after work-up and crude separation by vpc, approximately 100 mg of a 57:43 mixture, whose 94.1-MHz fmr spectrum showed a singlet (43%) at δ −57.94 and an ABX pattern, the latter being identical with that of the major component in the bromine monochloride addition to α,β,β-trifluorostyrene (see below).

Reaction of α,β,β-Trifluorostyrene with Bromine Monochloride. To a mixture of 10 ml of 18% hydrochloric acid and 5.9 g (37 mmol) of α,β,β-trifluorostyrene was added, with stirring, 3.1 g of *N*-bromoacetamide at 0° over a period of 20 min. The mixture was allowed to warm up to room temperature over a period of 2 hr, added to 5 ml of 5% sodium bisulfite solution, and extracted with ether. Work-up by distillation yielded 4.4 g of a mixture, shown by fmr to consist of 70% of **13** and 30% of a second component, presumably **19**: bp 92° (11 mm). A pure sample of **13** was obtained by preparative vpc: pmr (CCl_4) δ 7.7 (s).

Anal. Calcd for $C_8H_5BrClF_3$: C, 35.13; H, 1.84. Found: C, 35.34; H, 1.95.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund (Grant No. 4440-AC4), administered by the American Chemical Society, for support of this research. The XL-100-15 nmr instrument used in this investigation was acquired under National Science Foundation Equipment Grant No. GP-10383.

Time-Averaged Geminal Anisochronism and Molecular Energetics in Acyclic Systems. A Heuristic Mathematical Model

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Contribution from the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556. *Received April 10, 1972*

Abstract: An empirical relationship between the time-averaged anisochronism in asymmetric ethanes of the general formula RCG_2CXYZ and the free energy differences between the individual conformers is derived from heuristic arguments based on transformation properties and sum rules. The mathematical model is developed to first order in certain scalar quantities characterizing the ligands X, Y, and Z at the asymmetric center and applied to the experimental data of the preceding paper. It is found that the model correctly accounts for the qualitative trends in the populations of all 30 conformers of the 10 compounds $BrCF_2CXYZ$, in which the substitution pattern at the asymmetric center corresponds to all possible combinations of the five ligands hydrogen, fluorine, chlorine, bromine, and phenyl, and that the calculated ambient-temperature populations, obtained from the first-order model after scaling with the cubic root of the product of the free energy differences, agree with the experimental values to within an average precision of about 4%.

The work to be described in this paper was stimulated by an observation reported in 1965 by Ugi,[2] who found that the logarithms of the diastereomer ratios in two series of asymmetric syntheses could be fitted, with remarkable precision, to products of differences of scalar parameters characterizing the ligands at the asymmetric centers. An elaborate group-theoretical edifice has since been erected on this observation, culminating in a general algebraic theory of the chirality phenomenon in chemistry.[3] Fortunately, however, the salient features of this treatment relevant to the special case of interest in the context of the present paper are so simple and obvious that they can be derived and appreciated by inspection.

The geminal time-averaged anisochronism $\langle\Delta\rangle$ in molecules of the general formula RCG_2CXYZ is another example of a chirality observation describable by a chirality function, *i.e.*, a function χ satisfying the following two rigorous mathematical requirements: (1) χ must vanish identically if two of the ligands X, Y, or Z are the same; (2) χ must change sign, and sign only, if two ligands are interchanged. The latter of these two obvious properties of $\langle\Delta\rangle$ could previously not be fully exploited because all measurements have so far only yielded the magnitude of time-averaged geminal chemical shift differences. With the results of the preceding publication,[4] the missing piece of information is now available for 14 compounds, which include a complete set of 10 corresponding to the general formula $BrCF_2CXYZ$ where the ligands X, Y, and Z run through all combinations of five different substituents. It is of interest, therefore, to determine empirically the level of complexity in the chirality functions that is required to reproduce such experimental data to a desired degree of precision, and in particular to investigate whether a simple chirality product, involving only one scalar parameter per ligand, can give satisfactory results. In the latter case, as already stressed by Ugi[2] and Ruch,[3] the theory would yield nontrivial new information; only $n-1$ measurements are needed in principle to fix the parameters for n (>3) different ligands, so that $\langle\Delta\rangle$ could be predicted for $n!/(3!(n-3)!) - (n-1)$ additional systems.

