Table IX. T_1 Data for Aniline in Inert, Hydrogen-Bonding, and Acidic Solvent Systems

Solvent	Concn, % v/v	Visc, cP[b]	T_1, sec[a] Ortho	Meta	Para	$T_1^{o,m}/T_1^p$
Neat		3.62	5.4	5.3	4.4	1.32
CCl_4	20	2.6	11.5	11.7	8.8	1.32
Benzene-d_6	20	0.886	13.4	12.7	10.5	1.24
Acetone-d_6	20	0.602	10.5	11.7	11.2	0.99
DMSO-d_6	20	2.08	3.5	3.55	2.85	1.24
	10	2.0	3.5	3.47	3.13	1.11
CH_3CO_2H	20	5.08	1.29	1.35	0.44	3.00
	10	2.99	1.65	1.8	0.62	2.78
CF_3CO_2H	20	6.26	1.21	1.07	0.26	4.42

[a] 38°, 25.2 MHz. Samples undegassed. [b] Viscosities in centipoise calculated from solution densities and capillary viscometer measurements.

sistent attention to experimental details. Precision in duplicate runs with separate samples was <2%. ^{13}C T_1 data plots for the C–H carbons of PhOD in D_2O are given in Figure 6. In this case the $(T\text{-}90°_\infty\text{-}T\text{-}180°\text{-}t\text{-}90°_t)_x$ pulse sequence was repeated 16 times for each data point set. The decay was followed for $\approx 2 \times T_1$ at which time only 13.5% of the initial magnetization remains.

The last solvent system investigated for PhOH was CH_3COCH_3. Geometries of phenol–ketone complexes have not been elucidated. The $T_1^{o,m}/T_1^p$ ratio observed for 1:1 PhOH–CH_3COCH_3, 1.2, is significantly lower than the ratios observed in PhOH–CCl_4 or PhOH–H_2O solutions (~1.5–1.7). This indicates that PhOH–CH_3COCH_3 complexes may be "folded," or that the complex lifetime is short compared with the time for overall molecular reorientation of the PhOH molecules.

Relaxation behavior analogous to that observed for phenol is observed for aniline in inert and hydrogen-bonding solvents (Table IX). When aniline is protonated in acid solution the ring carbon T_1's decrease markedly, out of proportion to macroscopic viscosity measurements. In addition, the molecular tumbling of the anilinium ion becomes highly anisotropic, the $T_1^{o,m}/T_1^p$ ratio being *ca.* 3 (tumbling ratio $\approx$ 9) *vs.* 1.0–1.3 for aniline itself. The strongly anisotropic molecular motion arises from the ion being "locked" into the solvent lattice by ion pairing and electrostatic interactions.[29]

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(29) G. C. Levy, *Chem. Commun.*, 768 (1972).

Analysis of Isomerization in Compounds Displaying Restricted Rotation of Aryl Groups[1]

Devens Gust and Kurt Mislow*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received August 17, 1972*

Abstract: A general and systematic approach to the topological analysis of isomerism and isomerization has been developed for compounds belonging to the triaryl systems Ar_3ZX (*e.g.*, Ar_3CH, Ar_3P) and Ar_3Z (*e.g.*, Ar_3B), and also for the diaryl systems Ar_2ZXY (*e.g.*, Ar_2CHCl, Ar_2PH), Ar_2ZX_2 (*e.g.*, Ar_2CH_2, Ar_2O), and Ar_2ZX (*e.g.*, Ar_2CO, Ar_2O), where X and Y represent ligands or pseudo-ligands. The results may be displayed in the form of graphs, as illustrated by application to several examples from the literature. This method of analysis is broadly applicable to a large variety of molecular structures.

Recent years have witnessed the study of a great diversity of chemical systems which demonstrate isomerism due to restricted internal motions.[2] One group of compounds evincing such behavior consists of molecules containing two or more aromatic ring systems (Ar) bonded to a central atom (Z). Although these compounds often differ greatly in their constitution, they are all related in the elements giving rise to isomerism and in the pathways for interconversion of isomers (isomerization). The present paper presents an approach to a general, systematic, and exhaustive analysis of isomerism and isomerization in such systems, allowing a facile interpretation of relevant experimental data. The sometimes complex interconversion

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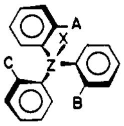
(1) This work was supported by the National Science Foundation (GP-30257), and was presented as a Solvay Lecture at the Free University of Brussels, March 1972.

(2) See, for example, I. O. Sutherland, *Annu. Rep. NMR (Nucl. Magn. Resonance) Spectrosc.*, 4, 71 (1971).

networks resulting from such an analysis are conveniently displayed as graphical representations, which greatly simplify a discussion of the stereochemical features of these systems. As detailed in the following sections, topological analyses have been carried out for the triaryl systems Ar$_3$ZX, where X represents either a ligand or a pseudo-ligand such as an electron pair (*e.g.*, Ar$_3$CH, Ar$_3$P), and Ar$_3$Z (*e.g.*, Ar$_3$B), and for the diaryl systems Ar$_2$ZXY (*e.g.*, Ar$_2$CHCl, Ar$_2$PH), Ar$_2$ZX$_2$ (*e.g.*, Ar$_2$CH$_2$, Ar$_2$O[3]), and Ar$_2$ZX (*e.g.*, Ar$_2$CO, Ar$_2$O[3]), where X and Y represent ligands or pseudo-ligands. In all cases under consideration, X and Y represent groups which have local conical symmetry on the time scale of measurement, as typified by groups such as methyl, cyano, hydrogen, and halogen.

Triaryl Systems

Systems of the Type Ar$_3$ZX. In structures of this type, all four ligands (or pseudo-ligands) are arranged approximately tetrahedrally about the central atom Z. The three aryl carbons bonded to Z define a plane hereafter called the *reference plane*. From the point of view of classifying the conformations of an Ar$_3$ZX molecule according to symmetry criteria, there are three ways a given aryl group may orient itself with respect to this plane: the plane of the aromatic ring may be perpendicular to the reference plane (case I), the normal to the ring which passes through the carbon atom attached to Z may lie in a plane perpendicular to the reference plane and containing the C–Z bond (case II), or the plane of the aromatic ring may assume an intermediate position (case III). Thus, there are two unique conformations (case I and case II) and an infinite number of case III conformations. In the Ar$_3$ZX systems studied thus far, all three rings are consistent with case III behavior in the ground state. In particular, these molecules have propeller-like conformations, and all three aromatic rings in a given molecule have the same sense of twist. This conformation is exemplified by the generalized structure shown in **1**, which is depicted in one of several possible propeller conformations.[4]



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Three structural features are present which give rise to isomerism in molecules having the propeller conformation, as will be exemplified by reference to the generalized molecule **1**, in which A $\neq$ B $\neq$ C. These features bear a direct relationship to the elements into which the overall chirality of the molecule may be factored.[8] We recognize that the choice of elements of chirality employed here is not unique. Other approaches to factorization would be equally valid. However, we believe that the analysis herein described is advantageous since its results are readily correlated with the isomerization mechanisms of interest.

First, the four ligands, tetrahedrally arranged about Z, are different, and hence Z is a *center of chirality*.

