59. How Good Are Quartic Functions to Describe Double-Minimum Energy Profiles? Nitrogen Inversion as Example

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Energy profiles for nitrogen inversion in ammonia (**1**), aziridine (**2**), 1*H*-azirine (**3**), *trans*-2,3-difluoroaziridine (**4**), *cis*-2,3-difluoroaziridine (**5**), 2,3-difluoro-1*H*-azirine (**6**), methanimine (**7**), and 2,2-difluoromethanimine (**8**) have been calculated at the 6-31G** and 4-21G* levels. If the reaction coordinate is chosen as the angle τ between the N–H bond and the C–N–C plane (or the N–C line for the imines **7** and **8**), the energy is reproduced quite well by a quartic function $V(\tau) = a\tau^4 - b\tau^2$ in all cases. Moreover, for this series of molecules the ratio a/b is approximately constant, which means that the inversion barrier is directly proportional to the quadratic force constant of the equilibrium structure along the reaction coordinate. The use of this and other simple relationships for automerization reactions is discussed. Some of the molecules studied show features that can be nicely interpreted in terms of stereoelectronic factors.

Introduction. – The notion that energy profiles for elementary chemical reactions can be described by simple analytic functions[1]) has an immediate appeal to the kind of chemist who is more interested in generalities than in details or fundamental principles. Recent work by *Bürgi* and *Dubler-Streudle* [2] has shown that the combination of experimental structural data for (η^4-s-*cis*-butadiene)metallocene complexes with activation barriers for metallacyclopentadiene ring inversion in these molecules (from NMR data) can be interpreted in terms of a quartic potential $\Delta E(x) = ax^4 - bx^2$, where x is the reaction coordinate for the ring inversion and a is approximately uniform for all the molecules included in the analysis. In analogous studies for a bond-breaking reaction (acetal hydrolysis), the combination of structural and kinetic data could be interpreted in terms of a modified *Morse* potential [3] or, even better, by a cubic potential [4] with a variable linear term.

One advantage of such simple, analytic potentials is that, once verified, they lead to functional relationships among the structural and energetic parameters. Thus, for the one-dimensional quartic potential describing a double minimum automerization reaction (*Fig. 1*):

$$V(x) = ax^4 - bx^2 \tag{1}$$

the equilibrium distance x_0, the quadratic force constant f, and the energy barrier E are not independent, but depend on the coefficients a and b as follows:

$$x_0 = (b/2a)^{1/2}, \quad f = 4b, \quad E = b^2/4a. \tag{2}$$

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[1]) For a brief discussion of analytic functions that have been used to represent the potential energy function for inversions and other large amplitude vibrations, see [1].

Thus, each may be evaluated from a knowledge of the other two:

$$x_0 = (8E/f)^{1/2}, \qquad f = 8E/(x_0)^2, \qquad E = (x_0)^2 f/8. \tag{3}$$

By eliminating b from *Eqns. 2*, we obtain

$$E = a(x_0)^4. \tag{4}$$

If a stays the same for a set of molecules, there is then a proportionality relationship between E and $(x_0)^4$ that has been shown to apply in practice for the reaction studied by *Bürgi* and *Dubler-Streudle* [2].

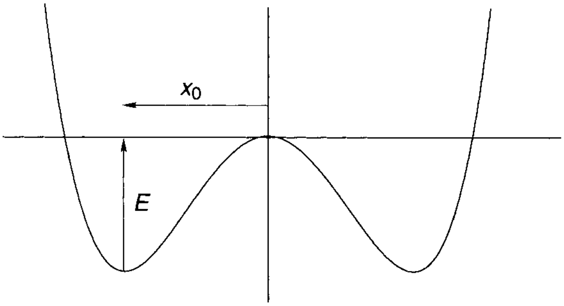


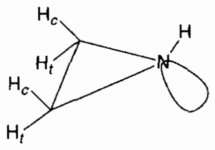
Fig. 1. *Quartic function representing symmetrical double minimum potential*

One can imagine many circumstances where one may wish to derive one of the three quantities, E, x_0, f, from known values of the other two. It is, therefore, of interest to enquire how closely quartic potentials actually fit energy profiles for automerization reactions. Also, if the quartic potential is indeed a good approximation for such energy profiles, we would like to know whether the assumption of uniform a for a set of related molecules can be justified, or whether other regularities among the coefficients might apply. We report here a preliminary study of these questions, using energy profiles calculated at the 4-21G* and 6-31G** levels for some simple automerization reactions involving nitrogen inversion.