Apart from and beyond such a possibility we had reasons to believe that in the present series there was a finite chance of arriving at a physical interpretation of the ligand parameters, an effort that has so far not been attempted. Most importantly, the prospect of discovering an empirical relationship between time-averaged intensive quantities satisfying the required

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[1] Alfred P. Sloan Research Fellow.

[2] I. Ugi, *Z. Naturforsch. B*, **20**, 405 (1965).

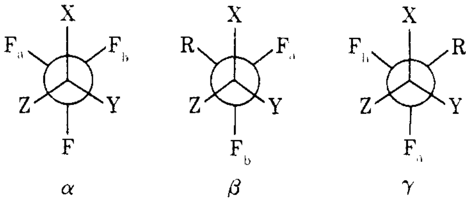
[3] For a review, see E. Ruch, *Accounts Chem. Res.*, **5**, 49 (1972).

[4] R. D. Norris and G. Binsch, *J. Amer. Chem. Soc.*, **95**, 182 (1973).

transformation behavior and the free energies of the individual conformers appeared especially attractive in view of its potential usefulness in amino acid and polypeptide chemistry. We should now like to present a simple heuristic mathematical model that seems to accomplish this purpose, even though it admittedly still contains an element of magic.

The Model

The convention consistently adopted throughout for referring to the individual conformers is depicted in the following drawing, where the clockwise arrangement of the ligands X, Y, and Z at the asymmetric carbon follows the decreasing order of priority in the Cahn–Ingold–Prelog sequence. The Greek indices α, β, γ refer to the specific conformers as shown and



the Greek indices μ, ν, σ to any cyclic permutation of α, β, γ. The compound key is that of the preceding paper.[4] In addition we use the shorthand notations

$$\Delta_\mu = \delta_\mu{}^a - \delta_\mu{}^b;\ \langle\Delta\rangle = \sum_\tau^{\alpha,\beta,\gamma} p_\tau \Delta_\tau$$

for the fluorine chemical shift differences in the individual conformers and their population-weighted averages, and

$$\Delta G^\circ{}_{\mu\nu} = G^\circ{}_\nu - G^\circ{}_\mu$$

for the standard free energy differences, thereby also defining the absolute signs of these quantities.

The chirality functions representing, to any desired degree of precision, the observed $\langle\Delta\rangle$ values of a complete or partial series of m compounds with n different ligands can be expressed mathematically in a variety of ways by a convergent expansion into a suitable set of basis functions with adjustable coefficients, the only requirement being the preservation of the transformation properties already mentioned. For instance, a convenient method consists in choosing orthogonal polynomials in certain scalar parameters λ characteristic of the ligands at the asymmetric center. A first-order theory is then obtained by truncating the expansions after the first nonvanishing term, which leads to simple chirality products of the form originally suggested by Ugi

$$\chi = (\lambda_X - \lambda_Y)(\lambda_Y - \lambda_Z)(\lambda_Z - \lambda_X) \quad (1)$$

whose correct transformation behavior is immediately verified. The ligand parameters could be determined by a least-squares principle, *i.e.*, by minimizing the functional

$$g = \sum_{j=1}^{m}(\langle\Delta\rangle_j - \chi_j)^2 \quad (2)$$

This means that the ligand parameters are chosen in such a way as to maximize the first nonvanishing term in the expansion in orthogonal polynomials. Ruch has repeatedly pointed out that for precisely that reason it is a strength of models of this kind that the ligand parameters are not preburdened with physical meaning. We fully concur with this view as long as one is mainly concerned with a mathematical fit to the experimental data. If one happens to be more interested in physical interpretations, however, this feature might occasionally turn out to be a weakness. In such cases it may be advantageous to adopt a slightly different approach. We intend to return to this point in a future publication.

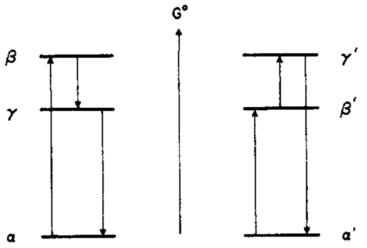


Figure 1. Schematic free energy diagrams for two enantiomeric triplets of conformers.

