compound larger than NH_3 would be impractical to calculate. On the other hand, rotational barriers are much less sensitive to the balanced or unbalanced nature of the basis set, as has been demonstrated in Pople's recent work[19] with a standard basis set substantially smaller than that employed here. In the present work we used the standard Huzinaga basis set[17b] in order to have results which are quantitative for rotation and semiquantitative for inversion, and thus suitable for a comparative study. (b) S. Huzinaga, *J. Chem. Phys.*, **50**, 1371 (1969). This basis set consists of 13^s, 6^p on carbon contracted to 4^s, 2^p; and 4^s on hydrogen contracted to 2^s. Thus for **4**, 84 primitive GTF's were employed, contracted to 28 functions. The geometrical parameters employed were: r(CH) = 1.086 Å (in **4**), 1.102 Å (in **1** and **3**), 1.117 Å (in **2**); r(CC) = 1.543 Å (in **1** and **3**).

(18) (a) A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.*, **52**, 4133 (1970); (b) R. E. Kari and I. G. Csizmadia, *ibid.*, **50**, 1443 (1969).

(19) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971).

(20) *I.e.*, a model which assumes that a lone electron pair behaves like a bonding electron pair.

the 0° conformation. Again, both predictions are incorrect; V_{ne} is a minimum (greatest attraction) in the 0° conformation and a maximum (least attraction) in the 180° conformation. Thus a directed lone-pair model is not supported by the results, but, significantly, the general shapes of both curves may be deduced if it is simply assumed that only those interactions associated with the nuclei and the bonding electron pairs show an angular dependence.[21]

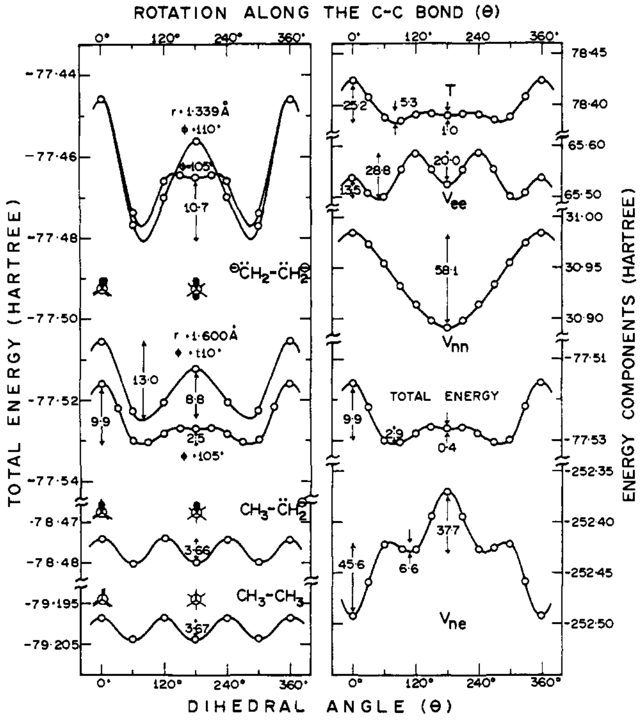

Figure 1. Left-hand side: the total energies of ethane (**1**), ethyl carbanion (**3**), and ethylene dicarbanion (**4**) as a function of rotation about the C–C bond (*θ*). In the direction of decreasing energy, the curves are as follows: **4** at the ethylenic C–C bond length and pyramidal angles 105 and 110° (top two curves); **4** at the optimized C–C bond length (1.60 Å) and pyramidal angles 105 and 110°; **3**; **1**. Right-hand side: the total energy of **4** and its components as a function of rotation about the C–C bond at the optimized C–C bond length (1.60 Å) and pyramidal angles (105°). The scale of the curve for total energy has been expanded fourfold with respect to those of the components. *Note*: in Figures 1 and 2, depiction of the electron pairs as directed ligands allows these to be employed as convenient reference points in the visualization of a particular conformation. However (see text), the most meaningful physical picture is that which describes the relative positions of the *nuclei*.

We now formalize this conclusion, and that reached in our earlier study,[5b,22] as *Rule 3*[5c] of the gauche effect; *viz.*, the relative importance of the gauche effects associated with polar bonds and lone electron pairs is polar bond–polar bond > polar bond–lone pair > lone pair–lone pair.