Computational Details. – The molecules for which we have made detailed calculations are: ammonia (**1**), aziridine (**2**), 1*H*-azirine (**3**), *trans*-2,3-difluoroaziridine (**4**), *cis*-2,3-difluoroaziridine (**5**), 2,3-difluoro-1*H*-azirine (**6**), methanimine (**7**), and 2,2-difluoromethanimine (**8**). In all of these molecules except **5** the transition state (TS) for nitrogen inversion has a higher symmetry than the ground state (GS). The GS and TS structures were derived for each molecule by complete geometry optimization with the *ab initio* gradient method employing both the 4-21G*[5] and 6-31G** [6][7] basis sets. The optimization process was terminated when the gradient length,

$$g = \left[\sum_{i}^{n} \left(\frac{\partial E}{\partial q_i}\right)^2 \frac{1}{n}\right]^{1/2}$$

(where the summation is carried out over all degrees of freedom) was reduced below 5×10^{-4} mdyn. The energy was then calculated by constrained minimization at several points along a one-dimensional driving coordinate selected to describe the automerization reaction involving inversion of configuration at the N-atom. The program system package MONSTERGAUSS [8] was used for all these calculations.



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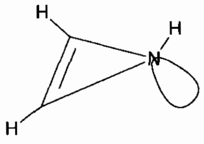

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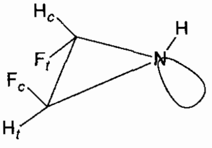

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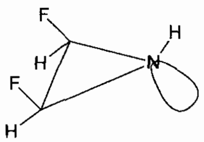

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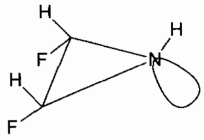

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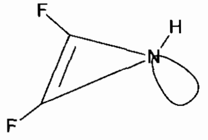

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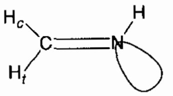

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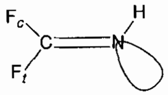

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Choice of Reaction Coordinate: Ammonia Inversion. – The reaction coordinate can be chosen in many ways. The first question to be decided involved the choice of the most suitable coordinate for nitrogen inversion, for it is obvious that, if the energy profile is exactly described by a quartic function of one coordinate, it will be less well described by a quartic function of any other coordinate that is not linearly related to the first. For a coordinate to be applicable in *Eqn. 1*, it must obviously have the value zero at the energy maximum and have equal values and opposite signs at the two minima. This zero value should result in a 'natural' way by symmetry and not merely by subtracting the value of some parameter from itself.

We can see the difference between a suitable and an unsuitable coordinate by studying the example of ammonia inversion. Some possible coordinates for following this inversion are indicated in *Fig. 2*. As the H–N–H bond angle α is 120° for the D_{3h} transition state, the zero condition (but not the sign-reversal condition) can be satisfied for this state by taking as coordinate $\alpha' = 120° - \alpha$ or $\sin\alpha'$ or $\tan\alpha'$ or other comparable quantities. Another possible choice is γ, the complement of the angle γ' between the molecular threefold rotation axis and a N–H bond direction ($\gamma = \pm\arccos(2\sin(\alpha/2)/\sqrt{3})$ for C_{3v} molecular symmetry); or $\sin\gamma$, *etc.* Still another choice is the angle τ between a N–H bond direction and the plane of the other two N–H bonds. For C_{3v} molecular symmetry, $\tau = \pm\arccos\{-\cos\alpha/\cos(\alpha/2)\}$.

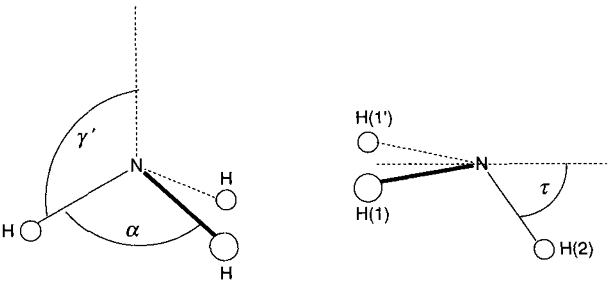

Fig. 2. *Possible coordinates for following inversion of ammonia molecule.* The angle γ is the complement of γ'.