The chirality products satisfy the following two additional properties

$$\chi(\lambda + c) = \chi(\lambda) \quad (3)$$

and

$$\chi(c\lambda) = c^3\chi(\lambda) \quad (4)$$

where c is an arbitrary constant. We can exploit eq 3 by fixing one λ parameter arbitrarily; we choose $\lambda_H = 0$ for convenience. The property (4) implies that χ can be partitioned into a product of two functions

$$\chi = \rho\chi' \quad (5)$$

This feature is useful if one has reason to suspect that the λ parameters extracted from one series might be transferable to another series with a different substituent R and/or to another type of chirality observation; the peculiarity of each series or each type of chirality observation can then be absorbed in the function ρ. In the present paper, in which we shall in the main be concerned with the fluorine anisochronism in the series corresponding to R = Br, we shall for simplicity put $\rho_{Br} = 1$ and thus write $\chi = \chi'$.

Let us now assume that the experimental data can indeed be represented satisfactorily by such a crude first-order model. To make the connection with the free energy differences between the individual conformers we first note that the product

$$\Gamma = (\Delta G^\circ{}_{\alpha\beta})(\Delta G^\circ{}_{\beta\gamma})(\Delta G^\circ{}_{\gamma\alpha}) \quad (6)$$

also obeys the transformation properties of a chirality function. This fact can easily be verified from schematic free energy diagrams of the type shown in Figure 1, in which the primed labels refer to the conformers of the series enantiomeric to α, β, γ obtained upon switching Y and Z, for example. We furthermore have the sum rules

$$(\lambda_X - \lambda_Y) + (\lambda_Y - \lambda_Z) + (\lambda_Z - \lambda_X) = 0 \quad (7)$$

and

$$\Delta G^\circ{}_{\alpha\beta} + \Delta G^\circ{}_{\beta\gamma} + \Delta G^\circ{}_{\gamma\alpha} = 0 \quad (8)$$

Equations 7 and 8 are invariant with respect to any permutation of the labels. The relationships (1) and

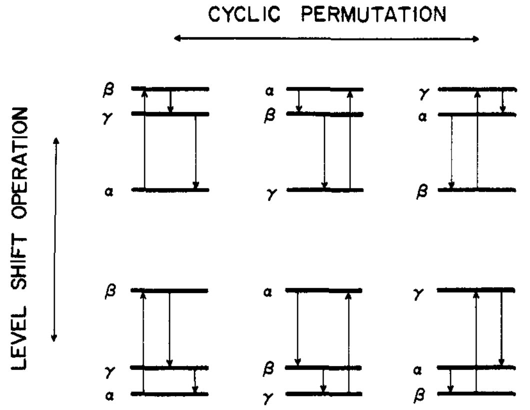


Figure 2. Schematic representation of the invariance properties of the quantity Γ.

(6) remain unchanged on cyclic permutations of the ligands and/or the conformers. Equation 6 exhibits an additional invariance property with respect to the "level shift" operation depicted schematically in Figure 2, which has its pendant also in eq 1.[5] It is therefore tempting to invoke the relationships[6]

$$\Delta G^\circ_{\xi\eta} = f(\lambda_U - \lambda_V) \tag{9}$$

in which the index pairs [$\xi\eta$, UV] correspond to the combinations [$\mu\nu$, XY], [$\nu\sigma$, YZ], and [$\sigma\mu$, ZX] or [$\mu\nu$, XY], [$\nu\sigma$, ZX], and [$\sigma\mu$, YZ]. The factor f must have the dimension of energy divided by the cubic root of a chemical shift, which leads us to the formula

$$f = (\Gamma/\chi)^{1/3} \tag{10}$$

There can be no question that this "derivation" of eq 9, which embodies the central hypothesis of our first-order mathematical model, largely relies upon a heuristic point of view. However, the following two additional considerations suggested that eq 9 might approximately apply to the data of the preceding paper.[4] (1) The quantity Γ of eq 6 must become zero for equal conformer populations. For this to be true also for χ of eq 1 demands a vanishing intrinsic anisochronism.[4,7] To the extent that this was found to be approximately valid[4] one can expect the λ values to contain "undiluted" information about population differences.[8] (2) The free energy differences between any two conformers will in general depend on all three ligands, but the heuristic eq 9 implies that this dependence can be approximated by a two-parameter function. This ought to be a good approximation if we can make the reasonable assumption that the relative free energies of the conformers are controlled by vicinal gauche interactions describable by products of two parameters. For then we can write, by inspection, eq 11a–c, where the l parameters characterize the ligands at the asymmetric center and the k parameters the ligands at the adjacent carbon. If the structures of the conformers do not deviate too drastically from idealized staggered geometry, k_{F_a} should be very similar to k_{F_b}, so that the eq 11 simplify to

