(16) In the closely related case of tris(*o*-tolyl)phosphine, all three methyl groups are in proximal positions (i.e., pointing toward the apex of the phosphine pyramid), both in the crystal lattice[17] and in solution.[18] The same situation obtains for the corresponding oxide in the solid state.[17] However, in the crystal lattice, the corresponding sulfide[19] and selenide[17] have two proximal and one distal methyl groups, and tris(*m*-tolyl)phosphine sulfide has one proximal and two distal methyl groups.[19]

(17) R. A. Shaw, M. Woods, T. S. Cameron, and B. Dahlen, *Chem. Ind.* (*London*), 151 (1971); R. A. Shaw, M. Woods, W. Egan, and J. Jacobus, ibid., 532 (1973).

(18) E. J. Halpern and K. Mislow, *J. Am. Chem. Soc.*, **89**, 5224 (1967).

(19) T. S. Cameron, K. D. Howlett, R. A. Shaw, and M. Woods, *Phosphorus*, **3**, 71 (1973).

(20) Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Tetrahydrofuran (THF) was dried over KOH and distilled from $LiAlH_4$ onto Linde type 4A molecular sieves. THF-d_8 (Stohler Isotope Chemicals, 99% D) was distilled either directly from $LiAlH_4$ into the reaction flask or onto 4A molecular sieves. Benzene was dried by refluxing over sodium and was distilled onto 4A molecular sieves. Dry solvents and reagents sensitive to air or moisture were transferred by syringe. The D_2O employed was 99.7% D. Unless specified otherwise, NMR spectra were recorded on a Varian A-60A spectrometer at ambient temperature (ca. 37°), refer to ca. 20% solutions in CS_2 containing tetramethylsilane (TMS) as internal reference, and are in parts per million from Me_4Si. Mass spectra were determined with an AEI MS-9 high-resolution mass spectrometer or a Du Pont 21-490 mass spectrometer[21] with an ionizing voltage of 70 eV. Fragmentation patterns include peaks with relative intensity ≥10% of the base peak. Melting points were determined with a Thomas-Hoover apparatus and are corrected.

(21) Purchased with funds from NSF Chemistry Section Grant No. GP-32826.

(22) Prepared in 54–69% yield from 2,6-dimethylaniline and sodium nitrite in 48% HBr, followed by cuprous bromide or copper powder.

(23) Obtained from Alfa Inorganics, Beverly, Mass.

(24) K. Biemann, "Mass Spectrometry Organic Chemical Applications", McGraw-Hill, New York, N.Y., 1962, pp 204–250.

Empirical Force-Field Calculations on a Model System for Trimesityl Derivatives of Group IIIa, IVa, and Va Elements. Investigation of Stereoisomerization Pathways[1,2]

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Abstract: Stereoisomerization in the class of compounds $(Mes)_3Z$ (Mes = mesityl; Z = B, CH, N, etc.) has been investigated using the technique of empirical force-field calculations. The study was made feasible by employing a simplified model based on trimesitylmethane in which the only distinction among molecules in this class was the difference in the preferred length of the Z–Mes bond. Calculated energies for the idealized transition states point to the two-ring flip mechanism as the pathway of lowest energy over a wide range of structures. Calculated energies for this mechanism follow a trend which parallels experimental values. Activation energies are predicted for $(Mes)_3N$, $(Mes)_3SnH$, and $(Mes)_3Bi$ of 25–27, 5–7, and 3–5 kcal/mol, respectively. Results for the higher energy mechanisms are discussed in terms of structural changes accompanying the change in bond length to the central atom. The three-ring flip is found to be consistently higher in energy than the two-ring flip in the region of interest.

The intricacies of isomerism and isomerization in compounds containing three aromatic rings bonded to a common central atom, Z, have been the subject of continuing investigation in recent years in our[4] and other[5-11] laboratories. The interest in such triaryl compounds arises from the great variety of stereoisomerization pathways available to these systems.[12] In a previous paper,[4f] the stereochemistry of a simple representative, trimesitylmethane (**1**), was examined in detail utilizing the approach of full relaxation empirical force-field calculations. The present paper describes an extension of this earlier work to the general class of compounds $(Mes)_3Z$ (**2**, Mes = mesityl; Z = B, CH, N, etc.) and represents an effort to determine to what extent generalizations developed for **1** may be applied to other members of the series **2** and, by extension, to the class of triaryl compounds in general.

Specifically, for the members of series **2**, we will be concerned with the identification of the threshold mechanism[4e] of stereoisomerization and with the relative ordering of the activation energies for the nonthreshold mechanisms.[13]

The Model

The subject compounds of this study, **2**, were chosen because (1) they typify highly congested triaryl compounds, the chemistry of which is dominated by steric effects, and (2) while their high symmetry precludes[4e] a detailed laboratory investigation of mechanism, it simplifies the study by empirical force-field calculations.

The particular compounds of interest are all trimesityl derivatives of groups IIIa, IVa, and Va, *e.g.*, those with Z = B, CH, SiH, GeH, N, P, and As. A proper conformational analysis of these compounds by empirical force-field calculations would demand the specification of a large number of parameters for the interactions of each Z with the surrounding carbon and hydrogen atoms. Reliable parameters for such interactions as bond stretching, bond angle bending, torsion, and nonbonded potentials are scarce for most of these elements, and achieving such a parametrization would prove to be both risky and difficult.[16] Although it is conceivable that these constants might have been estimated by a lengthy parametrization process, we decided not to pursue this complex and arduous undertaking and instead cut the Gordian knot by adopting a starkly simplified model force field.

