338 *J. Am. Chem. Soc.* **1987**, *109*, 338–341

Periodic Trends in the Edge and Vertex Inversion Barriers for Tricoordinate Pnictogen Hydrides and Fluorides

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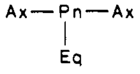
Received July 29, 1986

Abstract: The edge and vertex inversion barriers for PH_3, PF_3, AsH_3, AsF_3, SbH_3, and SbF_3 have been calculated by ab initio molecular orbital theory. Large basis sets were employed, and correlation corrections were included at the MP-2 level. The force fields were calculated to identify various transition states. The hydrides invert by a vertex inversion process through a planar trigonal D_{3h} transition state while the fluorides invert by an edge inversion process through a planar T-shaped C_{2v} transition state. The vertex inversion barrier heights including zero-point corrections for the hydrides are as follows: PH_3, 34.1 kcal/mol; AsH_3, 40.6 kcal/mol; and SbH_3, 42.1 kcal/mol. The edge inversion barriers including zero-point corrections for the fluorides are as follows: PF_3, 52.9 kcal/mol; AsF_3, 45.7 kcal/mol; and SbF_3, 38.3 kcal/mol. The vertex inversion barriers for the hydrides increase with increasing pnictogen atomic number while the edge inversion barriers for the fluorides decrease.

We have recently shown[1] that inversion at pnictogen[2] centers can proceed via an *edge* inversion process instead of the *vertex* inversion process typified by ammonia inversion. *Edge* inversion can occur if the pnictogen center is substituted by appropriate electronegative groups. The T-shaped transition state for edge inversion, A, can be stabilized by σ-acceptors in the axial positions (Ax) and π-donors in the equatorial (Eq) position. Our initial work focussed on inversion at phosphorus with varying degrees of fluorine substitution. It is of interest to understand the periodic trends as one goes down the pnictogen series. For example, theoretical calculations on the pnictogen hydrides show that the vertex inversion barriers for AsH_3[3] and SbH_3[4] are 10–12 kcal/mol higher than the inversion barrier in PH_3.[5] Furthermore, theoretical work[6] on the vertex inversion barriers for closed-shell first- and second-row tricoordinate hydrides of the form AH_3^-, AH_3, AH_3^+ have shown that correlation corrections are small; this is in agreement with Freed's theorem.[7]



A

$$\begin{array}{c} \mathrm{Ax{-}Pn{-}Ax} \\ | \\ \mathrm{Eq} \end{array}$$

We present ab initio molecular orbital calculations which examine the periodic trends in the inversion barrier for the trifluoro pnictogens PF_3, AsF_3, and SbF_3. We also examine the effects of correlation on these barriers at the MP-2 level[8] and on the barriers for the corresponding hydrides PH_3, AsH_3, and SbH_3.

Calculations

Most of the geometries of the C_{3v} ground states, the D_{3h} structures (possible vertex inversion transition state), and the C_{2v} structures (possible edge inversion transition state) were gradient optimized[9] at the SCF level with the program HONDO[10] on an IBM-3081 computer. If the structures were not optimized with HONDO, they were gradient optimized with the program GRADSCF[11] on a CRAY-1A computer. Force fields and MP-2 correlation corrections were determined with the rapid analytic techniques incorporated in GRADSCF.[12] Only the valence s and p electrons were incorporated in the MP-2 calculations.

For PF_3 and PH_3, the geometries were optimized with a DZ+P basis set of the form (11s7p1d/9s5p1d/4s1p)/[6s4p1d/3s2p1d/2s1p] in the order P, F, H.[13] The s, p, and d orbital coefficients are from Dunning and Hay[14] with $\zeta_P(3d) = 0.50$. The final force field and energy calculations were done with a slightly larger basis set of the form (13s9p1d/9s5p1d/4s1p)/[6s4p1d/4s2p1d/2s1p]. The exponents and coefficients for F and H are from Dunning,[15] those for P from McLean and Chandler,[16] and the polarization exponents are those given above. For AsF_3 and SbF_3, the [3s2p1d] basis set for F given above was employed. For AsH_3 and SbH_3 a (5s1p)/[3s1p] basis set on H was employed with $\zeta_H(2p) = 1.0$ as used above. For As the basis set is of better than DZ+P quality and has the form (14s11p6d)/[10s8p3d]. Following previous work,[17] the exponents and contraction coefficients are from Dunning's compilation.[18] The first five s orbitals are contracted together,