The energy of C_{3v} ammonia was calculated at the 6-31G** level for 22 values of the H–N–H bond angle α. The values obtained for the equilibrium bond length (1.001 Å) and angle (107.6°) agree with those obtained previously at this level [7], and the energy barrier (5.51 kcal · mol^{-1}) is close to the experimental value (~ 5.8 kcal · mol^{-1}). The reaction coordinate is not quite a straight line in coordinate space; as α is varied, there is a small but systematic change in the bond length d(N–H): for α = 100, 107.6 (equilibrium value), 120°, d(N–H) is 1.009, 1.001, 0.987 Å, respectively; as the N bonding orbitals acquire more s character, the bonds shorten. As we shall see, this effect is even more pronounced in some of the other examples we shall discuss.

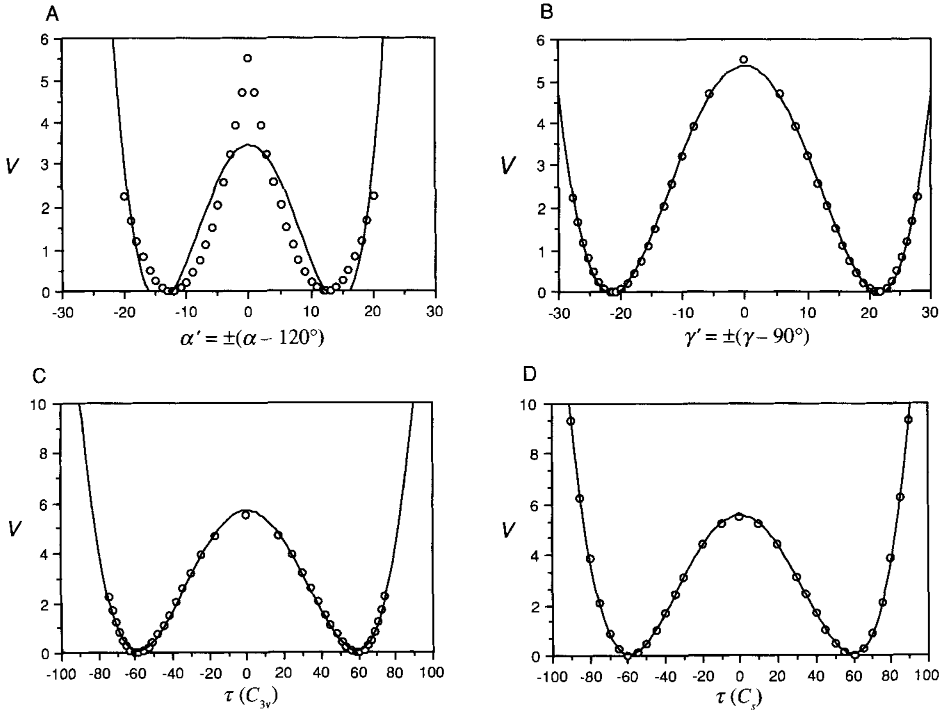

Fig. 3. *Ammonia-inversion energy profiles with various choices of the reaction coordinate* (see *Fig. 2* for explanation): A) $\alpha' = 120° - \alpha$; B) $\gamma = \gamma' - 90°$; C) τ (C_{3v} molecular symmetry); D) τ as driving coordinate (C_s molecular symmetry). Calculated energies at the 6-31G** level are indicated by small circles, fitted quartic functions as smooth curves.

The calculated energy values were fitted to a quartic polynomial against several types of parameter, such as α', γ, and τ (*Fig. 3*)[2]). The dependence of V on the bond angle deviation α' is not at all quartic-like (*Fig. 3A*). In fact, when the energy is expanded about the minimum, the calculated points give an almost perfect fit to a quadratic function with a force constant $f = 76$ cal · mol^{-1} · deg^{-2} (*Fig. 4*). A small cubic term lowers the quadratic potential energy by 0.17 kcal · mol^{-1} for a bond angle 10° larger than the equilibrium value and raises it by the same amount for a 10° smaller bond angle. Very similar curves are obtained with $\sin\alpha'$ and $\tan\alpha'$ as reaction coordinate as with α' itself. On the other hand, when either γ or τ is chosen as the reaction coordinate, the fit to a quartic potential is quite good, as can be seen from *Figs. 3B* and *3C*.