Second, isomerism results from the distribution of the substituents A, B, and C on the two sides of the reference plane.[9] For the purposes of our analysis, this plane may be treated as *a plane of chirality*. As shown in **1**, the substituents may all reside on the same side of this plane. Alternatively, A or B or C may be on the opposite side from the other two substituents. These four arrangements will be designated x, a, b, and c, respectively. Each of the four arrangements is chiral and thus may exist in two forms which differ in configuration with respect to the plane of chirality. Figure 1 illustrates the two x arrangements which differ in configuration only with respect to the plane of chirality for a hypothetical molecule in which all three rings demonstrate case I behavior. Isomerism arising from planar chirality is independent of central chirality. For example, the configuration at the chiral center of the molecule in Figure 1 is the same in both representations, and the two conformations shown are therefore diastereomeric.[10]

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(3) A molecule such as diphenyl ether may formally be classified as an Ar$_2$ZX$_2$ system if the two electron pairs are regarded as two pseudo-ligands. On the other hand, the two pairs may be viewed as a single pseudo-ligand (see S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B*, 136 (1971)), in which case diphenyl ether would be classified as an Ar$_2$ZX system.

(4) (a) X-Ray structure analyses[5] confirm such a propeller conformation in the solid state for a variety of molecules, and the results of nmr investigations of substituted triarylmethanes[5a,6] and triaryl derivatives of phosphorus and arsenic[6a] are consistent with this conformation in solution, on the nmr time scale. An electron diffraction study of triphenylmethane[7] indicates that the same conformation is favored in the gas phase. (b) Although the substituents (A, B, C) are depicted in ortho positions, no particular substitution pattern is implied. The essential point is that in the most general case, the aryl groups do not have local C_2 axes coincident with the C–Z bonds.

(5) (a) M. J. Sabacky, S. M. Johnson, J. C. Martin, and I. C. Paul, *J. Amer. Chem. Soc.*, **91**, 7542 (1969); (b) J. Trotter, *Can. J. Chem.*, **41**, 14 (1963); (c) J. Trotter, *Acta Crystallogr.*, **16**, 1187 (1963); (d) J. J. Daly, *J. Chem. Soc.*, 3799 (1964); (e) R. A. Shaw, M. Woods, T. S. Cameron, and B. Dahlén, *Chem. Ind.* (*London*), 151 (1971); (f) H.-J. Kuhn and K. Plieth, *Naturwissenschaften*, **53**, 359 (1966); (g) D. M. Hawley and G. Ferguson, *J. Chem. Soc. A*, 2059 (1968).

(6) (a) A. Rieker and H. Kessler, *Tetrahedron Lett.*, 1227 (1969); (b) H. Kessler, A. Moosmayer, and A. Rieker, *Tetrahedron*, **25**, 287 (1969).

(7) P. Andersen, *Acta Chem. Scand.*, **19**, 622 (1965).

(8) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

(9) Actually, the essential factor giving rise to isomerism is not the position of the substituent itself with respect to the reference plane, but rather the orientation of the plane of the ring bearing the substituent with respect to the reference plane. This orientation may be defined by considering that portion of the plane of the ring which lies on the side of the ring bearing the substituent in question with respect to a line, coextensive with the Z–C bond, which bisects the ring. The angle of rotation about the Z–C bond of this segment of a plane with respect to a case II orientation may then be used to define this type of isomerism. The orientations of all three aryl groups must be considered. Such a definition, although rigorous, would be cumbersome, and therefore isomerism arising from this source has been discussed in terms of the distribution of substituents with respect to the reference plane for the sake of convenience and ease of visualization. In principle, however, cases may be envisioned for which this simplified discussion is inapplicable. In such cases, for purposes of formal analysis, the aryl groups may be considered to be splayed out so that Z and the three carbon atoms bonded to it lie in a plane, with X lying above or below this plane. Such a formalism allows one to discuss isomerism in alternative and convenient terms without ambiguity, and at the same time clearly illustrates the relationship between the Ar$_3$ZX and Ar$_3$Z systems (see below).

(10) In previous discussions dealing with stereoisomerism of triarylcarbonium ions[11,12] the chiral plane does not appear to have been recognized as such. We do not believe that it is meaningful to refer to this feature as "biphenyl-type chirality."[11b] Such terminology is likely to engender confusion, since biphenyls are capable of exhibiting two types of chirality. First, in chiral conformations of, for example, 2,2′-dichlorobiphenyl (C_2), *axial* chirality exists even when the torsional angle (τ) equals $m\pi/2$ (m = odd) radians, *i.e.*, even when the biphenyl skeleton is achiral (local D_{2d} symmetry). This is the form of chirality which is analogous to the *planar* chirality discussed in the text, regardless of whether we are dealing with an Ar$_3$ZX or an Ar$_3$Z case. Second, in chiral conformations of unsubstituted biphenyl (D_2), axial chirality exists if and only if $\tau \neq n\pi/2$ (n = 0, 1, 2, ...) radians. This form of chirality is strictly analogous to the previously described "propeller

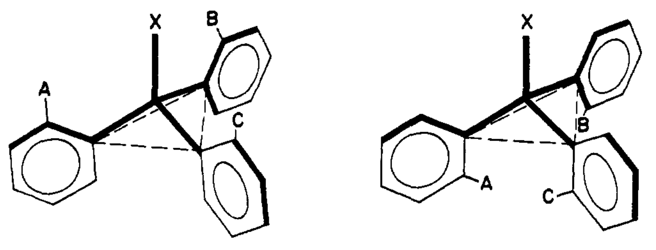

Figure 1. Illustration of isomerism arising from planar chirality. The dashed lines define the reference (chiral) plane, and all three aryl groups are perpendicular to this plane. The central atom Z resides at the intersection of the four heavy lines at the center of the figure. The two structures differ only in their configuration with respect to the chiral plane.

A third element of chirality is introduced by the fact that the molecule is propeller shaped. Each of the three aryl groups, in case III arrangements, is twisted about its Z–C axis in the same sense so that the basic framework has C_3 symmetry. The line perpendicular to the reference plane which passes through Z is thus recognized to be an *axis of chirality.*[14] The sense of twist may be that of either a right- or left-handed helix. The *helicity*,[8] *i.e.*, "propeller chirality"[13] is independent of the two other elements of chirality.

In order to completely identify an isomer for the general case, the configuration must be specified with respect to each of the three elements of chirality. We have arbitrarily chosen to designate the configuration in each case by a *plus* or *minus* sign. In the subsequent discussion, the configurational sign will be listed in the following order: (1) central chirality, (2) planar chirality, (3) axial chirality (helicity). For example, **1** has the x-type arrangement of substituents and might be arbitrarily designated as $(-+-)$x. The enantiomer of **1** is obtained by changing the sign with respect to all three elements of chirality, $(+-+)$x.[15]

It is apparent that for the general Ar_3ZX case illustrated by **1** there are $(2^3)4 = 32$ isomers possible (16 *dl* pairs). Degeneracies arise whenever two or more aryl groups are constitutionally identical (affecting central chirality) or whenever one or more of these groups has a local C_2 axis coincident with the Z–C bond (affecting planar chirality). Table I lists the number of isomers for each possible degeneracy.[16]

Two general classes of mechanisms will be considered for the interconversion of isomers within each of the sets listed in Table I, neither of which involves cleavage of the Z–C bond.