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[2] The terms "pnictogen" and "pnictide" have been used to refer to the main group 5 (group 15) elements (N, P, As, Sb, Bi). These terms are derived from the Greek work pniktos (suffocate – the origin of the prefix "pnicto"): see Brown, R. W.; George, W. *Composition of Scientific Words*; King Printing Co.: Baltimore, MD, 1954; p 620. The terms "pnigogen" and "pnicogen" have also been used to identify this family of elements (Suchow, L. *Inorg. Chem.* **1978**, *17*, 2041). The latter two terms are somehwat inappropriate since pnigo (the source of pnigogen) means "choke" rather than "suffocate", and "pnicogen" does not reflect the proper etymology (the "t" should not be omitted). For the spoken works, the terms "pnictogen" and "pnictide" are clearly and easily enunciated. Thus we prefer the terms derived from "pnicto" (pnictogen and pnictide).

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Table I. Optimized Geometry Parameters for Pnictogen Hydrides and Fluorides[a]

property	PH_3	PF_3	AsH_3	AsF_3	SbH_3	SbF_3
$r(C_{3v})$	1.407 (1.427)[b]	1.563 (1.561)[b]	1.508 (1.511)[b]	1.693 (1.709)[c]	1.707 (1.710)[b]	1.874 (1.879)[c]
$\theta(C_{3v})$	95.2 (93.3)	97.1 (97.1)	94.3 (92.1)	95.4 (95.9)	94.3 (91.7)	93.6 (94)
$r(D_{3h})$	1.371	1.664	1.458	1.799	1.652	1.960
$r_{Ax}(C_{2v})$	1.648	1.633	1.784	1.774	1.919	1.939
$r_{Eq}(C_{2v})$	1.402	1.533	1.503	1.676	1.710	1.862
$\theta_{Ax-Pn-Ax}(C_{2v})$	166.0	172.8	165.1	169.5	161.1	163.2
$\theta(_{Eq-Pn-Ax}(C_{2v}))$	83.0	86.4	82.5	84.8	80.5	81.6

[a] Bond distances in Å. Bond angles in deg. Experimental values in parentheses. [b] Reference 18. [c] Reference 19.

Table II. Total Energies (au) for the Pnictogen Hydrides and Fluorides

	E(SCF)	E(MP-2)
PH_3 (C_{3v})	−342.475 220	−342.606 415
PH_3 (D_{3h})	−342.417 431	−342.550 655
PH_3 (C_{2v})	−342.223 498	−342.351 600
PF_3 (C_{3v})	−639.240 822	−639.857 757
PF_3 (D_{3h})	−639.042 048	−639.721 743
PF_3 (C_{2v})	−639.131 879	−639.772 018
AsH_3 (C_{3v})	−2235.899 263	−2236.025 755
AsH_3 (D_{3h})	−2235.831 624	−2235.959 956
AsH_3 (C_{2v})	−2235.675 436	−2235.799 118
AsF_3 (C_{3v})	−2532.641 874	−2533.260 261
AsF_3 (D_{3h})	−2532.488 480	−2533.154 661
AsF_3 (C_{2v})	−2532.549 859	−2533.186 401
SbH_3 (C_{3v})	−6313.979 607	−6314.089 471
SbH_3 (D_{3h})	−6313.908 181	−6314.021 333
SbH_3 (C_{2v})	−6313.802 356	−6313.910 906
SbF_3 (C_{3v})	−6610.755 058	−6611.359 512
SbF_3 (D_{3h})	−6610.626 259	−6611.267 247
SbF_3 (C_{2v})	−6610.680 916	−6611.297 790

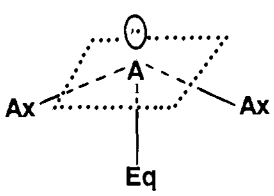
as are the first four p orbitals and the first four d orbitals. The remaining orbitals are left variationally free. The exponent of the final d function is 0.3269 obtained by a geometric progression based on the final two d exponents given by Dunning. For Sb, the basis set has the form (15s11p8d)/[10s7p5d] and was constructed in a similar fashion again from an atomic basis set of Dunning.[19] On the basis of the previous work on GeH_4,[17] we only contracted the first six s functions, the first five p orbitals, and the first four d orbitals. The final d orbital exponent was 0.247 obtained as described above.