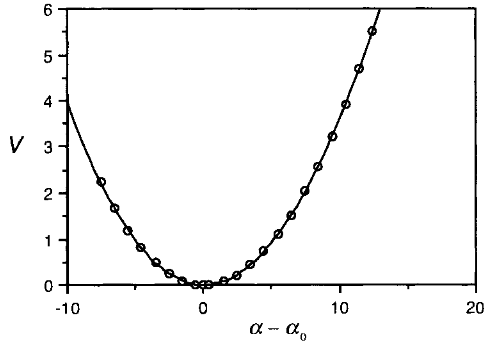

Fig. 4. *Ammonia-inversion energy profile with the reaction coordinate x chosen as $\alpha - \alpha_0$, the deviation of the bond angle α from its equilibrium value α_0* (see *Fig. 2*). The calculated energies at the 6-31G** level (small circles) are closely reproduced by a third degree polynomial (smooth curve) with only the quadratic term significantly different from zero: $V = 0.0009 + 0.00013x + 0.038x^2 - 0.00017x^3$

Once τ is accepted as a suitable coordinate, the effect of lowering the molecular symmetry from C_{3v} to C_s needs to be examined. In a separate set of calculations, one H-atom (H(2)) was moved out of the plane of the other three atoms and the molecular energy minimized with respect to α(H(1)–N–H(1')), d(N–H(1)) = d(N–H(1')) and d(N–H(2)) for a few values of τ, the driving coordinate (see *Fig. 2*). A preliminary run showed that the two symmetry-independent bond distances did not differ by more than 0.008 Å within the range of τ from 0 to 90° (the equilibrium value of τ is close to 60°); they were, therefore, constrained to be equal in the subsequent calculations. The results show an almost perfect fit of the energy to a quartic function in τ (*Fig. 3D*). Note that, although the quartics of *Figs. 3C* and *3D* are very similar, they describe physically different processes; for *Fig. 3C* the N-atom is displaced from the plane of the three

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[2]) With the available software (*StatView512+*™), it was more convenient to fit the calculated points describing the symmetrical curve to a general polynomial of the 4th degree with no symmetry constraints. Of course, the coefficients obtained for the odd powers are negligibly small but not identically zero (because of rounding errors). The energy barrier E determined by *Eqn. 2* as a function of a and b ($E = b^2/4a$) can be compared with the coefficient of the constant term (call it E_0) in the general 4th degree polynomial calculated in this way. The barriers estimated in these two different ways agree very closely (see *Table 2*).

H-atoms (preserving C_{3v} symmetry), whereas for *Fig. 3D* one H-atom is displaced from the plane of the other three atoms (preserving only C_s symmetry) so that the bond angles α(H(1)–N–H(1')) and β(H(1)–N–H(2)) are no longer constrained to be equal. While the first path corresponds to a motion along the A_1 symmetry coordinate[3], the second involves one of the degenerate pair of E coordinates as well – the one with C_s co-kernal symmetry[4]. Since the curves of constant τ are inclined to both symmetry coordinate axes, the constrained path obtained by searching for the minimum energy with respect to α at constant τ does not correspond to a true valley in the potential-energy surface.

The ammonia results provide justification for choosing as reaction coordinate for nitrogen inversion in the three-membered ring molecules **2**–**6** the angle τ between the N–H bond and the C–N–C plane. For the imines **7** and **8**, we choose as τ the analogous angle between the N–H bond and the C–N bond.

Results for Nitrogen Inversion in Other Molecules. – Ground-state (GS) and transition-state (TS) geometries obtained for the molecules **2**–**8** at the 6-31G** level are given in *Table 1*, together with the calculated energy barriers E. For **2** and **3** our results are in almost perfect agreement with recent work of *Alcamí et al.* [10], who have studied nitrogen inversion in three-membered rings from a different point of view. In particular, we find virtually the same shortening of the N–C (and N–H) bonds and lengthening of the C–C bonds on going from GS to TS as they did. The same kind of behaviour is found in the difluoro molecules **4**, **5**, and **6**. In the imines **7** and **8**, there is an analogous shortening (by 0.03–0.04 Å) of the C=N bond.

Table 1. *Optimized Ground-State* (GS) *and Transition-State* (TS) *Geometries from 6-31G** Calculations with Relative Energies*. Distances in Å, angles in degrees, energies in kcal · mol^{-1}.