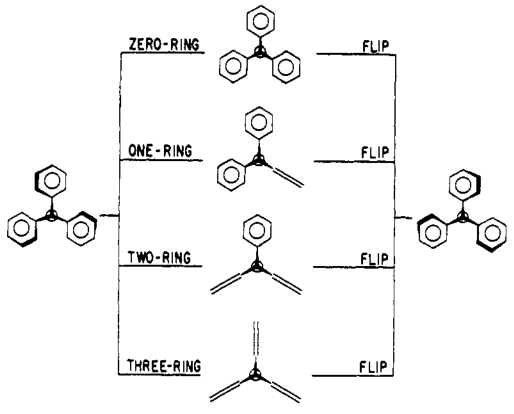

Figure 2. The four rotational (flip) mechanisms for the Ar_3ZX system. The small hollow circle represents the X group. The structures in the center of the figure indicate the approximate geometries of the transition states.

Table I. Number of Isomers for Ar_3ZX Systems

No. of identical rings	No. of rings with C_2 axes 0	1	2	3
0	32	16	8	4
2	16	8	4	2
3	8	0	0	2

The first of these classes consists of processes in which inversion occurs along a line defined by the Z–X bond. This may be pyramidal inversion, as encountered in amines, carbanions, etc., or it may be inversion resulting from displacements at Z, involving cleavage of the Z–X bond by any of a variety of processes. In the general case illustrated by **1**, inversion changes only the configuration of the chiral center. For example, inversion converts $(-+-)$x into $(++-)$x.

Isomerism may also occur by rotations about the Z–C bonds. Four rotational mechanisms have been postulated by Kurland, *et al.*,[17a] for triarylcarbonium ions. Analogous mechanisms can be envisioned for other Ar_3Z systems, as well as for Ar_3ZX and diaryl systems. These mechanisms will be called "flip" mechanisms in keeping with the nomenclature introduced by Kurland, *et al.* In these four mechanisms, zero, one, two, or three rings "flip," *i.e.*, rotate through orientations defined by case I above, while the remaining rings rotate in the opposite direction through orientations defined by case II (Figure 2). Each flip mechanism reverses the helicity of the structure; furthermore, in the general case, each flip leads to a different stereoisomer.[17b] The flip mechanisms have no effect on the central chirality.

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chirality,"[13] which will be discussed below. Thus, biphenyls such as 2,2′-dichlorobiphenyl exhibit axial chirality arising from two sources when $\tau \neq n\pi/2$ radians.

[11] (a) J. W. Rakshys, Jr., S. V. McKinley, and H. H. Freedman, *J. Amer. Chem. Soc.*, 92, 3518 (1970); (b) *ibid.*, 93, 6522 (1971).

[12] F. Strohbusch, *Tetrahedron*, 28, 1915 (1972).

[13] See the previous discussions[11,12] and references cited therein.

[14] The three Z-C axes may also be considered chiral axes. However, in propeller molecules of type 1, the specification of the chirality arising from these elements is subsumed by the specification of helicity.

[15] These designations are introduced only for convenience within the context of the present discussion and are not being recommended as a general nomenclatural proposal.

[16] A distinctive description of diastereomers in cases of degeneracy requires additional rules, and conventions may have to be coined for particular cases (*e.g.*, exo/endo, etc.). A thorough discussion of this issue is beyond the purview of this paper.

[17] (a) R. J. Kurland, I. I. Schuster, and A. K. Colter, *J. Amer. Chem. Soc.*, 87, 2279 (1965). (b) In all of these mechanisms, it is postulated that one of the aryl groups in a molecule having the propeller conformation in the ground state rotates from its position at a local minimum on the potential energy surface to one of the two adjacent local minima. The two other aryl groups must rotate concurrently to adjacent minima in order to maintain the propeller conformation in the product molecule. Thus, since there are three aryl groups in the molecule and two adjacent local minima for each aryl group, there are $2^3 = 8$ possible pathways for isomerization. These eight pathways are those specified by the four flip mechanisms. Although these mechanisms comprise all the pathways involving inter-dependent rotations of the three rings, other mechanisms may be envisioned if this constraint is removed. For example, a given aryl group may not rotate at all, or may rotate through two or more local minima. There are a great number of such mechanisms, and consideration of all of them is not contemplated in this paper. The flip mechanisms suggested by Kurland, *et al.*,[17a] appear to be chemically reasonable, and all experimental observations to date are interpretable in terms of them. Therefore, since it is necessary to place some limit on the scope of our discussion, we have chosen to restrict our analysis to these mechanisms, and to aim for an exhaustive treatment within this framework.

Table II. Inversion Matrix for Ar_3ZX System

	(+++)x	(+−+)x	(+++)a	(+−+)a	(+++)b	(+−+)b	(+++)c	(+−+)c	(++−)x	(+−−)x	(++−)a	(+−−)a	(++−)b	(+−−)b	(++−)c	(+−−)c
(−++)x	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
(−−+)x	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
(−++)a	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
(−−+)a	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
(−++)b	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
(−−+)b	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
(−++)c	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
(−−+)c	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
(−+−)x	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
(−−−)x	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
(−+−)a	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0
(−−−)a	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0
(−+−)b	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0
(−−−)b	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0
(−+−)c	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0
(−−−)c	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1

The 32 possible isomers may be divided into two sets of 16 having opposite configurations at the chiral center. An isomer belonging to one set may be converted into one of the other set only by an inversion mechanism. Within each of these two sets, interconversions may occur only by means of flip mechanisms. For a given isomer, nine isomerizations are possible by way of five mechanisms: one inversion, one zero-ring flip, one three-ring flip, three two-ring flips, and three one-ring flips. Hence, there are a total of $(32 \times 9)/2 = 144$ interconversion paths.

In order to visualize the consequences of a given set of interconversions, a systematic representation is desirable. The matrix display in Tables II–IV depicts all interconversions possible by the five mechanisms. A glance at these tables immediately gives some insight into the stereochemical results of three of these mechanisms. As stated above, inversion changes only the configuration at the chiral center, *i.e.*, for the inversion matrix (Table II) all off-diagonal elements are zero. If one now examines the four matrices for the set of isomers corresponding to a given configuration at the chiral center (*i.e.*, either Table III or Table IV), it is evident that a three-ring flip changes only the helicity of a molecule, and does not affect isomerism arising from the other elements, and that a zero-ring flip reverses only the sign of the helicity and that of the planar chirality. In both cases, for a given row or column only one element is not zero, since, for a given isomer, only one zero-ring flip and one three-ring flip are possible.

In contrast, it may be difficult to use the matrices to grasp the effects of the one- and two-ring flips, or of a combination of mechanisms, even though all the necessary information is contained in the tables. A topological representation is therefore of some advantage. In principle, a graph could be constructed which would consist of 32 vertices representing the 32 isomers, each of which would have a connectivity of 9. The resulting 144 edges would represent the interconversion pathways. It is more convenient, however, to consider the different mechanisms separately, and thus to depict only the relevant portions (subgraphs) of this graph. These subgraphs, as well as the other graphs discussed in this paper, may be delineated in any one of an infinite number of images. The choice of images presented here is based on convenience for the purposes of this analysis.