Results and Discussion

The optimized geometry parameters are given in Table I, while the total energies are given in Table II. The experimental geometries for the pyramidal C_{3v} structures have all been reported in the literature.[20,21] The bond lengths for PH_3 and AsH_3 are shorter than the experimental values by 0.020 and 0.003 Å, respectively. The error for PH_3 is typical of that found for large basis set SCF calculations while the difference for AsH_3 is somewhat smaller than normally found. The bond distance for SbH_3 is also calculated to be 0.003 Å less than the experimental value. The bond angle is 1.9° too large for PH_3 and 2.2° too large for AsH_3. The difference increases to 2.6° for SbH_3. Previous SCF-CI calculations on PH_3[4] have shown that the bond distances for PH_3 increase and that the bond angles decrease when correlation corrections are included.

The Pn–H bond distances decrease in the D_{3h} structure of the hydrides as expected if the lone pair is in the out-of-plane p orbital of a_2'' symmetry. The magnitude of the decrease in the Pn–H bond distances increases with increasing atomic number, for PH_3, −0.036 Å; for AsH_3, −0.050 Å; and for SbH_3, −0.055 Å.

The T-shaped C_{2v} structures for the hydrides show very long bonds from the pnictogen to the axial hydrogens and essentially no change in the equatorial Pn–H bond distance. The increases for the Pn–Ax bond distances are 0.241 Å for PH_3, 0.276 Å for AsH_3, and 0.212 Å for SbH_3. The Ax–Pn–Ax bond angles are all less than 180° and decrease with increasing pnictogen atomic number from 166.0 for PH_3 to 161.1 for SbH_3. As a consequence, a plane which includes the pnictogen center and is normal to the equatorial bond–lone pair axis separates all of the substituents from the lone pair.



The optimized bond distances for the fluorides agree well with the experimental values. For PF_3, the calculated value is 0.002 Å longer than the experimental equilibrium value,[20] while for AsF_3 the calculated value is 0.016 Å shorter.[21] For SbF_3,[21] the calculated value is only 0.005 Å shorter. For the fluorides, the calculated values for θ(FPnF) are slightly smaller than the experimental values, 0.6° for PF_3 and 0.5° for AsF_3.

The Pn–F bond lengths increase in the planar D_{3h} structures as compared to the pyramidal C_{3v} structures (contrary to the decrease observed for the hydrides). For PF_3 this increase is 0.101 Å, for AsF_3 it is 0.106 Å, and for SbF_3 it is 0.086 Å. This is a result of the orbital occupancy in the D_{3h} structure for PnF_3 which places the lone pair in a delocalized s orbital of a_1' symmetry, not in an out-of-plane p orbital of a_2'' symmetry. This in-plane lone pair leads to increased repulsions with the bond orbitals causing the bond distances to increase. Indeed as shown below the D_{3h} structures are not minima or even transition states and will become C_{2v} structures.

The geometries of the T-shaped C_{2v} structures for the fluorides differ from those observed for the hydrides. The Pn–Ax bonds are longer than those in the pyramidal C_{3v} form by only 0.070 Å for PF_3, 0.081 Å for AsF_3, and by 0.065 Å for SbF_3; these differences are much smaller than those found in the hydride series. The Pn–Eq bond lengths are now shorter than the C_{3v} distances by 0.030 Å for PF_3, 0.017 Å for AsF_3, and 0.014 Å for SbF_3. The Ax–Pn–Ax bond angles are again all less than 180° and are larger than those in the corresponding hydrides. These bond angles show the same periodic trend of a decrease with increasing pnictogen atomic number as found for the hydrides.

In order to assess whether the calculated structures are minima or transition states and to determine the magnitude of the zero-point corrections to the barrier heights, the molecular force fields were determined analytically. We present here only the zero-point energies and the number of imaginary frequencies for each structure in Table III. As expected, the pyramidal C_{3v} structures are all minima on the surface with no imaginary frequencies. For the hydrides, the D_{3h} structures are transition states characterized by one imaginary frequency corresponding to the vertex inversion mode. The T-shaped C_{2v} structures of the hydrides with the lone pair in the molecular plane correspond to minima on their appropriate energy hypersurfaces (see below). For the fluorides, the T-shaped C_{2v} structures are transition states with one imaginary frequency corresponding to the edge inversion motion discussed earlier. The D_{3h} structures with an a_1' s orbital lone pair have three imaginary frequencies and are thus not even saddle points. The most appropriate description is that they are high-energy forms (distorted) of the C_{2v} structures which is confirmed by the normal modes for the imaginary frequencies. There is, of course,