Turning to the inversion barriers[23] (Figure 2), we note that both barriers in $CH_3CH_2^-$ are lower than in CH_3^-, in agreement with the view[7c] that inductive and steric effects introduced by the methyl group should facilitate pyramidal inversion at the adjacent center. For $^-CH_2CH_2^-$, the barrier to single inversion is higher than in CH_3^-. In terms of group electronegativities, electron release to CH_2^- is expected to be in the direction $CH_2^- > CH_3 > H$. Since the effect of electron release is to *lower* barriers to pyramidal inversion,[24] it appears that, in the symmetrical species ethylene dicarbanion, electron-pair–electron-pair effects[5a,7] outweigh electronegativity effects and lead to an increase in the barrier. The barrier to double inversion in **4** is almost twice that of the single inversion. The energy maximum for this process corresponds to a structure having two planar CH_2 groups at right angles to each other. This structure has been suggested as a model for the gauche effect ("conjugative destabilization"),[25] but it is not supported by the present work.

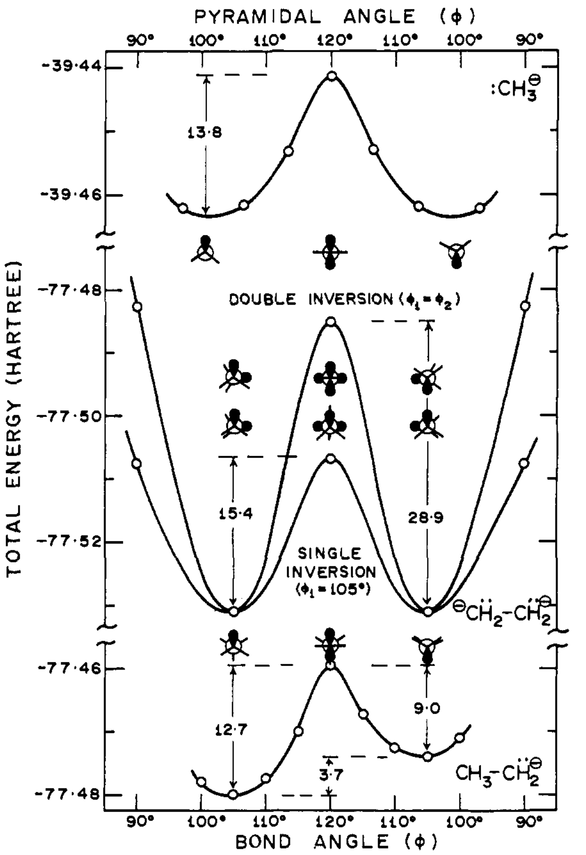

Figure 2. Inversion curves of methyl carbanion (**2**) (upper curve), ethyl carbanion (**3**) (lower curve), and the curves for single inversion and double inversion of **4**; the latter two cross sections were taken near the absolute minimum of the hypersurface of **4**.

Acknowledgments. We thank the National Research Council of Canada for continuing support of this

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[21] This is readily seen upon inspection of a molecular model, assuming the lone pairs to be "invisible," as in the Harvey effect (see ref 5b, footnote 95), and, for V_{ee}, taking into account both the Coulombic (V_{ee}^{Coul}) and exchange (V_{ee}^{exch}) terms, as previously described.[5b] Separation of V_{ee} into its two components will be presented in our full paper, together with suggested rules for derivation of the shapes of the components in a qualitative manner.

[22] A less formal statement of Rule 3 has been given in ref 5b as a note added in proof.

[23] Both barriers are attractive dominant.[8]

[24] R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **93**, 773 (1971).

[25] K. Müller and A. Eschenmoser, *Helv. Chim. Acta*, **52**, 1823 (1969).

work, and for the award of a Special Grant, and the Institute of Computer Science, University of Toronto, for allocation of computer time.