$$\Delta G^\circ_{\alpha\beta} = k_R(l_X - l_Y) + k_{F_a}(l_Y - l_Z) + k_{F_b}(l_Z - l_X) \tag{11a}$$

$$\Delta G^\circ_{\beta\gamma} = k_R(l_Y - l_Z) + k_{F_a}(l_Z - l_X) + k_{F_b}(l_X - l_Y) \tag{11b}$$

$$\Delta G^\circ_{\gamma\alpha} = k_R(l_Z - l_X) + k_{F_a}(l_X - l_Y) + k_{F_b}(l_Y - l_Z) \tag{11c}$$

$$\Delta G^\circ_{\alpha\beta} = (k_R - k_F)(l_X - l_Y) \tag{12a}$$

$$\Delta G^\circ_{\beta\gamma} = (k_R - k_F)(l_Y - l_Z) \tag{12b}$$

$$\Delta G^\circ_{\gamma\alpha} = (k_R - k_F)(l_Z - l_X) \tag{12c}$$

It should be borne in mind, however, that because of the invariance properties of the heuristic model the relationships 12 are subject to the scrambling operations of Figure 2.

Tests of the Model

(1) For solving the least-squares problem of eq 2, any standard procedure should be applicable in principle, but the structural similarity of these third-degree equations to certain notoriously ill-behaved functions in numerical mathematics, for instance that widely known as "Rosenbrock's Valley,"[9] led us to anticipate trouble. Indeed, even using such powerful algorithms as those developed by Marquardt[10] or Fletcher and Powell[11] did not prevent the computations from frequently running aground in exceedingly narrow hypervalleys with almost horizontal floors. It was therefore deemed necessary to conduct a semisystematic exploration of the parameter hypersurface, for which we developed a "breathing grid" method. The grid asynchronously stretches and shrinks so as to follow most rapidly a downhill path, even in the presence of extreme curvatures, and the algorithm is designed so as to render divergence logically impossible.[12] Starting at 81 widely spaced fixed grid points, the breathing grid arrived in the same general region after less that 10 iterations for 28 of the cases, whereupon it proceeded to shrink without limit, producing identical results. In the other 53 cases the breathing grid ended up in a variety of higher lying hypervalleys, signaled by the grid step size becoming quasi-stationary at a level of 10^{-3} to 10^{-5}. Two of these hypervalleys were followed for an additional 300 iterations, which resulted in large changes in the parameters, but reduced the sum of the squares of the residuals by less than $10^{-3}\%$. In view of all these computer experiments we feel reasonably confident that we have located the

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(5) These properties can be expressed more elegantly in formal group-theoretical language, but we refrain from doing that here.

(6) The heuristic equation (9) has the form of a linear free energy relationship and might hence be dubbed the "Hammett equation of conformational analysis."

(7) G. R. Franzen and G. Binsch, *J. Amer. Chem. Soc.*, **95**, 175 (1973).

(8) The assumption of a negligible intrinsic term would undoubtedly be a very poor approximation for the corresponding chirality observation of optical rotation. Otherwise one would generally have to find a much smaller optical rotation for compounds of the type G_3CCXYZ as compared to RG_2CCXYZ, which is at variance with a large body of experience. On the other hand, such an assumption might well hold for the asymmetric syntheses discussed by Ugi.[2] The data to test this latter hypothesis directly are unfortunately not available, but Ugi's observation that his λ values conformed to an intuitively reasonable measure of steric bulk is highly suggestive.

(9) H. H. Rosenbrock, *Comput. J.*, **3**, 175 (1960).

(10) D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).

(11) R. Fletcher and M. Powell, *Comput. J.*, **6**, 163 (1963); R. Fletcher, *ibid.*, **10**, 392 (1968).

(12) Details of this procedure, which is based on a further development of ideas described by J. G. Becsey, L. Berke, and J. R. Callan, *J. Chem. Educ.*, **45**, 728 (1968), will be communicated on request.