	2		**3**		**4**		**5**			**6**	
	GS	TS	GS	TS	GS	TS	GS1	GS2	TS	GS	TS
d(N–H)	1.000	0.984	1.009	0.979	1.000	0.988	1.002	0.998	0.989	1.011	0.982
d(N–C)	1.448	1.391	1.490	1.447	1.425, 1.419	1.37	1.426	1.417	1.370	1.479	1.455
d(C–C)	1.470	1.511	1.255	1.273	1.454	1.484	1.458	1.457	1.488	1.243	1.255
d(C–H$_c$), d(C–H$_t$)	1.078	1.083	1.065	1.064	1.075, 1.073	1.076	– , 1.073	1.075, –	1.077		
d(C–F$_c$), d(C–F$_t$)					1.348, 1.340	1.354	1.344, –	– , 1.338	1.350	1.286	1.286
α(NCH$_c$), α(NCH$_t$)	118.6, 115.2	119.0	137.6	141.0	120.3, 117.7	121.6	– , 117.4	120.7, –	121.6		
α(NCF$_c$), α(NCF$_t$)					117.3, 115.9	118.3	118.1, –	– , 115.6	118.6	136.6	139.2
τ	64.7	0	69.3	0	60.4	0	62.5	–57.5	1.7	68.1	0
Relative energy	0	18.7	0	44.2	0	10	0	0.7	9.7	0	44.6

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[3] The relevant symmetry coordinates are conveniently chosen as: $S_1(A_1) = (\alpha + 2\beta - 332.71)/\sqrt{3}$, $S_2(E) = \sqrt{2}\,(\alpha - \beta)/\sqrt{3}$, where the bond angles α(H(1)–N–H(1')) and β(H(2)–N–H(1)) are measured in degrees. The constant term 332.71 is $3\alpha_0$. In the range covered ($0 \leq \tau \leq 90°$) the largest value of S_2 occurs at $\tau = 90°$, where $\alpha = 102.83°$, $\beta = 90°$.

[4] A table of co-kernal symmetries of the common point groups is given in [9].

Table 1 (cont.)

	7		**8**	
	GS	TS	GS	TS
d(N–H)	1.006	0.976	1.001	0.976
d(N–C)	1.250	1.220	1.224	1.183
$d(\mathrm{C–X}_c)$, $d(\mathrm{C–X}_t)$	1.085, 1.081	1.095	1.306, 1.291	1.313
$\alpha(\mathrm{NCX}_c)$, $\alpha(\mathrm{NCX}_t)$	124.6, 119.3	123.2	127.4, 123.9	127.2
τ	68.5	0	67.9	0
Relative energy	0	31.8	0	21.1

The bond angles in the imines provide a beautiful example of the application of *Bent*'s rule: atomic p character concentrates in orbitals directed towards electronegative substituents [11]. The F–C–F angles in the GS and TS of **8** are 108.7° and 105.6°, respectively, both *ca.* 8° smaller than the corresponding H–C–H angles in **7**.

The small but systematic variation of the C–F bond lengths in the difluoro molecules can be attributed to a stereoelectronic factor. When the C–F bond is *syn* to the N–H bond, *i.e. anti* to the nitrogen lone pair[5]), it is 0.006 to 0.012 Å longer than when it has the opposite configuration. In the corresponding TS's, where the lone pair is p-like, there is a further, small increase in the C–F bond lengths.

A comparison of the total energies of the stereoisomers **4** and **5** shows that the *trans*-isomer **4**, ($E = -330.752859$ au) has a lower energy than the more stable of the *cis*-isomers (**5A**), with both F-atoms *syn* to the N–H bond (*i.e. anti* to the lone pair), by 2.32 kcal · mol^{-1}; the energy of the other isomer, with the inverted N-atom, is raised further by 0.66 kcal · mol^{-1}. The relative instability of the *cis*-isomers can be attributed to the roughly parallel alignment of the highly polar C–F bonds, and the small energy difference between the *syn*- and *anti*-forms has an obvious interpretation in terms of stereoelectronic factors[6]).

Alcamí et al. [10] found that the nitrogen-inversion barriers in three-membered rings were sensitive to choice of basis set and to correlation effects. For **2**, their calculations at 6-31G* level with (and without) MP3 correlation correction led to barriers of 20.6 (and 19.4) kcal · mol^{-1}; for **3**, the corresponding barriers were 45.6 (and 45.5) kcal · mol^{-1}. For comparison, the barriers we obtain with 6-31G** (without correlation correction) are 18.7 and 44.2 kcal · mol^{-1}, respectively. Thus, for these molecules at least, the correlation effects at this level are small and our values are in good agreement with theirs. Our calculations at the 4-21G* level lead to consistently higher barriers (by 5–15%) than those given in *Table 1*. For all the molecules included in our study, the more extended basis set lowers the TS energy more than it does the GS energy.