In this model, the entire class of compounds $(Mes)_3Z$ is represented by one member of that class, trimesitylmethane (**1**). This molecule was chosen because, being a hydrocarbon, its force-field parametrization is the most reliable available.[20] Each compound of series **2** is treated here as being identical with **1** except for the C–Mes bond length, which has been allowed to assume different values depending on the nature of the central atom. This model is founded on the deliberately complete disregard of a number of factors, such as differences in force constants, in electronic configuration, and in geometry at the central atom. In short, *all distinctions between the individual molecules have been neglected, with the single exception of differences in Z-Mes bond length.*

There are two fundamental assumptions behind this model. First, it is assumed that the differences in magnitudes of the activation energies for stereoisomerization of the compounds **2** are principally due to steric interactions involving the carbon and hydrogen atoms of the mesityl rings. Second, the assumption is made that differences in these intramolecular interactions arise mainly from differences in the bond lengths r(Z-Mes).

It is evident that this model is exceedingly simple in concept and in application; this simplicity is of course its most attractive feature. It was recognized that vindication for the above assumptions would have to come from the results of the calculations. Fortunately, as will be shown below, this simple model proved capable of yielding results sufficiently in harmony with existing information so that the effort required for any refinement to achieve closer agreement between calculated and found values of activation energies would far outweigh any possible gains.

Description of Calculations

The method employed was the one developed by us in connection with our study of **1**.[4f] To allow a "semiquantitative" comparison of the different flip mechanisms, a crude approximation of the transition states was conceived and implemented into the computer program; thus, during minimization, the motion of each mesityl ring can be constrained such that the plane of the ring maintains a given dihedral angle ϕ with respect to the plane containing the central C-H and C-Mes bonds. For the transition states, two particular orientations were required: (1) $\phi = 0°$, for a flipping ring, and (2) $\phi = 90°$, for a nonflipping ring.[22] Thus, in the zero-ring flip, three rings maintain orientation 2; in the one-ring flip, one maintains orientation 1, and two maintain orientation 2; in the two-ring flip, two maintain orientation 1 and one orientation 2; and in the three-ring flip, all three rings maintain orientation 1. For the calculation of ground-state structures, the dihedral angles of the rings were not constrained.

Using these idealized transition states and the molecular model described above, energies were calculated[23] for the ground and transition states for several values of r(C-Mes) in the range 1.4-2.2 Å. These limits were chosen since they represent roughly the range of bond lengths covered by the actual trimesityl compounds. The extremes of this range approximate the C-Z bond lengths in, for example, triphenylamine [r(C-N) = 1.42 Å[24]] at the short end and triphenylbismuthine [r(C-Bi) = 2.24 Å[25]] at the long end.

The input for every calculation was the parametrization and structure of **1** used in our previous study,[4f] except that the preferred length[26] of the C-Mes bond, r_0(C-Mes), and the input length of the C-Mes bond [set equal to r_0(C-Mes)] were assigned arbitrary values between 1.36 and 2.10 Å. The specific preferred lengths used were r_0(C-Mes) = 1.36, 1.50,[27] 1.60, 1.80, 2.0, and 2.10 Å. During minimization of the ground states, the bonds relaxed in response to internal forces to yield bond lengths r(C-Mes) in the range 1.4-2.2 Å. Ground-state and two-ring flip conformations were determined for all preferred bond lengths studied; three-ring flip conformations were determined for all except r_0(C-Mes) = 2.0 Å; zero- and one-ring flip conformations were calculated for only three and four values of r_0(C-Mes), respectively, for reasons which are discussed below.

During minimization, the central carbon was held fixed at the origin, and the methine hydrogen was restricted to motion along the input methine C-H bond axis. For the ground state calculations, all other atoms were allowed full freedom of movement. For the idealized transition states, each six-membered aromatic ring obeyed constraint 1 or 2. Since movement of the individual aromatic carbons might destroy the required orientations of the rings, the atoms of each mesityl ring were only moved as groups so that the rings retained regular planar hexagonal geometry throughout minimization. Methyl groups and hydrogens attached to the rings were not constrained during minimization. In order to maintain the appropriate ring orientations in the transition states, a special routine was included in the program to move the mesityl groups in spherical coordinate space, with the methine C-H bond defining the z axis;[4f] this enables the relaxation of the bonds to the central carbon and angles at the central carbon while maintaining constraint 1 or 2. Further details, including a description of the empirical force-field parameters and the computer program employed, are given in our previous paper.[4f]

Results

The bond lengths r(C-Mes) calculated for the ground states are given in Table I. Tabulated alongside these are the strain energies computed for the idealized transition states. These values are all relative to the ground-state energy for each bond length; ground-state energies are not listed since they are relative to an arbitrary zero and hence are meaningless.

Principal structural features of calculated conformations are given in the remaining tables. Table II lists those of the ground states; Tables III-VII list those of the transition states.

The following discussion of the calculated energies and conformations considers first the relationship between experimentally determined activation energies and calculated energies for the transition state of the threshold mechanism. Second, an analysis of the structural changes of the transition states accompanying the change in r(C-Mes) is performed with the aim of gaining insight into the intramolecular interactions which most affect the changes in steric energy.