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Table III. Zero-Point Energies and Number of Imaginary Frequencies for the Pnictogen Hydrides and Fluorides

molecule	ZPE[a] (kcal/mol)	no. imaginary ν	$i\nu$ (cm^{-1})
PH_3 (C_{3v})	16.19 (14.58)[b]	0	
PH_3 (D_{3h})	15.18	1	1238*i*
PH_3 (C_{2v})	14.43	0	
PF_3 (C_{3v})	5.83 (5.41)[b]	0	
PF_3 (D_{3h})	2.63	3	827*i*, 308*i* (E′)
PF_3 (C_{2v})	4.81	1	365*i*
AsH_3 (C_{3v})	14.69 (13.25)[b]	0	
AsH_3 (D_{3h})	13.90	1	1235*i*
AsH_3 (C_{2v})	13.14	0	
AsF_3 (C_{3v})	4.66 (4.31)[c]	0	
AsF_3 (D_{3h})	2.45	3	492*i*, 201*i* (E′)
AsF_3 (C_{2v})	3.96	1	263*i*
SbH_3 (C_{3v})	12.88 (11.60)[b]	0	
SbH_3 (D_{3h})	12.10	1	1128*i*
SbH_3 (C_{2v})	13.26	0	
SbF_3 (C_{3v})	4.08	0	
SbF_3 (D_{3h})	2.41	3	356*i*, 150*i* (E′)
SbF_3 (C_{2v})	3.60	1	199*i*

[a] Experimental values in parentheses. [b] Reference 20 [c] Reference 21.

an out-of-plane mode, and the two in-plane bends lead to the C_{2v} structure.

The imaginary inversion frequencies for the inversion motion show different periodic trends. For the hydrides, the imaginary inversion frequencies for PH_3 and AsH_3 for the D_{3h} structure are essentially the same. The inversion frequencies at the C_{3v} structure differ significantly—PH_3: 1113 cm^{-1} (calcd), 992 cm^{-1} (expt);[22] and AsH_3: 1020 cm^{-1} (calcd), 906 cm^{-1} (expt).[22] The imaginary frequency for the inversion motion is higher than the C_{3v} inversion frequency. For SbH_3, the imaginary frequency at the D_{3h} structure decreases but is still significantly above the C_{3v} inversion frequency: 889 cm^{-1} (calcd), 782 cm^{-1} (expt).[22] Thus the transition states are actually tighter in the harmonic approximation for this mode than the ground states.

For the fluorides, the imaginary frequencies for the C_{2v} structure show a clear periodic trend, decreasing with increasing pnictogen atomic number. Due in part to increased masses of the fluorines, the frequencies are significantly lower in the fluorides than in the hydrides. The imaginary frequency in the fluorides is slightly lower than that for the degenerate bend to which it corresponds in the C_{3v} structure—PF_3: 374 cm^{-1} (calcd), 344 cm^{-1} (expt);[22] AsF_3: 287 cm^{-1} (calcd), 262 cm^{-1} (expt);[23] and SbF_3 222 cm^{-1} (calcd).

In order to correct the calculated inversion barriers for zero-point effects, it is necessary to scale the calculated differences in the zero-point energies (ΔZPE). The calculated frequencies are too high due to neglect of correlation effects and anharmonic effects. For the hydrides, the scale factor for the C_{3v} structures is 0.90 for all three structures. For PF_3 and AsF_3 the scale factor is 0.925 and this was used for SbF_3.

From our geometric results, it is apparent that the hydrides invert through a planar D_{3h} transition state representing *vertex* inversion while the fluorides invert through a T-shaped C_{2v} transition state representing *edge* inversion based solely on the number of imaginary frequencies. This is shown very explicitly by the energetics in Table IV. The hydrides clearly do not invert by the edge inversion process since the C_{2v} structures are clearly much higher in energy than the corresponding D_{3h} vertex inversion transition states. (In fact the C_{2v} structures with an in-plane lone pair are above the Pn–H bond strengths.[24]) For the hydrides, the barriers to inversion are expected to show an increase with increasing atomic number of the pnictogen although the differences get smaller as the pnictogens get larger. There is also not as large a difference among the three pnictogens P, As, and Sb as compared to the difference in barrier heights between NH_3[6b] and PH_3.[5] As expected from previous work, correlation corrections lower the barrier heights by 1–2 kcal/mol. This very small correlation effect is excellent agreement with Freed's theorem.[7]

Table IV. Calculated Inversion Barriers (kcal/mol) for Pnictogen Hydrides and Fluorides[a]

	vertex		edge	
molecule	SCF	MP-2	SCF	MP-2
PH_3	36.3	$\underline{35.0}$	158.0	159.9
PF_3	124.7	85.3	68.4	$\underline{53.8}$
AsH_3	42.4	$\underline{41.3}$	140.5	142.2
AsF_3	96.3	66.3	57.7	$\underline{46.3}$
SbH_3	44.8	$\underline{42.8}$	111.2	112.0
SbF_3	80.8	57.9	46.5	$\underline{38.7}$

[a] Underlined values represent the best values for ΔE_0 used in determining the barrier heights.