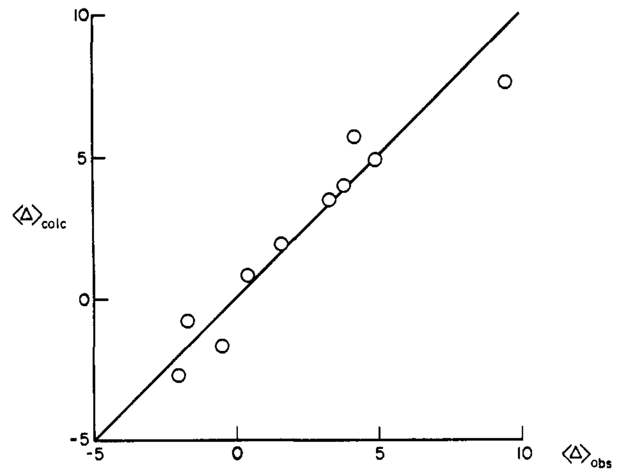

Figure 3. Regression line for the data of Table I.

global minimum of the functional g.[13] The results for one series of ambient-temperature (302°K) data[4] are collected in Table I and a regression line is shown in Figure 3.

Table I. Ligand Constants and Calculated Ambient-Temperature Anisochronism (ppm) for the Series $BrCF_2CXYZ$[a]

Compd[b]	X	Y	Z	$\langle\Delta\rangle_{calcd}$	$\langle\Delta\rangle_{obsd}$[b]
1	Cl	F	H	4.079	3.829
2	Br	F	H	5.858	4.178
3	Br	Cl	H	3.594	3.297
4	Br	Ph	H	7.475	9.498
5	Cl	Ph	H	4.676	4.915
9	F	Ph	H	−0.864	−1.728
10	Br	Cl	Ph	0.795	0.0
11	Br	F	Ph	−2.482	−1.952
13	Cl	F	Ph	−1.460	0.463
14	Br	Cl	F	1.816	1.648

[a] λ_{Br} −3.104, λ_{Cl} −2.671, λ_F −0.830, λ_{Ph} −1.517 (λ_H 0).
[b] Reference 4.

(2) If the ligand constants are transferable to the series with R = Cl, we should now be able to predict the $\langle\Delta\rangle$ values for $ClCF_2CBrPhH$ (**6**), $ClCF_2CClPhH$ (**7**), and $ClCF_2CClFPh$ (**12**).[4] Although the conversion factor will in general have to be determined empirically, eq 12 indicate that it should be given approximately by $[(\lambda_{Cl} - \lambda_F)/(\lambda_{Br} - \lambda_F)]^{3/2}$, leading to the following calculated (observed) values: **6**, 5.457 (6.282); **7**, 3.413 (3.130); **12**, −1.066 (0.621). The agreement is of a quality comparable to that of Table I and the analogous compounds **12** and **13** fall more noticeably out of line in both series. In any case it remains a weak test, however, whose significance would assume genuine meaning only after more data have been collected.

(3) It follows from eq 9 and 10 that the normalized quantities $\Delta\lambda^0 = (\lambda_U - \lambda_V)\chi^{-1/3}$ should be independent of temperature, provided that temperature effects on the chemical shift differences in the individual conformers and entropy differences between them can be nelected.[14] A least-squares calculation on the low-temperature data of the preceding paper,[4] after conversion to the common temperature of 123°K, yielded the ligand constants λ_{Br} −3.793, λ_{Cl} −3.311, λ_F −0.788, λ_{Ph} −1.712 (λ_H 0). A regression plot of the 30 $\Delta\lambda^\circ$ differences for the $BrCF_2CXYZ$ series is shown in Figure 4.