Figure 3 shows the subgraph for the two-ring flip, consisting of four unconnected cubes in each of which the vertices represent eight diastereomers and the edges interconversions by way of this mechanism. These four cubes may be divided into two sets, A/B and $\bar{A}/\bar{B}$, in each of which two cubes represent the 16 isomers with a given configuration at the chiral center. Since the four cubes are not connected, four noninterconvertible isomers exist even when interconversions by the two-ring flip are rapid, consisting of two diastereomeric *dl* pairs, A/$\bar{A}$ and B/$\bar{B}$. Since any flip reverses the helicity of a given isomer, any two vertices on this graph which are connected by a path consisting of an odd number of edges necessarily represent isomers having opposite helicities. Diagonally opposite corners (vertices) of any cube, such as (+++)x and (+−−)x, represent isomers which differ configurationally both in helicity and in planar chirality. A given edge and all those

Table III. Flip Matrices for (+) Configuration at Z; Ar$_3$ZX System

	Three-ring flip								One-ring flip							
	(++−)x	(+−−)x	(++−)a	(+−−)a	(++−)b	(+−−)b	(++−)c	(+−−)c	(++−)x	(+−−)x	(++−)a	(+−−)a	(++−)b	(+−−)b	(++−)c	(+−−)c
(+++)x	1	0	0	0	0	0	0	0	0	0	0	1	0	1	0	1
(+−+)x	0	1	0	0	0	0	0	0	0	0	1	0	1	0	1	0
(+++)a	0	0	1	0	0	0	0	0	0	1	0	0	1	0	1	0
(+−+)a	0	0	0	1	0	0	0	0	1	0	0	0	0	1	0	1
(+++)b	0	0	0	0	1	0	0	0	0	1	1	0	0	0	1	0
(+−+)b	0	0	0	0	0	1	0	0	1	0	0	1	0	0	0	1
(+++)c	0	0	0	0	0	0	1	0	0	1	1	0	1	0	0	0
(+−+)c	0	0	0	0	0	0	0	1	1	0	0	1	0	1	0	0
	Two-ring flip								Zero-ring flip							
(+++)x	0	0	1	0	1	0	1	0	0	1	0	0	0	0	0	0
(+−+)x	0	0	0	1	0	1	0	1	1	0	0	0	0	0	0	0
(+++)a	1	0	0	0	0	1	0	1	0	0	0	1	0	0	0	0
(+−+)a	0	1	0	0	1	0	1	0	0	0	1	0	0	0	0	0
(+++)b	1	0	0	1	0	0	0	1	0	0	0	0	0	1	0	0
+−+)b	0	1	1	0	0	0	1	0	0	0	0	0	1	0	0	0
+++)c	1	0	0	1	0	1	0	0	0	0	0	0	0	0	0	1
+−+)c	0	1	1	0	1	0	0	0	0	0	0	0	0	0	1	0

Table IV. Flip Matrices for (−) Configuration at Z; Ar$_3$ZX System

	Three-ring flip								One-ring flip							
	(−+−)x	(−−−)x	(−+−)a	(−−−)a	(−+−)b	(−−−)b	(−+−)c	(−−−)c	(−+−)x	(−−−)x	(−+−)a	(−−−)a	(−+−)b	(−−−)b	(−+−)c	(−−−)c
(−++)x	1	0	0	0	0	0	0	0	0	0	0	1	0	1	0	1
(−−+)x	0	1	0	0	0	0	0	0	0	0	1	0	1	0	1	0
(−++)a	0	0	1	0	0	0	0	0	0	1	0	0	1	0	1	0
(−−+)a	0	0	0	1	0	0	0	0	1	0	0	0	0	1	0	1
(−++)b	0	0	0	0	1	0	0	0	0	1	1	0	0	0	1	0
(−−+)b	0	0	0	0	0	1	0	0	1	0	0	1	0	0	0	1
(−++)c	0	0	0	0	0	0	1	0	0	1	1	0	1	0	0	0
(−−+)c	0	0	0	0	0	0	0	1	1	0	0	1	0	1	0	0
	Two-ring flip								Zero-ring flip							
(−++)x	0	0	1	0	1	0	1	0	0	1	0	0	0	0	0	0
(−−+)x	0	0	0	1	0	1	0	1	1	0	0	0	0	0	0	0
(−++)a	1	0	0	0	0	1	0	1	0	0	0	1	0	0	0	0
(−−+)a	0	1	0	0	1	0	1	0	0	0	1	0	0	0	0	0
(−++)b	1	0	0	1	0	0	0	1	0	0	0	0	0	1	0	0
(−−+)b	0	1	1	0	0	0	1	0	0	0	0	0	1	0	0	0
(−++)c	1	0	0	1	0	1	0	0	0	0	0	0	0	0	0	1
(−−+)c	0	1	1	0	1	0	0	0	0	0	0	0	0	0	1	0

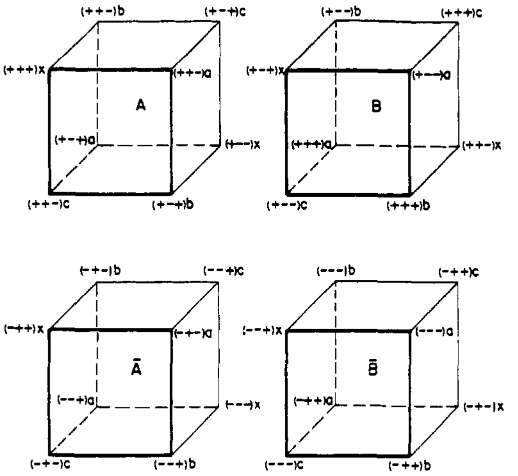


Figure 3. The two-ring flip subgraph for the Ar_3ZX system. Vertices represent isomers and edges signify interconversions by the two-ring flip.

parallel to it represent two-ring flips by the same two rings.

A similar subgraph may be constructed for the one-ring flip mechanism using the matrices in Tables III and IV. This graph also consists of four unconnected cubes which may be ordered into two sets differing in configuration at the chiral center. Each cube represents eight diastereomers. In each of these cubes, diagonally opposite corners represent isomers differing only in helicity.

If it is necessary to discuss a system in terms of more than one mechanism, one must resort to the appropriate combination of subgraphs. For example, Figure 4 is the graph for a combination of the two-ring flip and inversion mechanisms. It consists of two unconnected figures, each one of which, in the particular image which we have chosen, is made up of two cubes, one wholly contained within the other, whose vertices are connected pairwise by eight edges. In each figure, the edges which make up the faces of the cubes represent two-ring flips, and the edges joining the two nested cubes signify inversions. It is interesting to note that even when both mechanisms are allowed, the system still consists of two noninterconvertible diastereomers. Other graphs may be similarly constructed for any combination of mechanisms using the information in the matrices (Tables II–IV).

Tables I–IV may also be used in conjunction to construct graphs for each of the possible degenerate cases of the Ar_3ZX system. A complete exposition of all possible combinations would serve no purpose, but the utility and advantages of the graphical analysis will be illustrated by an example from the literature. Before doing so, it should be noted that although the method of analysis presented here enumerates the possible isomerization pathways for a given system, spectral and/or other evidence must be used to determine which of the pathways are energetically favored. In addition, experimental limitations (*e.g.*, accidental isochrony) may on occasion render it impossible to differentiate mechanisms or isomers which are readily distinguishable on theoretical grounds.

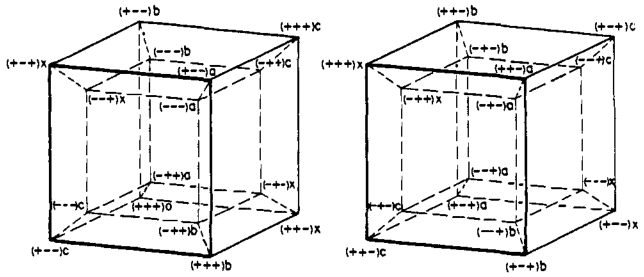
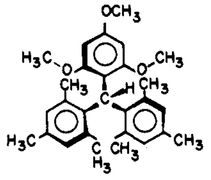


Figure 4. Subgraph for the combination of the two-ring flip and inversion mechanisms for the Ar_3ZX system. The edges of the nested cubes represent two-ring flips, and the edges joining these cubes signify inversions.