Comparison of Experimental Barriers with Calculated Energies of the Threshold Mechanism

Examination of Table I reveals that, over the entire bond-length range, the lowest calculated transition-state energy is that of the two-ring flip. *This result represents the first explicit indication that the two-ring flip is the threshold mechanism for an entire class of triaryl compounds, namely, those of the form (Mes)$_3$Z.* The present computations thus corroborate previous arguments that the two-ring flip pathway is the lowest energy enantiomerization mecha-

Table I. Calculated Energies (kcal/mol) for Idealized Transition States

r_0(C-Mes), Å	r(C-Mes),[a] Å	Zero-ring flip[c]	One-ring flip	Two-ring flip	Three-ring flip
1.36	1.43			39.4	97.5
1.50[b]	1.55		46	31.0	80.0
1.60	1.64	[62]	41	26.7	68.5
1.80	1.82	[60]	35	19.0	45.2
2.00	2.02			12.2	
2.10	2.11	[44]	34	9.8	23.1

[a] Average bond length calculated for ground state (see Table II).
[b] For r_0(C-Mes) = 1.50 Å, results are for calculations on **1**, ref 4f.
[c] See text for discussion of zero-ring flip energies.

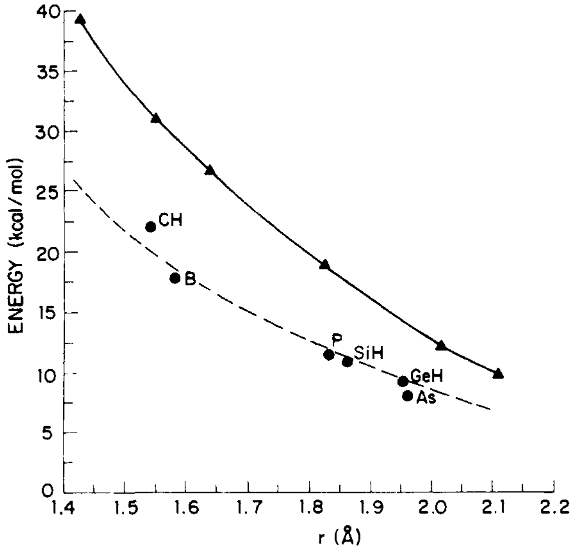

Figure 1. Circles: experimental[28] activation energies for stereoisomerization of $(Mes)_3Z$. Triangles: energies calculated for idealized transition states of the threshold mechanism in the model $(Mes)_3Z$ system (Z = CH). r = length of the Z–Mes bond. For a given value of r, the energy values on the dashed line are 0.645 times the corresponding values on the solid line (see text).

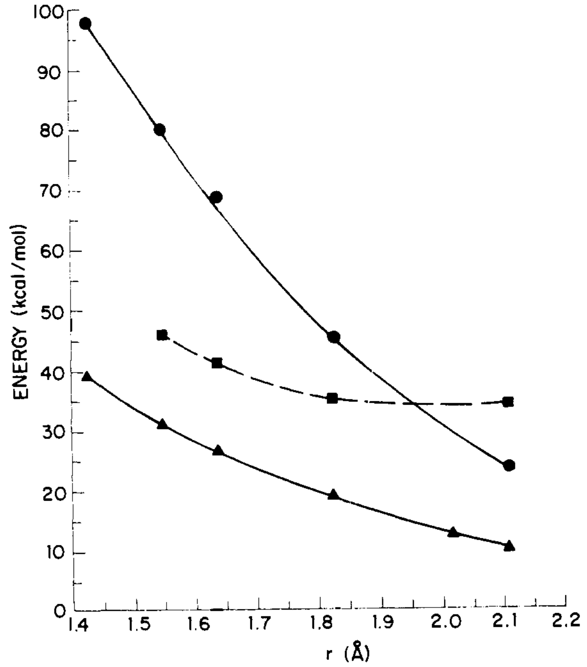

Figure 2. Calculated energies for the idealized one-, two-, and three-ring flip transition states. Energies are relative to the ground state for each bond length. Squares: one-ring flip. Triangles: two-ring flip. Circles: three-ring flip. r = calculated length of the C–Mes bond.

nism in trimesityl systems and provide firm support for the suggestion[4g] that the two-ring flip is the preferred mechanism in all similar compounds.

When plotted as a function of r(C–Mes), the two-ring flip energies lie on a smooth curve which is roughly parallel to the trend of experimental barriers[28] (Figure 1). That the trends of calculated and experimental threshold energies are parallel demonstrates the fundamental soundness of our approach. Indeed, the only discrepancy between the calculated and experimental values is that the former are consistently higher than the latter, the deviations being greatest for short bond lengths. The discrepancy can be attributed to artificial constraints imposed upon the molecule by the idealized transition states (such as maintaining ϕ at 0 or 90°). When these constraints were relaxed in the calculation of the detailed isomerization pathway of **1**,[4f] the resulting energy (20 kcal/mol) was in excellent agreement with experiment (21.9 kcal/mol).[4e]

Although it is in principle possible to determine a detailed pathway for each value of r(C–Mes), in order to improve the calculated barriers, not only would such a procedure be costly and time consuming, but it would also be contrary to the spirit in which the present model was conceived, *i.e.*, a model characterized by the deliberate neglect of details. The same effect was achieved simply and directly by making the assumption that the percentage error introduced by the artificial constraints is the same for all values of r(C–Mes). With this assumption, the results[4f] of the computations on **1** can be used to determine a correction factor which can then be applied to the energies of the idealized two-ring flips for all other systems. The ratio of the energy of the calculated transition state of **1** (20 kcal/mol) to the energy of the idealized two-ring flip of **1** (31 kcal/mol) has been used for this purpose; this factor, 20/31 = 0.645, transforms the solid curve to the dashed curve in Figure 1.