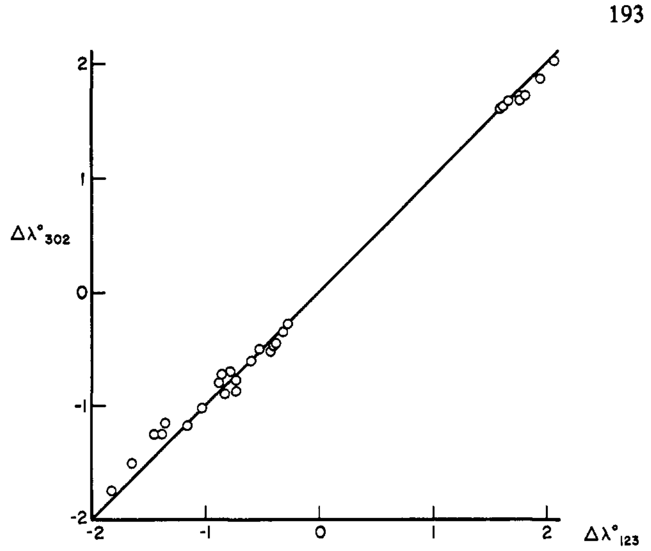

Figure 4. Regression line for the $\Delta\lambda^0$ differences at 123 and 302°K.

(4) The consequence of greatest practical importance consists in the conclusion that the normalized quantities $\Delta\lambda^0$ should be proportional to the free energy differences. To test this hypothesis we have calculated the ambient-temperature populations by using the proportionality factors $\Gamma^{1/3}$ obtained from the low-temperature data of the preceding paper,[4] except for **4** and **11** for which Γ is not available. In these two cases we have taken $(\Delta G^\circ{}_{\gamma\alpha})_4(\lambda_{Ph} - \lambda_H)/\chi_4{}^{1/3}$ and $(\Delta G^\circ{}_{\gamma\alpha})_{11}\cdot(\lambda_F - \lambda_{Ph})/\chi_{11}{}^{1/3}$ as scaling factors. In Table II the theoretical results are compared with the values extrapolated from the measured low-temperature populations.[4]

Table II. Calculated and Observed Ambient-Temperature Populations for the Series $BrCF_2CXYZ$

	p_α		p_β		p_γ	
Compd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
1	0.41	0.41	0.24	0.21	0.35	0.38
2	0.47	0.50	0.17	0.19	0.36	0.31
3	0.41	0.43	0.29	0.28	0.30	0.29
4	0.78	0.81	0.04		0.18	0.19
5	0.46	0.52	0.23	0.22	0.31	0.26
9	0.29	0.29	0.33	0.33	0.38	0.38
10	0.46	0.58	0.25	0.20	0.29	0.22
11	0.66	0.70	0.05		0.29	0.30
13	0.49	0.47	0.18	0.13	0.33	0.40
14	0.51	0.53	0.38	0.32	0.11	0.15

Conclusion

Before one can hope to exploit the heuristic theory of the present paper for the practical conformational analysis of acyclic systems, without the benefit of low-temperature information, the following three problems have to be faced. (1) The absolute sign

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[13] For a comprehensive account of the current status of research concerned with systems of nonlinear equations, see J. M. Ortega and W. C. Rheinboldt, "Iterative Solution of Nonlinear Equations in Several Variables," Academic Press, New York, N. Y., 1970.

[14] The entropy differences between the conformers of **3** were found to be zero within an experimental error of about 1 eu: A. Trifunac and G. Binsch, unpublished results.

of the geminal anisochronism must be known for each compound in a series. If one has crude qualitative information about chemical shift trends, either from approximate chemical shift theories or from suitable model compounds, this problem will hardly cause difficulties for the large time-averaged chemical shift differences in the series. It becomes progressively more difficult as the numbers approach zero, but, fortunately, this increase in uncertainty is compensated by the corresponding decrease in the importance of sign information for the least-squares calculation. (2) As apparent from the peculiar invariance properties of the model and from Figure 2, applications of the theory require knowledge about the relative ordering of the free energy levels. Here again, crude qualitative information is adequate. Some information of this kind is, in fact, already contained in the ligand constants. For instance, the perhaps somewhat surprising conclusion[4] that phenyl is "smaller" than chlorine only emerged after extensive low-temperature work,[4] but is at once clear from the relative magnitudes of the λ values. (3) We have seen that the model does not yield the absolute populations, since the free energy differences can only be calculated to within a proportionality factor. To extract this factor from time-averaged measurements, one needs values of $\langle\Delta\rangle$ at three, and preferably more, different temperatures.

It is impossible to say at this stage how well the first-order model will perform for other systems. The data are still too limited to exclude the possibility that some of the agreements found in the present paper are accidental. We are inclined to believe, however, that the results are encouraging enough to warrant further efforts.