Several studies are reported of conformational dynamics involving Ar_3ZX systems, in which all three rings have local C_2 axes coincident with the Z–C bond,[18] and in which either two or three of the rings are identical.[5a,6] Only two isomers are possible in all of these cases (Table I); these are enantiomers differing only in helicity. One such system (2) was examined by Martin



2

and coworkers,[5a] who reported that below −30° the ^1H nmr spectrum of 2 displays three *o*-methyl resonances and two *o*-methoxyl resonances. At −20° the *o*-methyl signals coalesce to a singlet, while the two *o*-methoxyl resonances remain distinct. The *o*-methoxyl signals finally coalesce at about 145°.[19] These observations were rationalized[5a] in terms of a "gear meshing" rotational mechanism, which explains the coalescence at −20°, and a "gear clashing" mechanism, which explains the coalescence at 145°. No alternative mechanisms were discussed.

The compound represented by 2 exists as a *dl* pair in the ground state, and the effect of each of the five mechanisms discussed above may therefore be depicted by a graph (Figure 5) which consists of two vertices, representing the two enantiomers, connected by eight edges, representing flip mechanisms. Each vertex is also connected to itself by a loop, representing an inversion mechanism.[20] In Figure 5, each edge of the graph is identified by the appropriate mechanism, the numbers in brackets indicating the rings (with reference to the structural formula shown in Figure 5) which flip during the specified interconversion. The [1,2]- and [1,3]-flips are enantiomeric, as are the [2]- and [3]-flips. These enantiomeric processes must occur at identical rates in an achiral medium, and they have therefore been considered together in terms of their effect on the spectrum. Each edge of the graph is also labeled with the number of *o*-methyl and *o*-methoxyl resonances to

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[18] In many of these cases the para positions are occupied by methyl, dimethylamino, or methoxyl groups. Although these groups do not have local C_2 symmetry they may be regarded as having, in effect, local $C_{\infty v}$ symmetry on the nmr time scale.

[19] In the conformation shown, 2 (or its enantiomer) has four diastereotopic *o*-methyl groups and two diastereotopic *o*-methoxyl groups. Thus, two of the *o*-methyl signals are apparently accidentally isochronous in the slow exchange limit.[5a]

[20] Since both loops and multiple edges are required, Figure 5 might properly be termed a "pseudograph" (F. Harary, "Graph Theory," Addison-Wesley, Reading, Mass., 1969, p 10).

be expected when interconversion by the pathway in question is rapid (*i.e.*, at the fast exchange limit) on the nmr time scale.[21]

The two-ring flip mechanism will be discussed first. The graph indicates that if interconversion by all three of the two-ring flips occurs rapidly, only one *o*-methyl and one *o*-methoxyl signal will be observed. This result is consistent with the 145° spectrum. On the other hand, if the [2,3]-flip is slow and the other two-ring flips are rapid, one *o*-methyl and two *o*-methoxyl signals are in principle observable. This result is consistent with the spectrum at $-20°$. These explanations are also favored by Martin and coworkers,[5a] who have argued that above $-20°$ the [1,2]- and [1,3]-flips ("gear meshing") are occurring rapidly because of the relatively low degree of steric repulsion of the *o*-methyl and *o*-methoxyl groups which are forced together in the transition state. The [2,3]-flip ("gear clashing"), however, requires that two methyl groups be forced together in the transition state, and since a methyl group is larger than a methoxyl,[5a] the barrier to this flip is higher. At 145° this two-ring flip is also said to have become rapid, whence it follows that coalescence of the *o*-methoxyl signals is accounted for.[5a]

Examination of Figure 5 indeed indicates that in the absence of accidental isochrony, none of the other four mechanisms is capable of explaining the coalescence observed at $-20°$, thus providing strong evidence for the proposed[5a] mechanism.[22] However, even granted rapid interconversion by [1,2]- and [1,3]-flips above $-20°$, the graph indicates that the zero-ring flip, the [2]- and [3]-flips, and the inversion mechanism are also all consistent with the coalescence at 145°. Thus, nmr evidence alone does not rule out three alternatives to the proposed mechanism at the higher temperature.[23] The zero-ring flip may be safely eliminated for steric reasons, and arguments against the inversion mechanism have been presented for a similar case.[6a] However, the [2]- and [3]-flips remain as viable alternatives. Such flips involve merely the interaction of one *o*-methyl and one *o*-methoxyl group in the transition state, and result in exchange among all four *o*-methyl positions and between both *o*-methoxyl positions. Thus, by [2]- and [3]-flips the required coalescence at 145° is achieved without the need to postulate a pathway, *i.e.*, the [2,3]-flip, which requires large steric repulsion of two methyl groups. The evidence to date does not allow us to choose between the previous[5a] and the present explanations for the coalescence at 145°; the point at issue is that only through an exhaustive analysis of the mechanistic alternatives, based on the information contained in Tables I–IV, can it be established that such alternatives exist.

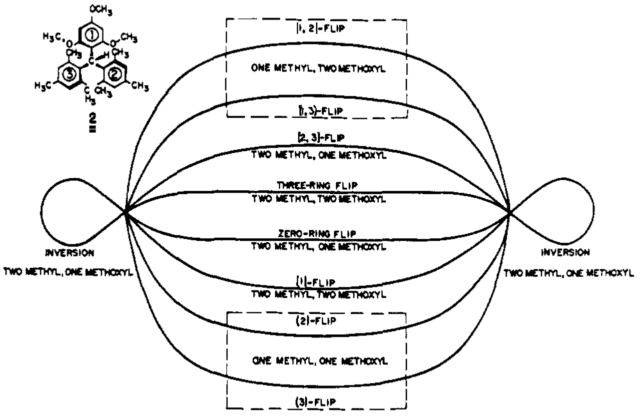
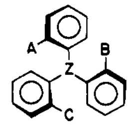


Figure 5. Graph depicting all possible interconversions of **2**. The dashed boxes identify the two sets of enantiomeric mechanisms. Each edge is labeled with the number of *o*-methyl and methoxyl signals to be expected when interconversion by the given pathway is rapid on the nmr time scale.

Kessler and coworkers[6] determined barriers to rotation of aryl groups for several triarylmethanes and -arsines, and a triarylphosphine, by ^{1}H-nmr coalescence measurements. Although these workers did not discuss the different rotational mechanisms which might account for the observed spectra, analysis in the manner described above makes it readily apparent that, with the exception of the three-ring flip, any one or a combination of the mechanisms here discussed is capable of explaining the nmr data.

Systems of the Type Ar$_3$Z. All molecules belonging to this class which have been studied to date have a propeller conformation similar to those of the Ar$_3$ZX system, as illustrated by the generalized structure shown in **3**.[4b,24] This system is a special case of the general



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(21) The transition states of the zero-, [1]-, [2,3]-, and three-ring flips are achiral, and the results of rapid interconversions may be easily ascertained by inspection of the transition state geometries (see Figure 2). In the case of the enantiomeric two-ring flips and one-ring flips, the results of rapid interconversion are represented by the achiral (racemic) combination of enantiomeric transition states, since no single conformation on the reaction surface connecting the two enantiomers by a combination of [2]- and [3]-flips, or a combination of [1,2]- and [1,3]-flips, is achiral. (In this connection, see K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1965, p 93.)