It is evident that the corrected line faithfully follows the experimental data. One can make predictions, based on the dashed curve, of activation energies for several compounds of special interest. A fascinating example is trimesitylamine (**3**), which has not yet been synthesized. The C–N bond length in triphenylamine is 1.42 Å;[24] a reasonable guess of r(C–N) in **3**, by analogy with the difference in C–Ar bond lengths between triphenylmethane (1.53 Å)[29] and **1** (1.54 Å),[30a] is 1.43 Å. The isomerization barrier, as predicted from Figure 1, should be 25–27 kcal/mol. Such a high barrier suggests the possibility that **3** should be resolvable and optically stable at room temperature. It is also possible, by extrapolating the curve in the other direction, to make predictions about compounds with very long Z–Mes bond lengths. Two such compounds are $(Mes)_3SnH$ and $(Mes)_3Bi$. For the former, an upper limit to the activation energy of 8 kcal/mol has been determined.[31] For the latter, Rieker and Kessler[7] report only that nmr line broadening was not observed in the available temperature range. By assuming the Z–C bond lengths in methylstannane (2.14 Å)[32] and triphenylbismuthine (2.24 Å),[25] activation energies of 5–7 and 3–5 kcal/mol can be predicted from Figure 1 for $(Mes)_3SnH$ and $(Mes)_3Bi$, respectively. These results are consistent with the experimental observations.

Analysis of Structure and Energy of the Idealized Transition States

In Figure 2, the calculated energies of the idealized one-, two-, and three-ring flip transition states are plotted against r(C–Mes). As noted above, the two-ring flip energies are consistently the lowest. The three-ring flip energies, though much higher than the two-ring flip energies, nevertheless follow a similar trend: both curves gradually flatten as r(C–Mes) increases and appear to move asymptotically toward some small energy value. The one-ring flip and zero-ring flip (not included in Figure 2, for reasons outlined below) behave differently. There are extended regions in which steric energy remains practically constant despite the change in bond length. For the zero-ring flip, this occurs between 1.64 and 1.82 Å (Table I); for the one-ring flip, this occurs between 1.82 and 2.11 Å.

The following analysis, which is intended to provide insight into the energetic behavior depicted in Figure 2, focuses on the variations in structure which result from the change in central bond length. An alternative analysis in terms of trends in component energies was not made for two reasons. (1) The only clear-cut trends in component energies are those which are also obvious from structural

Table II. Calculated Ground-State Conformations

r_0(C–Mes), Å	r(C–Mes),[a] Å	C–C–C[b] (deg)	H–C–C[c] (deg)	H–C–C_{ar}–C_{ar}[d] (deg)
1.36	1.428	118.1	97.8	41.2
	1.428	117.8	97.9	40.2
	1.430	118.8	97.3	41.7
1.50[e]	1.550	117.0	99.0	40.2
	1.551 (1.539)[f]	117.9 (115.9)[f]	98.7 (101.8)[f]	41.4 (37.7)[f]
	1.549	118.1	98.9	40.5
1.60	1.640	117.0	100.0	41.5
	1.639	116.8	100.2	40.9
	1.640	117.4	99.6	41.4
1.80	1.825	116.3	101.4	41.8
	1.825	116.0	101.5	41.3
	1.826	116.5	101.0	42.0
2.00	2.015	114.7	103.7	42.1
	2.015	114.0	104.0	42.9
	2.016	114.5	104.1	42.9
2.10	2.111	114.0	104.4	43.3
	2.110	114.0	104.4	42.2
	2.112	114.4	104.0	43.1

[a] Bond length calculated for each of the three rings. [b] Angles between the bonds to the rings at the central carbon. [c] Angles between the C–H and C–Mes bonds at the central carbon. [d] Angle representing the amount of twist of the rings with respect to the methine C–H bond; equivalent to the angle ϕ defined in the text. [e] Results for r_0(C–Mes) = 1.50 Å are those calculated for **1** in ref 4f. [f] From crystal structure of **1**, ref 30a.

changes; for example, increases in angle strain energies are mirrored by increased angle distortions. (2) Energy differences of less than 1 kcal/mol, which are often observed, are certainly not beyond the range of error in force-field parametrization. Schleyer and coworkers[21] have observed for a number of hydrocarbons that the calculated *structures* are "...remarkably consistent despite the wide variety of force fields employed," whereas component energies "vary considerably" for different force fields. Thus, any strain component analysis presented here might prove to be valid only for the particular force field used in these calculations and therefore of limited significance.