Acknowledgments. I am indebted to Professor Ivar Ugi, who in a personal conversation in June 1967 implanted the seed of an idea in my mind. Acknowledgment is made to the donors of the Petroleum Research Fund (Grant No. 4440-AC4), administered by the American Chemical Society, for support of this research.

Stable Carbocations. CXLI.[1] The 3-Homoadamantyl Cation

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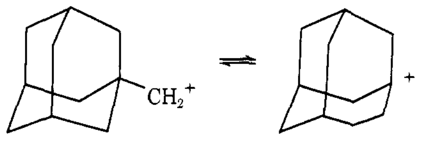
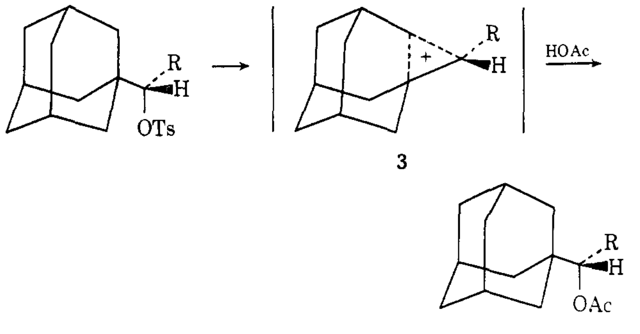
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received June 17, 1972*

Abstract: The 3-homoadamantyl cation (**1**) was obtained in superacid solutions at −78°. Ion **1** was found to be stable and did not rearrange. Both ^{1}H and ^{13}C nmr spectroscopic studies indicate the classical nature of the 3-homoadamantyl cation, a trivalent bridgehead carbenium ion. The cage effect in ion **1** was found unimportant in comparison with the 1-adamantyl cation.

The formation of bridgehead carbenium ions,[2] such as the 3-homoadamantyl cation (**1**),[3] has been suggested in connection with studies in the Koch reaction.[3f,4] Solvolysis studies indicated the equilibration between the tertiary homoadamantyl (**1**) and the primary 1-adamantylcarbinyl cation (**2**). However, bridged structure **3** (R = D) of the 3-homoadamantyl cation recently has been suggested as the transition state (or intermediate) involved in the acetolysis of chiral 1-adamantylcarbinyl-*1′*-*d* tosylate.[5] Schleyer also suggested that simple primary carbenium ions were energetically inaccessible in usual solvolytic systems.[2,5] Theoretical calculation of the stabilities of bridgehead carbenium ions[6] showed that 3-homoadamantyl cation



2 **1**



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(1) Part CXL: G. A. Olah, G. D. Mateescu, and Y. K. Mo, *J. Amer. Chem. Soc.*, **95**, in press.

(2) (a) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964); (b) U. Schollkopf, *Angew. Chem.*, **72**, 147 (1966); (c) R. C. Fort, Jr., in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. 4, Wiley-Interscience, New York, N. Y., 1972, Chapter 32.

(3) (a) H. Stetter and P. Goebel, *Chem. Ber.*, **96**, 550 (1963); (b) S. P. Jindal, Ph.D. Thesis, Case Western Reserve University, 1965; (c) J. E. Nordlander, S. P. Jindal, P. v. R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, **88**, 4475 (1966); (d) R. C. Fort, Jr., and R. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966); (e) B. R. Vogt, *Tetrahedron Lett.*, 1575 (1968); (f) F. N. Stepanov and S. S. Guts, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 439 (1970); (g) I. Tabushi, Z. Yoshida, and N. Takahashi, *J. Amer. Chem. Soc.*, **92**, 6670 (1970); (h) J. B. Hamilton, Jr., Ph.D. Thesis, Case Western Reserve University, 1971.

(4) (a) F. N. Stepanov and S. S. Guts, *Zh. Org. Khim.*, **4**, 1933 (1968); (b) J. A. v. Zorge, J. Strating, and H. Wynberg, *Recl. Trav. Chim. Pays-Bas*, 89, 781 (1970).

(5) S. H. Liggero, R. Sustmann, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 91, 4571 (1969).

(6) (a) G. J. Gleicher and R. v. R. Schleyer, *ibid.*, **89**, 582 (1967); (b) R. C. Bingham and P. v. R. Schleyer, *ibid.*, **93**, 3189 (1971); (c) R. C. Bingham, Ph.D. Thesis, Princeton University, 1970, and references quoted therein.