The energies of the T-shaped C_{2v} structures for the hydrides also show very small effects due to correlation corrections. In this case, the energies increase by 1–2 kcal/mol. The periodic behavior of the energies of these structures is more pronounced with a large decrease in energy as the pnictogen atomic number increases.

There are a number of previous calculations on the vertex inversion barriers of the hydrides. The best calculated ΔE[5] for PH_3 is 34.4 kcal/mol determined from a near Hartree–Fock basis set of STO's and including correlation correction at the CI-SD with a correction for quadruple excitation (CI-SDQ). Our value of 35.0 kcal/mol is in excellent agreement considering that our basis set is smaller, our correlation correction is simpler, and our use of SCF geometries. For AsH_3, the previous calculation[3] was done at the SCF level with a large STO DZ+P basis set and estimated geometries. The calculated barrier of 46.4 kcal/mol is in reasonable agreement with our SCF value of 42.4 kcal/mol. Our basis set is somewhat better in the valence space, and our geometries are better in the SCF limit. The correlation correction is again small. The inversion barrier for SbH_3 was calculated[4] previously with an STO basis set that was of minimum basis set quality in the inner shells and of DZ+P quality in the valence space. The barrier at this level was 46.2 kcal/mol as compared to our slightly lower barrier of 44.8 kcal/mol.

The ΔZPE corrections are 0.7–0.9 kcal/mol and give final inversion barriers of 34.1, 40.6, and 42.1 kcal/mol at the MP-2 level. For PH_3, the best value for the inversion barrier is 33.5 by using our ΔZPE correction and the previous CI-SDQ calculation. For AsH_3 and SbH_3 our values represent the best available values for these barrier heights.

The fluorides clearly will invert through the T-shaped C_{2v} transition state for *edge* inversion. Previous work on PF_3[25,26] has shown that the lowest energy D_{3h} structure has an s orbital lone pair of a_1' symmetry with the state with the p orbital lone pair of a_2'' symmetry 55 kcal/mol higher in energy. This has also been found in AsF_3 where the energy difference is 59 kcal/mol.[27] Our work clearly demonstrates that the T-shaped C_{2v} transition state for *edge* inversion is of lower energy than the D_{3h} structure with a_1' s orbital occupancy for the lone pair, and, in fact, this D_{3h} structure is simply a high-energy form of the C_{2v} structure. The edge inversion barriers for the fluorides show a much larger correlation correction in the direction of decreasing the barrier height than do the vertex inversion barriers of the hydrides. For PF_3 the MP-2 correlation correction is 21% of the SCF barrier height, for AsF_3 it is 20%, and for SbF_3 it is 17%. For the hydrides, the correlation corrections are 2–5% of the SCF value. The correlation correction for the edge inversion process for the fluorides thus does not appear to follow the conclusions usually derived from Freed's theorem.[7] The large correlation effects for the C_{2v} structures are consistent with previous estimates[25b] based on simple calculations on the inversion barrier for PF_3. The

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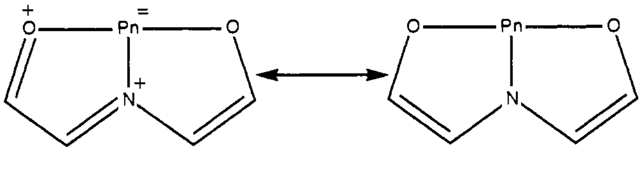
fluorides also show the opposite periodic trend in the inversion barriers with SbF_3 having the lowest edge inversion barrier. Thus the barriers decrease with increasing pnictogen atomic number, and, in fact, the difference is approximately constant in contrast to the leveling effect observed for the hydrides. The ΔZPE correction to the edge inversion barriers for the fluorides is again small being -0.9 kcal/mol for PF_3, -0.6 kcal/mol for AsF_3, and -0.4 kcal/mol for SbF_3. The final corrected, correlated barriers for *edge* inversion in the fluorides are 52.9, 45.7, and 38.3 kcal/mol for PF_3, AsF_3, and SbF_3, respectively. It is of interest to note that the edge inversion barrier for SbF_3 is actually lower than the vertex inversion barrier for SbH_3.