It should be noted that despite our belief in the validity of the present analysis in terms of structural changes, we do not place any heavy emphasis on the exact conformations calculated for the idealized transition states. Just as the calculated energies were consistently too high, reflecting the artificiality of the idealized transition states, so too the conformations are expected to deviate, though in a less obvious way, from the correct structures. We therefore focus our attention in the discussion on the *trends* in calculated geometries, and deviations from these trends, seeking only to derive a gross, qualitative interpretation of the interactions which lead to these trends.

Ground State. Whereas calculated ground-state energies are meaningless in absolute terms since they are relative to an arbitrary zero, ground-state structures are listed in Table II. It is seen that each structure is a propeller possessing approximate threefold symmetry, and that bond angles and bond lengths deviate less from their preferred positions as r_0(C–Mes) increases. All of this is intuitively reasonable.

For comparison, some dimensions reported for crystalline **1**[30a] are included in Table II alongside the calculated dimensions of **1**. The two are in general agreement; it is likely that what discrepancies there are can be attributed (at least in part) to crystal packing forces, which are not considered in the type of calculations done here. On the other hand, bond-angle deformations at the central atom appear to be generally overestimated. In the case of **1**, the computed value of 117–118° for the C–C–C angle is only slightly in excess of the value (115.9°) determined[30a] by X-ray analysis, but for trimesitylphosphine (**4**) the discrepancy is more serious. On the basis of Table II, a trimesityl compound with r(Z–Mes) equal to r(P–Mes) in **4** [1.83 Å,[30b] essentially the same as r(P–C) in triphenylphosphine[33]] should possess a C–P–C angle of roughly 116°. However, the X-ray structure of **4**[30b] shows C–P–C bond angles of 108–111°, *i.e.*, substantially smaller than calculated.[34] This discrepancy is inevitable from the nature of our model.

Table III. Angle Deformation in the Two-Ring Flip[a]

r(C–Mes),[a] Å	C(F)–C–C(F)[b]	H–C–C(F)[b]	H–C–C(F)[b]	H–C–C(NF)[b]
1.43	105.7	107.2	83.5	97.2
1.55[c]	107.4	106.7	82.7	97.2
1.64	109.0	107.5	83.0	98.5
1.82	112.8	105.7	84.7	100.5
2.02	117.2	95.5	93.2	103.0
2.11	117.8	95.2	94.7	104.7

[a] r(C–Mes) is the average bond length calculated for the ground state (see Table II). The dihedral angles refer to C(F) and C(NF) as the atoms bonded to the central carbon in flipping and nonflipping rings, respectively. [b] In degrees. [c] Results calculated for **1**, ref 4f.

Two-Ring Flip. In Table III are listed values for some angles in the calculated two-ring flip conformations; C(F) and C(NF) are the atoms bonded to the central carbon in flipping and nonflipping rings, respectively.

Two important trends may be discerned. First, C(F)–C–C(F) decreases as r(C–Mes) decreases. Second, of the two angles H–C–C(F), one increases by about 12°, whereas the other decreases by the same amount over the range of bond lengths, reflecting a shearing motion of the two flipping rings. The latter two angles appear to approach 95° for large values of r(C–Mes). The last angle, H–C–C(NF), changes in a predictable fashion, following almost exactly the pattern displayed by the H–C–C angles in the ground state (Table II).

The behavior of the angles involving the flipping rings can be accounted for by considering the principal nonbonded contacts in these systems, *viz.*, those in which the ortho-methyl groups participate. As r(C–Mes) becomes smaller, the interaction between the flipping rings and the ortho-methyl groups of the nonflipping ring must increase. In response to this, the molecule can distort in such a way that C(F)–C–C(F) becomes smaller, as Table III indicates. Another consequence of shortening the C–Mes bond is greater contact among the four ortho-methyl groups on the flipping rings. These contacts would tend to open the C(F)–C–C(F) angle, were it not being forced closed by the interactions described above. The molecule therefore adopts a second mechanism, the shearing motion of the flipping rings, to relieve the second type of strain. The reason that the H–C–

Table IV. Angle Deformation in the Three-Ring Flip[a]

r(C–Mes),[a] Å	C(*F*)–C–C(*F*)[b]	C(*F*)–C–C(*F*)[b]	C(*F*)–C–C(*F*)[b]	H–C–C(*F*)[b]	H–C–C(*F*)[b]	H–C–C(*F*)[b]
1.43	122.0	118.1	119.2	98.7	84.2	95.2
1.55[c]	119.8	119.9	120.0	99.0	85.7	91.0
1.64	118.2	120.5	121.1	95.7	89.5	90.0
1.82	120.7	119.5	119.7	92.0	90.7	90.0
2.11	120.2	119.2	120.4	92.2	91.2	91.2

[a–c] Footnotes correspond to those in Table III.

C(*F*) angles approach 95° is that the distal[4f] methyl groups of the adjacent flipping rings are in very close proximity. Since the rings may not rotate in the idealized transition states, there is a tendency to equalize the strain at the proximal[4f] and distal positions by flattening the structure at the central atom. Even for the longest bond length used, the distal interactions prevent the attainment of the preferred angles. This tendency is even more pronounced and more clearly exhibited in the three-ring flip structures.