(22) A combination of the three-ring flip and the [1]-flip is also consistent with the data, providing that the activation energies for the two processes are the same, within experimental error. Such a combination is probably sufficiently unlikely that it may be neglected in a first analysis.

(23) Since the three-ring flip and the [1]-flip do not interconvert *o*-methoxyl groups, they do not explain the coalescence at 145° in the absence of accidental isochrony. Although these processes might in fact be occurring rapidly above $-20°$, their detection is precluded in this system, since only one *o*-methyl resonance is observed under these conditions.

(24) There is evidence supporting this conformation in the crystal lattice, in solution, and in the vapor phase.[11a,25]

(25) (a) G. N. Lewis and M. Calvin, *Chem. Rev.*, **25**, 273 (1939); (b) G. N. Lewis, T. T. Magel, and D. Lipkin, *J. Amer. Chem. Soc.*, **64**, 1774 (1942); (c) F. Seel, *Naturwissenschaften*, **31**, 504 (1943); (d) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954); (e) N. C. Deno, P. T. Groves, and G. Saines, *J. Amer. Chem. Soc.*, **81**, 5790 (1959); (f) D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 674 (1957); (g) R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959); (h) R. Dehl, W. R. Vaughan, and R. S. Berry, *J. Org. Chem.*, **24**, 1616 (1959); (i) R. S. Berry, R. Dehl, and W. R. Vaughan, *J. Chem. Phys.*, **34**, 1460 (1961); (j) D. E. O'Reilly and H. P. Leftin, *J. Phys. Chem.*, **64**, 1555 (1960); (k) I. I. Schuster, A. K. Colter, and R. J. Kurland, *J. Amer. Chem. Soc.*, **90**, 4679 (1968); (l) A. H. Gomes de Mesquita, C. H. MacGillavry, and K. Eriks, *Acta Crystallogr.*, **18**, 437 (1965); (m) P. Andersen and B. Klewe, *Acta Chem. Scand.*, **19**, 791 (1965); (n) *ibid.*, **21**, 2599 (1967); (o) M. Szwarc, *Discuss. Faraday Soc.*, **2**, 39 (1947); (p) F. C. Adam and S. I. Weissman, *J. Amer. Chem. Soc.*, **80**, 2057 (1958); (q) P. Andersen, *Acta Chem. Scand.*, **19**, 629 (1965); (r) J. S. Hyde, R. Breslow, and C. DeBoer, *J. Amer. Chem. Soc.*, **88**, 4763 (1966); (s) R. Hoffmann, R. Bissell, and D. G. Farnum, *J. Phys. Chem.*, **73**, 1789 (1969); (t) M. Ballester, *Pure Appl. Chem.*, **15**, 123 (1967); (u) M. Ballester, J. Riera, J. Castañer, C. Badía, and J. M. Monsó, *J. Amer. Chem. Soc.*, **93**, 2215 (1971).

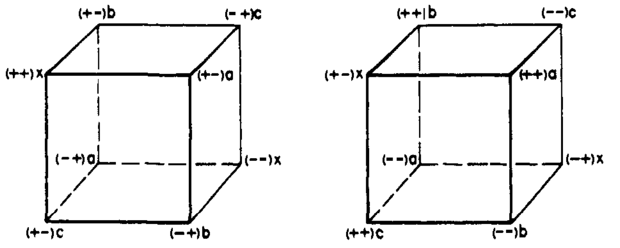

Figure 6. Subgraph depicting the two-ring flip mechanism for the Ar_3Z system.

Ar_2ZX system in which X has become a phantom ligand, and in which the possibility of isomerism due to central chirality has thus been eliminated. This point is well illustrated by the example of the triarylamines. If one were to undertake an nmr study of isomerism and isomerization of the compound ArAr'Ar''N, one might choose to treat it as a pyramidal molecule of the type Ar_3ZX where X represents an electron pair, the pseudo-ligand. In that case, the system could be analyzed exactly as described above. Alternatively, it might be argued that the barrier to pyramidal inversion for triarylamines is so low that this process is rapid on the nmr time scale at all readily accessible temperatures,[26] and that the molecule may therefore be treated as if it were lacking an element of central chirality on the time average.[27] In that case, the system would be considered as belonging in type to Ar_3Z, and would be analyzed as such. The results of both these analyses, however, would be identical.

For the general Ar_3Z system, 16 isomers are possible. Degeneracies arise from the same sources as in the Ar_3ZX system, and the number of isomers possible in these cases is shown in Table V.

Table V. Number of Isomers for Ar_3Z Systems

No. of identical rings	No. of rings with C_2 axes 0	1	2	3
0	16	8	4	2
2	8	6	2	2
3	4	0	0	2

Since the inversion mechanism is no longer applicable, only the four flip mechanisms need be considered. The results of interconversions by these mechanisms ($(16 \times 8)/2 = 64$ pathways) are given by a set of four matrices which may be derived from those in Table III or IV by deleting the sign denoting the configuration at the chiral center from each isomer designation. A study of these matrices indicates that the three-ring flip changes only the helicity of an isomer, as in the Ar_3ZX system. The zero-ring flip now interconverts enantiomers. The two-ring flips may be graphically displayed by a set of two cubes derived either from the upper (A/B) or from the lower ($\bar{A}/\bar{B}$) set in Figure 3 by deleting the signs denoting configuration at the center of chirality (Figure 6). The diagonally opposite corners (*e.g.*, (++)x and (−−)x) now represent enantiomers, and each of the diastereomeric cubes contains four *dl* pairs. Interconversion of enantiomers by this mechanism requires a minimum of three two-ring flips. An analogous graph may be constructed for the one-ring flip. In this case, the two cubes, each of which contains eight diastereomers, are enantiomeric, and thus racemization by this mechanism is impossible. Diagonally opposite corners of each cube represent isomers which differ only in helicity, just as in the Ar_3ZX case.

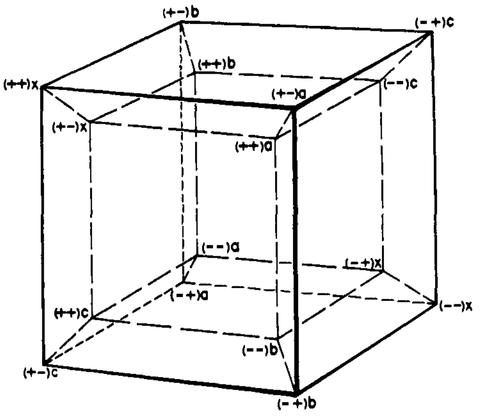

Figure 7. Subgraph for the combination of the two-ring flip and the three-ring flip mechanisms for the Ar_3Z system. Note that each of the nested cubes is identical with one of those in Figure 6. The eight edges joining the cubes represent three-ring flips.

Graphs depicting the effects of several mechanisms in combination are readily prepared. For example, if the two cubes in Figure 6, representing the possible two-ring flips, are nested, and the eight vertices of one are joined to those of the other by eight edges representing three-ring flips, as shown in Figure 7, the resulting graph represents a combination of the two- and three-ring flip mechanisms.[28] Similarly, if the two cubes representing one-ring flips are nested, and the vertices of one are joined to those of the other by eight edges representing zero-ring flips, the resulting graph depicts a combination of the one- and zero-ring flip mechanisms.