The decrease in the edge inversion barrier with increasing pnictogen atomic number is not surprising and correlates well with the increasing stability for increasing pnictogen atomic number observed for ADPnO complexes which have a T-shaped structure.[28]



Our SCF inversion barrier for PF_3 for vertex inversion through the D_{3h} transition state is in reasonable agreement with the value found by Marynick[25a] of 121.5 kcal/mol considering the differences in geometries and basis sets. For AsF_3, our SCF calculation is with a much larger basis set and with much better geometries. Marynick's value[27] of 111.9 kcal/mol is 15.6 kcal/mol higher in energy than our value showing the necessity of a good basis set and a good set of geometries in these calculations.

Finally, returning to the observation that the T-shaped C_{2v} structures for the hydrides are minima on a potential energy hypersurface,[29] we note that these structures may be accessed by electronic excitation. Including corrections for ΔZPE, the 0-0 transition of these states are calculated to be at 158.1 (55, 335 cm^{-1}), 140.6 (49, 210 cm^{-1}), and 112.4 (39, 340 cm^{-1}) kcal/mol above the ground state. The observed absorption spectra[30] are quite complex and have been assigned to Rydberg transitions. We do note that the continuous absorption in PH_3 has the maximum intensity at 1800 Å (55, 556 cm^{-1}) which is in an energy region consistent with our result. However, for AsH_3, the maximum is at 1830 Å (54, 645 cm^{-1}) which is higher than our result. For SbH_3, the continuum has a maximum intensity at 1970 Å (50, 781 cm^{-1}), clearly much higher than our value. However, it would seem useful to reinvestigate the UV spectra of these hydrides to look for evidence of the states having C_{2v} structure.

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[29] The T-shaped C_{2v} structures for the hydrides were calculated with an in-plane lone pair. If the lone pair is an out-of-plane p orbital then the C_{2v} structure is simply a distorted D_{3h} structure..

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Steric Effects on Atropisomerism in Tetraarylporphyrins

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Abstract: The rate of aryl ring rotation in a series of 5,10,15,20-tetrakis(2-X-5-methoxyphenyl)porphyrins, where X = H, F, Cl, Br, and I, was studied by NMR spectroscopy and chromatography. Where X = Cl, Br, and I, the four atropisomers *αβαβ*, *ααββ*, *αααβ*, and *αααα* were isolated and were stable at 298 K. When X = H or F, facile interconversion of the atropisomers at 298 K prevented isolation of pure atropisomers, but for X = F samples of >80% isomeric purity were isolated at low temperatures. The approach of nonequilibrated mixtures of atropisomers to equilibrium at elevated temperatures was monitored by HPLC experiments for X = Cl, Br, and I, and ^{19}F NMR spectroscopy for X = F. Rate constants were obtained for the six processes by which the atropisomers can interconvert. The rotational barriers increased monotonically as the van der Waals radii of the substituent X. The rotational barriers were correlated with the "apparent overlap" of the ortho substituents, Σr^*, a geometric parameter previously proposed to quantify steric interactions on the internal rotation in biaryls.

Biphenyl-type atropisomerization in ortho-substituted tetraphenylporphyrins was first reported by Gottwald and Ullmann[1] who separated the atropisomers of 5,10,15,20-tetrakis(*o*-hydroxyphenyl)porphyrin. X-ray structures of several 5,10,15,20-tetraarylporphyrins show that the aryl rings are inclined roughly perpendicular (60–90°) to the plane of the porphyrin ring in both free-base and metallo derivatives in the solid state,[2] and thus the ortho substituents project above and below the porphyrin plane. Aryl ring rotation in solution has been shown to be slow on the NMR time scale at ambient temperature, and the aryl ring, on average, is orthogonal to the plane of the porphyrin.[3] The atropisomerism, due to restricted rotation of the aryl rings about the porphyrin-arene bond, gives rise to four atropisomers (e.g., Figure 1). In an equilibrated mixture the four atropisomers *αβαβ*, *ααββ*, *αααβ*, and *αααα* are present in the statistical ratio of 1:2:4:1, respectively.

The restricted rotation which results when an amido substituent is placed on the ortho positions of the meso aryl rings has been exploited in the design and synthesis of a number of chemical models for heme-containing biological systems.[4] On the basis

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