Three-Ring Flip. Energies for the three-ring flip are not only considerably higher than two-ring flip energies, but they are also more sensitive to changes in bond length. This is again rationalized by analysis of the conformational changes at the central carbon (see Table IV). Note first that the three angles C(*F*)–C–C(*F*) for each bond length are practically equal. This is a result of the need to distribute evenly the strain imposed by the three flipping rings. In particular, due to the strain introduced by the distal ortho-methyl groups, the angles remain roughly at 120°, regardless of the value of r(C–Mes), over the entire range from 1.43 to 2.11 Å. Again there is shearing by two of the rings, as evidenced by the H–C–C(*F*) angles, though not quite as much as in the two-ring flip.

In the two-ring flip, as the bond length is shortened, the molecule adjusts to the greater strain by suffering greater angle distortion at the central atom [*i.e.*, diminution of the C(*F*)–C–C(*F*) angle and augmentation of the C(*F*)–C–C(*NF*) angles]. This mechanism of strain relief is not available to the three-ring flip. Because of the need to equalize the strain on the three equivalent rings and the need to minimize the interactions between the ortho-methyl groups on opposing rings, the structure tends toward planarity at the central carbon. Apparently, the three-ring flip is so crowded that it attains the optimum geometry (all three central angles 120°) even for the longest bond lengths studied (Table IV). Hence, when the bond length is shortened, no reduction in strain can be achieved by further distortion of the central angles. The result is that the strain is shifted to other parts of the molecule, especially the C–Mes bonds and the angles at the ortho positions on the rings. Table V compares distortions of these structural components for the two- and three-ring flips. The stretching of the C–Mes bond and the bending of the angles β are consistently greater in the three-ring flip than in the two-ring flip. It might be argued that the two-ring flip exhibits smaller distortions of these components, because it is able to undergo more out-of-plane distortion of the methyl groups on its flipping rings than in the three-ring flip; this would be rationalized by noting symmetry differences between the two transition states. However, examination of the out-of-plane angles has revealed no clear evidence that either transition state is more subject to this type of distortion than the other. For example, when r(C–Mes) = 1.43 Å, the out-of-plane angle of the distal methyl group on one of the flipping rings of the two-ring flip is 16.5°; for the corresponding methyl group in the three-ring flip, the angle is 15.0°. On the second flipping ring of the two-ring flip, the distortion of the distal methyl group from the plane is 4.4°, while for the remaining two rings in the three-ring flip, the angles are 8.0 and 8.1°. It is apparent, in this case, that neither transition state is distinguished from the other by the magnitude of its out-of-plane distortions. The remaining angles likewise indicate no uniform trend.

Table V. Comparison of Strain Components in Two- and Three-Ring Flips

	Two-ring flip[b,c]			Three-ring flip[b,d]		
r(C–Mes),[a] Å	Δr, Å	β_p, deg	β_d, deg	Δr, Å	β_p, deg	β_d, deg
1.43	0.10	110	109	0.18	107	103
1.55[e]	0.07	113	111	0.12	106	104
1.64	0.06	113	112	0.11	107	107
1.82	0.05	115	114	0.08	110	110
2.11	0.03	118	117	0.04	115	115

[a] Average bond length calculated for the ground state (see Table II). [b] Δr is the difference between the calculated bond length in the transition state and r_0(C–Mes), averaged over the three C–Mes bonds. β is the angle defined by an ortho-methyl group, an ortho aromatic carbon, and a meta aromatic carbon; the subscripts p and d denote proximal and distal positions, respectively. [c] Angles are averages for the flipping rings only. [d] Angles are averages for all three rings. [e] Results calculated for **1**, ref 4f.

The steepness of the three-ring flip curve compared with the two-ring flip curve follows simply from the nature of the potentials used in the force field. Typically, they are parabolic;[4f] hence the slope of the potential is proportional to the amount of strain present. Since the total potential function of a molecule is essentially a sum of this type of potential, the total energy should exhibit similar behavior. Therefore, the three-ring flip energies, which are higher than the two-ring flip energies, are more sensitive to changes in factors which affect the amount of strain, particularly r(C–Mes).

Zero- and One-Ring Flips. These two transition states are treated together since they share in common an important characteristic: both idealized transition states entail the placement of two methyl groups in essentially the same location. This situation is obviously unreasonable and led us to omit the calculation on the zero-ring flip in our previous paper[4f] "on simple steric grounds." The present calculations vindicate this decision. The strain caused by three pairs of overlapping methyl groups causes such distortion of the central angles (see Table VI) that the resulting geometry does not even remotely resemble the idealized zero-ring flip. In fact, although each ring faithfully obeys constraint 2, the angles H–C–C(*NF*) are bent so that the resulting structure appears[23] to be a *two*-ring flip. For a clearer picture of how such a conformation is attained, let us imagine that associated with each ring is an axis which contains the central carbon atom and which is perpendicular to both the C–Mes and C–H bond vectors. For r(C–Mes) = 1.64 and 1.82 Å, two of the rings rotate about these axes in such a way that the H–C–C angles decrease, while the third ring rotates in such a way that the angle increases. This motion does not in any way affect the requirement (constraint 2) that the planes of the rings be perpendicular to the planes of the C–H and C–Mes bonds, yet the result of this motion, coupled with some additional lesser distortions of the central C–C–C bond angles, is that the C–H bond vector is *coplanar* with, and almost exactly bisects, one of the C–C–C angles,

Table VI. Angle Deformations in the Zero-Ring Flip

r(C–Mes),[a] Å	C(NF)–C–C(NF)[b]	C(NF)–C–C(NF)[b]	C(NF)–C–C(NF)[b]	H–C–C(NF)[b]	H–C–C(NF)[b]	H–C–C(NF)[b]
1.64	130	114	114	65	66	169
1.82	139	118	103	74	66	166
2.11	105	114	113	127	128	50

[a] Average bond length calculated for ground state (see Table II). [b] In degrees.