A precedent for the topological analysis of isomerizations in the Ar_3Z system exists in the thoroughly studied isomerization of octahedral complexes of transition metals.[29] It does not appear to have been heretofore recognized that a subclass of these complexes, the transition metal tris chelates, has features which are symmetry equivalent to systems of the type Ar_3Z,[30] and that some of the isomerization mechanisms in both

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[26] (a) For a recent review of inversion at nitrogen, see J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970); (b) Y. Sasaki, K. Kimura, and M. Kubo, *J. Chem. Phys.*, 31, 477 (1959); (c) W. S. Kelley, L. Monack, P. T. Rogge, R. N. Schwartz, S. P. Varimbi, and R. I. Walter, *Justus Liebigs Ann. Chem.*, **744**, 129 (1971).

[27] It must be emphasized that the central atom need not lie in the reference plane of Ar_3Z systems. This condition is fulfilled only if the reference plane is also a plane of symmetry, or if there is at least one molecular C_2 axis which coincides with one of the Z-C bonds. For conformations such as the one shown in 3, neither of these conditions is met, and Z will therefore not lie in the reference plane on the time average. Although Z thus becomes, in a sense, a chiral center, this feature does not give rise to isomerism and can thus be ignored in the discussion of Ar_3Z systems.

[28] Isomerism and isomerization in triarylcarbonium ions have recently been analyzed by Strohbusch,[12] making use of some of these representations.

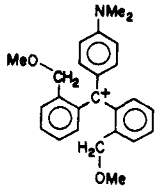
[29] See, for example, (a) E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968); (b) *ibid.*, **91**, 1636 (1969); (c) M. Gielen and C. Depasse-Delit, *Theor. Chim. Acta*, **14**, 212 (1969); (d) M. Gielen, G. Mayence, and J. Topart, *J. Organometal. Chem.*, 18, 1 (1969); (e) M. Gielen and J. Topart, *ibid.*, 18, 7 (1969).

[30] For example, $Co(en)_3{}^{3+}$ and $(C_6H_5)_3C^+$ both have the symmetry of a three-bladed propeller (D_3). The number and types of isomers are also the same in both systems (Table V).

systems bear a formal analogy. Accordingly, topological analyses in one system have their counterpart in the other. Thus, for example, the Bailar and Ray–Dutt intermediates proposed for interconversions in the tris chelates are analogous to the three- and two-ring flip transition states, respectively.[31]

Rotational isomerism in Ar_3Z systems has been reported for triarylcarbonium ions,[11,17,25k,32] a triarylmethyl radical,[25r] and triarylboranes.[33] The utility and advantages of the graphical analysis may be illustrated by several examples from the literature.

Breslow, *et al.*,[32b] in the course of their study of several relatively complex degenerate systems, found that the ^{1}H nmr spectrum of **4** at ambient temperature shows two methoxyl singlets with a 60:40 ratio of intensities. This observation was interpreted by postulating the presence of a mixture of two sets of two conformers each (A/$\bar{\mathrm{A}}$ and B/C in Figure 8). It was proposed that interconversion of the two conformers within each set occurred rapidly on the nmr time scale by the three-ring flip, while interconversion between the sets was slow.



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Six isomers are possible for this system (Table V). These are depicted in Figure 8, along with a graphical representation of each of the four possible interconversion mechanisms. An examination of the graph for the three-ring flip indicates that rapid interconversion by this mechanism gives rise to three kinds of methoxyl groups on the time average, two of which (arising from $\bar{\mathrm{B}}$/C and $\bar{\mathrm{C}}$/B) are enantiomeric and thus give rise to isochronous signals in an achiral medium. Therefore, the three-ring flip mechanism is indeed consistent with the observed spectrum. However, plausible alternatives are not excluded.

The graph for the two-ring flip connects all six isomers. Thus, if all the edges represented rapid interconversions, only one methoxyl signal would result. However, each of the edges marked with a pair of short lines corresponds to a pathway which involves the rotation of a ring bearing an *o*-CH_2OMe group through the reference plane, while the unmarked edges involve rotation of the ring bearing only hydrogens in the ortho positions through the reference plane. The marked pathways might be presumed to be less favorable for steric reasons than the unmarked pathways, and if interconversion by the marked pathways is slow, the corresponding edges of the graph may be deleted. The result is a disconnected subgraph which is identical with that for the three-ring flip. Thus, the two-ring flip mechanism with constraints is also consistent with the reported[32b] observations, and, by analogy with similar systems,[11b] may well be the lowest energy mechanism.

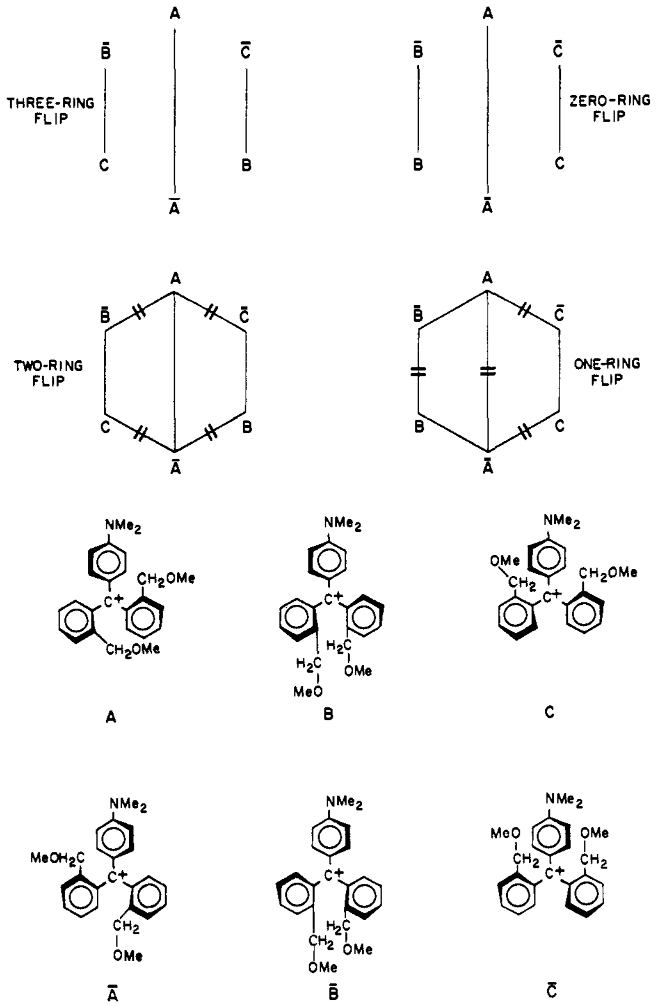

Figure 8. Possible isomers and isomerization pathways for **4**. The letters at the vertices identify isomers. A pair of identical letters, one of which is barred, represents a *dl* pair. For significance of short double lines across edges, see text.

Similarly, although the graph for the one-ring flip connects all isomers, the marked pathways involve a sterically unfavorable interaction between an *o*-CH_2-OMe group and an ortho hydrogen (or another *o*-CH_2OMe group) when both lie in or near the reference plane, while the unmarked edges of the graph do not involve such interactions. If the marked pathways are deleted, the time average result is a pair of enantiotopic methoxyl groups (arising from B/$\bar{\mathrm{A}}$ and $\bar{\mathrm{B}}$/A) which appear as a singlet, and another methoxyl group (arising from C/$\bar{\mathrm{C}}$) which also appears as a singlet. This mechanism is therefore also consistent with the observed[32b] spectrum.