The increase in the barrier on going from **2** to **3** is well understood as a consequence of the contraction of the C–N–C ring angle to 49.8° in the GS of **3**. Approximately the same barrier (44.6 kcal · mol^{-1}) is calculated for the unsaturated difluoro derivative **6**. Less well

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[5]) Note that, because of the geometry of the three-membered ring, the *syn*-relationship is *syn*-periplanar, whereas the *anti* one is *anti*-clinal.

[6]) We postpone a more detailed discussion of stereoelectronic effects involving the interaction between C–F bonds and nitrogen (and oxygen) lone pairs to a forthcoming publication.

understood is the drop in the barrier from 18.7 kcal · mol^{-1} to *ca.* 10 kcal · mol^{-1} on passing from aziridine (**2**) to its difluoro derivatives **4** and **5**. One might argue that the TS's of **4** and **5** are relatively stabilized by interaction of the nitrogen p lone pair with the σ^* orbitals of the polar C–F bonds. In the difluoroazirine **6**, this interaction is forbidden by symmetry, and, accordingly, the barriers in **3** and **6** are practically equal (as are also the C–F distances in the GS and TS of **6**). On the other hand, the barrier in difluoromethanimine **8** is again *ca.* 10 kcal · mol^{-1} lower than in the methanimine (**7**).

Both in the three-membered-ring molecules **2**–**6** and in the imines **7** and **8**, inversion of the N-atom is described reasonably well by quartic functions in the out-of-plane angle τ (*Fig. 5*). A summary of the relevant calculated quantities is given in *Table 2*, together with the parameters describing the quartics fitted by polynomial regression [2]. Inspection of the curves in *Fig. 5* shows that, in spite of the close agreement between the optimized quartics and the calculated points, the deviations have a systematic character: the quartics tend to give too low energy values at the maxima and the minima, and too high ones in between. This can be corrected by inclusion of a 6th power term with the same sign as the quadratic term, but, as our interest here is in the quartic approximation, we shall restrict our attention to this.

Table 2. *Values of Equilibrium Out-of-Plane Angle* $x_0(\tau)$[°], *Quadratic Force Constant* f [kcal · mol^{-1} · deg^{-2}], *and Energy Barrier* E [kcal · mol^{-1}] *as Calculated at the 6-31G** Level and as Estimated from the Coefficients of the Best Fitted Quartic Function* (*Eqns. 2*) *and from the Other Two Calculated Values* (*Eqns. 3*). The coefficients of the quartic functions are also given.

Molecule	6-31G** Results			Quartic coefficients			Estimated from *Eqns. 2*			Estimated from *Eqns. 3*		
	x_0	f	E	$a \cdot 10^6$	$b \cdot 10^3$	E_0	x_0	f	E	x_0	f	E
2	64.7	0.0294	18.7	0.99	8.5	18.1	65.5	0.0340	18.2	71.3	0.0357	15.4
3	69.3	0.0478	44.2	1.83	18.0	42.1	70.1	0.0720	44.3	86.0	0.0746	28.7
4	60.4	0.0196	10.0	0.73	5.4	9.8	60.8	0.0216	10.0	63.9	0.0219	8.9
5A	57.5	0.0195	9.1	0.70	5.1	9.6	60.4	0.0204	9.3	61.1	0.0220	8.1
5B	62.5	0.0186	9.7									
6	68.1	0.0484	44.6	1.95	18.0	41.9	67.9	0.072	41.5	85.9	0.0769	28.1
7	68.5	0.0399	31.8	1.39	13.0	30.7	68.4	0.052	30.4	79.8	0.0542	23.4
8	67.9	0.0309	21.1	0.98	9.1	20.7	68.1	0.0364	21.1	73.9	0.0366	17.8

It is not too surprising that x_0, f, and E values derived with *Eqns. 2* from the coefficients of the best quartic approximations agree quite well with the calculated values; one may note, however, that the quadratic force constants f estimated in this way are systematically too large. More interesting is the question, how well do *Eqns. 3* hold? In other words, how well can x_0, f, or E be expected to be estimated from a knowledge of the other two? From *Table 2*, it is seen that x_0 and f values estimated in this way from *Eqns. 3* are consistently too large, while estimated E values are too small.