Table VII. Angle Deformations in the One-Ring Flip

r(C–Mes),[a] Å	C(NF)–C–C(NF)[b]	C(F)–C–C(NF)[b]	C(F)–C–C(NF)[b]	H–C–C(F)[b]	H–C–C(NF)[b]	H–C–C(NF)[b]
1.55[c]	103	130	120	94	59	142
1.64	104	129	120	96	60	139
1.82	109	126	117	100	62	133
2.11	140	103	97	120	93	106

[a] Average bond length calculated for ground state (see Table II). [b] In degrees. [c] Results calculated for **1**, ref 4f.

and that the two attached rings lie perpendicular to the plane defined by that angle. They thus resemble flipping rings. For r(C–Mes) = 2.11 Å, an equivalent result is achieved by increasing, rather than decreasing, the values of two H–C–C angles, while decreasing, rather than increasing, the third. This motion also takes place about the axes described above, so that constraint 2 is once again maintained. The energies of these calculated conformations bear no relationship to the zero-ring flip energies. The results corroborate this: for r(C–Mes) = 1.64 Å, the "zero-ring flip" energy is *lower* than the three-ring flip energy (Table I), contrary to reason and intuition, but not surprisingly since it is well known that excessive angle bending (>25°) leads to unreliable results,[21] and the values of H–C–C(NF) given in Table VI represent distortions of 40° or more, in some cases, from preferred angles.[4f]

A similar situation occurs for the one-ring flip, which also has overlapping methyl groups. However, only one pair of methyl groups is in this condition, as opposed to three pairs in the zero-ring flip. In this case, the structure is driven not to a two-ring flip but to a propeller, even though the rings obey the proper constraints. The deformations in the one-ring flip can be visualized much as were those of the zero-ring flip. For r(C–Mes) = 1.55, 1.64, and 1.82 Å, rotation of the nonflipping rings about the axes containing the central carbon and perpendicular to the H–C–C plane results in shearing of the two rings (Table VII, columns 6 and 7). The three rings now have the same sense of twist, not with respect to the C–H bond (they are all still either parallel or perpendicular to the H–C–C plane) but with respect to an axis perpendicular to the reference plane of the distorted conformation and containing the central atom; thus, the structure has a propeller conformation. For r(C–Mes) = 2.11 Å, the minimization pathway selected by the program is different. Overlap of the methyl groups is, at this bond length, sufficiently small that shearing by the two nonflipping rings is no longer the most efficient mechanism for strain relief; note that the distortion of the H–C–C(NF) angles is much less for this bond length than for the other bond lengths (Table VII). Rather, the greatest deformation occurs in the C(NF)–C–C(NF) angles. The effect of this change in minimization pathway is that the final conformation in fact appears to be a one-ring flip and not a propeller. It is probable that the energy for this last structure is reasonable, while the remaining values become more unacceptable as bond length decreases. It is expected that the calculated energies err in the negative direction, that is, they are too low, since eliminating the excessive angle bending would create greater nonbonded interactions. These observations bring into question the crossover of the one- and three-ring flip energies depicted in Figure 2. Does the crossover actually occur, and if so, where? Since uncertainties in the calculated one-ring flip energies have not been resolved, the curve through the appropriate points in Figure 2 is represented as dashed.

References and Notes

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(2) Taken in part from the senior thesis of M.R.K., Princeton University, 1974.

(3) NATO Fellow, 1972–1973, on leave of absence from the University of Catania, Catania, Italy.

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(12) For a detailed analysis, see ref 4a.

(13) All experimental results to date[4–11] are consistent with the two-ring flip[14] as the threshold mechanism.[15] Empirical force-field calculations[4f] bear out this conclusion in the case of 1.

(14) Stereoisomerization of triaryl compounds has commonly been discussed in terms of the four mechanisms (zero-, one-, two-, and three-ring flips) postulated by Kurland, *et al.*,[5b] in their study of triarylcarbonium ions. In this interpretation, the aromatic rings rotate in a correlated[4b,h] fashion, such that each ring passes through one of two orientations. In one of these orientations, the plane of the ring is perpendicular to the "reference plane"[4a] defined by the three carbon atoms attached to the central atom; rings passing through that orientation are said to flip. In the other orientation, the plane normal to the plane of the ring and containing the bond to the central atom lies perpendicular to the reference plane. *Each of the four flip mechanisms leads to a reversal of propeller helicity.* See also ref 4a and 4j.

(15) Only recently has *direct* experimental evidence appeared, in the case of a borane,[4i] indicating that the two-ring flip is indeed the lowest energy pathway of stereoisomerization (threshold mechanism), to the exclusion of all others.

(16) Bond stretching force constants, k_r, might be estimated by assuming a relation between k_r and the bond length r(Z–Mes); bond length and force constant data indicate that this might be a reasonable approach,[17,18] and several empirical relations have been published.[18] A similar relation may also exist between the angle bending force constant, k_θ, and bond length, though the data are not as consistent, and the trends are not as clear as for k_r.[19] Data for torsional and nonbonded constants are even less plentiful.