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Variations of Heavy-Atom Kinetic Isotope Effects in SN2 Displacement Reactions[1]

Sir:

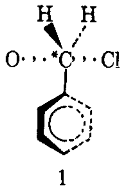
The primary hydrogen isotope effect has been widely utilized as a mechanistic probe of hydrogen-transfer reactions. Theoretical calculations[2-5] involving transfer of H from A to B using three center models A–H–B for the transition state indicate that the isotope effect should go through a maximum when H is symmetrically bonded to atoms A and B, when asymmetric motion of H from A to B is taken as the reaction coordinate. These results have been criticized,[6] since the calculations neglect effects of bending vibrations and of proton tunneling, but recent experimental results[7] support this behavior for a number of reactions. The concept is of considerable mechanistic usefulness, since it provides at least a qualitative correlation of the magnitude of the primary hydrogen isotope effect and transition state structure.

Several years ago, Fry[8] suggested that the carbon-14 (*C) kinetic isotope effect in an SN2 displacement reaction should exhibit similar behavior, whereas the isotope effect for labeled X should increase monotonically as F_1, the stretching force constant for bond 1, decreases. Experimental isotope effects for carbon-14 labeling at *C and chlorine-37 labeling at X have been obtained[9] for the benzyl chloride system, with Y = H_2O, CN^-, or $S_2O_3^{2-}$ and with R = para-substituted phenyl, p-Z-C_6H_4, with Z = CH_3O, CH_3, H, Cl, and NO_2. Recently, we have carried out a large number of calculations of the isotope effects expected for labeling at various positions in these systems for numerous models of the transition state for both SN1 and SN2 reactions. We present here some results from the calculations for the SN2 reactions of benzyl chloride.

$$Y + R^*CH_2X \longrightarrow [Y\overset{2}{\cdots}R^*CH_2\overset{1}{\cdots}X]^{\ddagger} \longrightarrow R^*CH_2Y + X \quad (1)$$

Carbon-14 and chlorine-37 isotope effects (k/k^*) were calculated using the complete transition state theory expression.[4,10] Moments of inertia and vibration frequencies were determined from complete vibrational analyses of the reactant and transition state models assumed. Extensive calculations have shown that in some cases one can extend the "cutoff" procedures of Stern and Wolfsberg[11] to include cutting through aromatic rings to conserve computer time. The validity of this cutoff procedure is indicated by the results in Table I for the complete models (**1**) of the reactants and complexes and for two cutoff models (**2**, **3**) of them. Force constants for the complex were calculated from the assumed bond orders for the *C···Cl bond (n_1) and for the Y···*C bond (n_2) in a manner similar to that used recently by other workers[5,12]

Table I. Calculated Kinetic Isotope Effects at 30° for Reaction 1 of Text[a]



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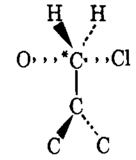
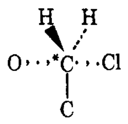


2



3

n_1	Complete model	Cutoff model	
	1	2	3
0.9	1.03764	1.03894	1.04531
	1.00348	1.00208	1.00048
0.7	1.05576	1.05750	1.06907
	1.01077	1.00924	1.00607
0.5	1.05473	1.05619	1.06788
	1.01702	1.01582	1.01265
0.3	1.03922	1.04022	1.04939
	1.02123	1.02064	1.01784
0.1	1.01090	1.01158	1.01689
	1.02451	1.02386	1.02493

[a] Values in the table correspond to the nucleophile Y in reaction 1 of text taken as oxygen, as in hydrolysis: upper entries, k^{12}/k^{14}; lower entries, k^{35}/k^{37}. Reactant models corresponding to those shown for the complex in **1–3** were employed. A zero reaction coordinate frequency $\nu_L^{\ddagger}$ was produced in these calculations as explained in the text.

$$\text{stretching of bond ab:} \quad F_{ab} = n_{ab}F^0_{ab}$$

$$\text{bending of angle abc:} \quad F_{abc} = n_{ab}n_{bc}F^0_{abc}$$

where the F^0's refer to reactant (or product) force constant values. The present calculations have assumed $n_1 + n_2 = 1$, which corresponds to constant total bonding during the course of the reaction.

The calculated k/k^* values were not sensitive to geometrical parameters of the complex, but to render the model realistic, bond distances for Y···*C and *C···Cl were adjusted from the assigned bond orders by Pauling's rule,[13] and the geometry about *C was varied

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