For the molecules studied here, the assumption of uniform a does not seem to be justified. Instead, another kind of regularity is found. From *Table 2*, it is seen that the coefficients of the quartic term a and the quadratic term b maintain approximately the

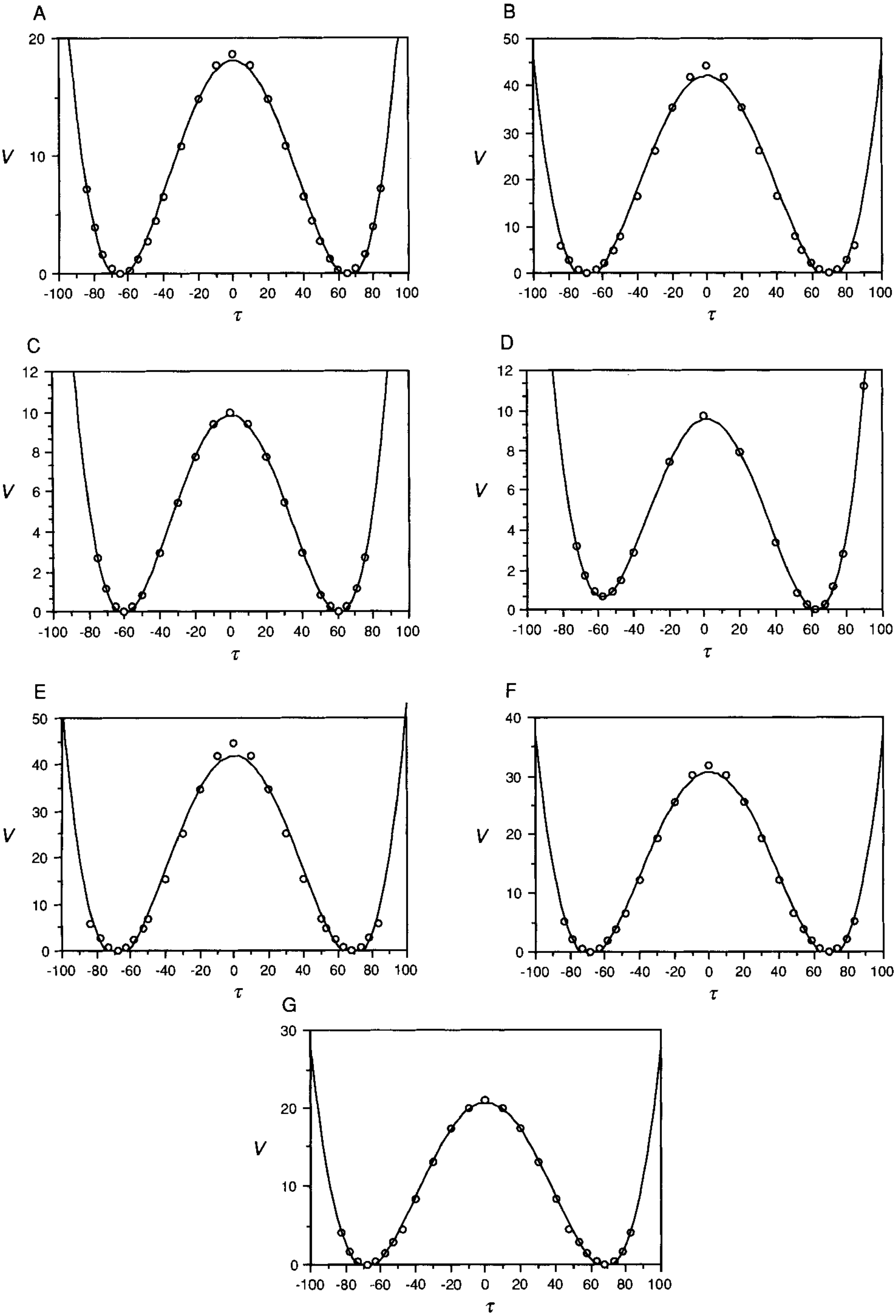

Fig. 5. *Nitrogen-inversion energy profiles for* A) *aziridine* (**2**); B) *1*H-*azirine* (**3**); C) trans-*2,3-difluoroaziridine* (**4**); D) cis-*2,3-difluoroaziridine* (**5**); E) *2,3-difluoro-1*H-*azirine* (**6**); F) *methanimine* (**7**); G) *2,2-difluoromethanimine* (**8**). The reaction coordinate is taken as the angle τ between the N–H bond and the C–N–C plane (or the C–N bond in the imines). Calculated energies at the 6-31G** level are indicated by small circles, fitted quartic functions as smooth curves. For the coefficients of the quartic functions, see *Table 2*.