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(22) These conventions do not follow the definitions of flipping and nonflipping rings given in ref 4a, in which ring orientations are described with respect to the reference plane. The definitions used here were chosen for programming considerations.

(23) Calculations were performed on an IBM 360/91 computer using double precision arithmetic. Analysis was aided by viewing all structures in three dimensions using the facilities of the Princeton Computer Graphics Laboratory (E & S LDS-1/DEC PDP-10), supported in part by a grant from the National Institutes of Health.

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(26) The equilibrium position, or energy minimum, of the harmonic potential used to approximate bond stretching forces. See ref 4f.

(27) Results for r_0(C–Mes) = 1.50 Å are those calculated for 1 in ref 4f.

(28) Experimental data in Figure 1 are taken from the following sources: (a) bond lengths, r(Z–C): Z = CH, ref 30; Z = B, ref 4c; Z = P, for triphenylphosphine, ref 33; Z = SiH, for tetraphenylsilane, M. Yokoi, *Bull. Chem. Soc. Jap.*, **30,** 100 (1957); Z = GeH, for tetraphenylgermane, A. Karipides and D. A. Haller, *Acta Crystallogr. Sect. B*, **28,** 2889 (1972); Z = As, for tri-*p*-tolylarsine, J. Trotter, *Can. J. Chem.*, **41, 14** (1963). (b) Activation energies: Z = CH, ref 4e; Z = B, for bis(2,6-xylyl)-1-(3-isopropyl-2,4,6-trimethylphenyl)borane, ref 4i; Z = P, As, ref 7. Since ΔG^* values reported in ref 7 are not those for the two-ring flip (see footnote 20 in ref 4e), ΔG^* values reported here are appropriately corrected as previously described.[4e] Z = SiH, ref 4d; Z = GeH, R. J. Boettcher, unpublished results.

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(34) It had earlier been concluded,[35a] on the basis of the essential identity of the dipole moments of triphenylphosphine and **4,** that the C–P–C bond angles in the latter should not be appreciably larger than those in the former,[33] *i.e.*, that they should assume a value near 103°. Evidently the rehybridization accompanying expansion of the C–P–C bond angles from 103 to 108–111° produces compensatory changes in the dipole moment, as discussed elsewhere.[35b]

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Special Effect of Pressure on Highly Hindered Reactions as a Possible Manifestation of the Hammond Postulate[1]

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Abstract: In this paper, we attempt to reach an understanding of the phenomenon that among those reactions which are promoted by the application of hydrostatic pressure, the most highly hindered ones tend to be accelerated most. The example discussed here is the Menshutkin reaction of methyl, ethyl, and isopropyl iodide with pyridine and with 2,6-dimethyl-, -ethyl-, isopropyl- and -*tert*-butylpyridine; the known activation volumes for these reactions in acetone steadily become more negative as the interfering groups are made larger. We now report the partial molal volumes of the free bases and the alkylating agents in acetone and methanol and of the *N*-methylpyridinium iodides in methanol. The data do not support the Gonikberg theory, according to which the progressive shrinking of the transition state with increased hindrance is due to "interpenetration" of the interfering groups. Instead, the observations can be accounted for by the Hammond postulate, according to which the transition states in the more hindered reactions should be more "product-like". We also report an anomalously large volume increase from 2,6-diisopropyl- to -*tert*-butylpyridine in methanol and conclude that hydrogen bonding to the latter base is extremely weak or absent altogether.

Among chemists interested in the effects of pressure on the rate constants of reactions in solution,[2] it is a well-known fact that pressure induced accelerations are generally greatest for sterically hindered reactions. These accelerations are related to the activation volume by the expression

$$-\partial \ln k/\partial p = \Delta V^*/RT$$

ΔV^* is therefore negative in a reaction promoted by pressure,[3] the more so the greater the acceleration. Some extreme examples have been noted; in fact, Okamoto has encountered sterically hindered reactions under pressure which are apparently not detectable at 1 atm at all.[4] This generalization—the greater the hindrance, the greater the acceleration—is of obvious interest in that it may have synthetic applications, and hence in several high pressure laboratories further examples have been sought and discovered. Most of these instances have centered around the Menshutkin reaction; most recently, a report from our laboratory[5] listed the systematic increase in the pressure-induced rate accelerations as the number of carbon atoms is increased in the reaction of methyl, ethyl, and isopropyl iodide with pyridine and 2,6-dimethyl-, -ethyl-, -isopropyl-, and -*tert*-butylpyridine. The observations in this report may be summarized by the statement that $\Delta V_0^‡$ becomes more negative by about 2 cm^3/mol for each additional methylene group near the reaction site.

To date, only the late Gonikberg and his coworkers have ventured an explanation of this phenomenon.[6] They assume that the length of the newly forming C–N bond is equal in the transition states of all these reactions (and 10% longer than the normal equilibrium value), and that no distortions occur except in the flattening methyl group, and they propose that the increasingly negative activation volume is due to "overlapping volumes", i.e., to increased "interpenetration" of the interfering groups. This proposal was supported by calculations showing that these assumptions can produce remarkably good agreement with experiment.[7] This agreement must be largely fortuitous, however. First of all, the assumption of a bond length in the transition state only 10%