same ratio. In fact, linear regression of a on b shows a good correlation with only a small constant term:

$$a = 0.18 \times 10^{-6} + 94.3\, b \times 10^{-6} \quad R = 0.99.$$

If a and b were exactly proportional, then, from *Eqns. 2*, we would have:

$$x_0 = c, \quad f = 4b, \quad E = fc^2/8 \tag{5}$$

where x_0 is fixed at $c = (b/2a)^{1/2}$ and E is directly proportional to the force constant f. For our selection of molecules, while x_0, the distance of the equilibrium structure along the reaction coordinate differs from molecule to molecule, it does not differ much. Relationships (*Eqns. 5*) can, therefore, be expected to hold approximately. From a linear regression of the calculated energy barriers E against force constants f (*Fig. 6*), we obtain:

$$E = 1193f - 14.2 \quad (R = 0.99).$$

Values of E estimated with this relationship agree much better with the calculated values than those estimated from *Eqns. 3*, involving f and x_0. (Virtually perfect agreement is obtained by quadratic regression: $E = 190f + 15050f^2 + 0.4$.)

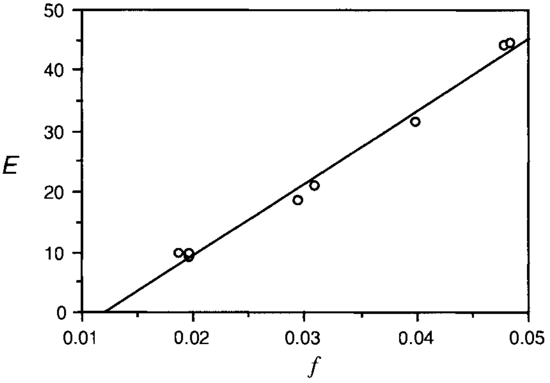

Fig. 6. *Approximately linear dependence of calculated energy barriers* E *on quadratic force constants for the molecules included in this study*

Of the molecules discussed here, the only one for which the out-of-plane angle τ is not fixed at zero in the TS by symmetry is the *cis*-difluoroaziridine **5**. Here, the quartic function fitted to the calculated points (*Fig. 5D*) has a and b coefficients very close to those of the *trans*-isomer, but it also contains small but significantly non-zero linear and cubic terms. As seen in *Table 2*, the more stable *syn*-structure (GS1) has $\tau = 62.5°$, and the *anti*-structure (GS2), less stable by 0.7 kcal · mol^{-1}, has $\tau = -57.5°$. The TS occurs at $\tau = +1.7°$, roughly midway between the two minima but displaced slightly towards the lower one. It is remarkable how closely the energy curves for the *cis*- and *trans*-isomers agree (*Fig. 5C* and *D*).

Tentative Conclusions and Unanswered Questions. – Our calculations show that, for nitrogen inversion, energy profiles can be fitted reasonably well by quartic functions (*Figs. 3* and *5*), when the out-of-plane angle τ (*Fig. 2*) is chosen as the reaction coordinate.

Energy barriers can thus be estimated from GS properties, using either the quartic approximation or other empirically derived *ad hoc* relationships. Moreover, quartics for molecules with similar barriers, *e.g.* **2** and **6**, or **4** and **5**, have similar coefficients.

For the series of molecules studied here, the ratio of the a and b coefficients of the quartic function (*Eqn. 1*) stays roughly uniform. This nearly constant ratio follows from the narrow range of variation in the equilibrium values of the out-of-plane angle τ (*Fig. 2*), and it leads to an approximate proportionality between the inversion barrier E and the quadratic force constant f in τ for the various members of the series (*Fig. 6*). Other types of regularity can be imagined. If the coefficient a of the quartic term is uniform, then the barrier E becomes proportional to $(x_0)^4$, as observed in the series of automerization reactions studied by *Bürgi* and *Dubler-Streudle* [2]. Possibly, in another series of molecules, the coefficient b of the quadratic term is uniform, in which case all the members would have the same quadratic force constant $f = 4b$, and the barrier E would be proportional to $(x_0)^2$ for all the molecules in that series. Thus, the energy barrier can depend on GS properties within a series of molecules in different ways, and it is not clear what structural and electronic factors are responsible for these different kinds of regularity.

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