The graph for the zero-ring flip indicates that rapid interconversion by this mechanism requires three diastereomers (A/$\bar{\mathrm{A}}$, B/$\bar{\mathrm{B}}$, and C/$\bar{\mathrm{C}}$), resulting in four methoxyl signals. In the absence of accidental isochrony, this mechanism is not consistent with the data.[34]

As the exhaustive analysis of isomerization in **4** indi-

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(31) Relevant topological analyses of isomerizations in the tris chelates have been presented by Muetterties[29a] and by Gielen, *et al.*[29c,e]

(32) (a) A. K. Colter, I. I. Schuster, and R. J. Kurland, *J. Amer. Chem. Soc.*, 87, 2278 (1965); (b) R. Breslow, L. Kaplan, and D. LaFollette, *ibid.*, 90, 4056 (1968); (c) B. L. Murr and C. Santiago, *ibid.*, 90, 2964 (1968); (d) B. L. Murr and L. W. Feller, *ibid.*, 90, 2966 (1968).

(33) (a) H. C. Brown and S. Sujishi, *ibid.*, 70, 2793 (1948); (b) T. J. Weismann and J. C. Schug, *J. Chem. Phys.*, 40, 956 (1964).

(34) This mechanism may also be excluded on the basis of the prohibitive steric repulsions which arise in the transition states.

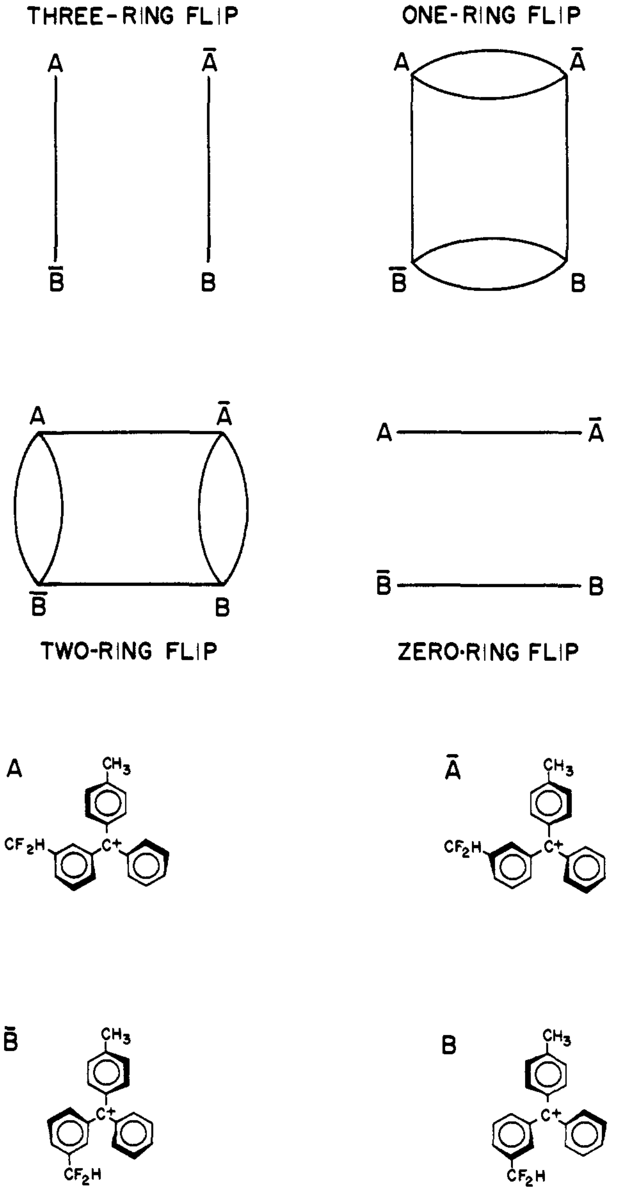

Figure 9. Possible isomers and isomerization pathways for m-CF$_2$H, p'-CH$_3$ trityl cation. Multiple edges represent diastereomeric pathways which interconvert the same two stereoisomers.

cates, the problem is much more complex than originally indicated. More to the point, the systematic approach rules out one mechanism (the zero-ring flip) while indicating that the three others are consistent with the spectral data, granted reasonable constraints. The evidence to date[32b] does not allow us to choose among these three alternatives.

Restricted rotation in molecules of the Ar$_3$Z type in which all aryl rings are different and two rings possess local C_2 axes has been studied by several groups.[11,32b,c,d] Four isomers are expected for this type of system (Table V). One such system, the "m-CF$_2$H, p'-CH$_3$ trityl cation," was studied by Freedman and coworkers,[11a] who reported that the ^{19}F nmr spectrum of this compound at −71° consists of two equal intensity ABX octets, each of which arises from the diastereotopic fluorines of one of the two possible diastereomeric *dl* pairs (Figure 9). Upon warming to 25°, this pattern collapses to a doublet. It was asserted that this spectral behavior is consistent with both the two-ring flip and the three-ring flip mechanisms.[11a]

A topological analysis of this system (Figure 9) immediately reveals that the one- and two-ring flip mechanisms may exchange all four diastereotopic fluorine nuclei, whereas the three- and zero-ring flips are incapable of doing so. In particular, since the three-ring flip is incapable of exchanging the diastereotopic fluorines of a given stereoisomer, this mechanism cannot account for the experimental observations, barring accidental isochrony. The advantages of a systematic analysis, such as the one in Figure 9, are thus once again clearly demonstrated.[35]

Diaryl Systems

Compounds belonging to this class include diaryl ethers and sulfides, diarylboranes, diarylmethanes, diarylcarbonium ions, etc. The ground state conformations of such molecules have been the subject of much study. The evidence to date has been interpreted[36–51] as indicating that these molecules may assume one of two conformations: either both aryl

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(35) In a subsequent paper,[11b] Freedman and coworkers have provided evidence favoring the two-ring flip mechanism as an explanation for the observed interconversions, and have recognized the necessity of invoking accidental isochrony in order to explain the observed coalescence of nmr signals by the three-ring flip.

(36) W. R. Blackmore and S. C. Abrahams, *Acta Crystallogr.*, 8, 329 (1955).

(37) W. R. Blackmore and S. C. Abrahams, *ibid.*, 8, 323 (1955).

(38) W. R. Blackmore and S. C. Abrahams, *ibid.*, 8, 317 (1955).

(39) (a) D. M. McEachern B. and P. A. Lehmann F., *J. Mol. Struct.*, 11, 127 (1972); (b) V. Cody, W. L. Duax, and D. A. Norton, *Chem. Commun.*, 683 (1971).

(40) (a) E. J. W. Whittaker, *Acta Crystallogr.*, **6**, 714 (1953); (b) B. Chaudhuri and A. Hargreaves, *ibid.*, **9**, 793 (1956).

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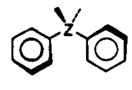
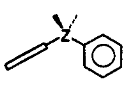
groups are arranged as in case III with respect to the C–Z–C plane (**5a**, hereafter called the *helical conformation*[52]), or one ring ideally assumes a case I position and the second ring a case II orientation (**5b**, hereafter called the *perpendicular conformation*).



5a

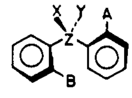


5b

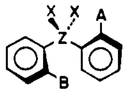
X-Ray structure determinations on a diaryl sulfide,[36] selenide,[37] and telluride,[38] and on diaryl ethers,[39] several diarylmethanes,[40] diaryl ketones,[41] and diarylarsines[42] indicate that these compounds assume the helical conformation in the solid state, although one of the ethers[39b] approaches the perpendicular conformation.[43,53]

However, evidence for the conformation of compounds of this type in solution is more ambiguous.[44a] Although from dipole moment studies it has been suggested[39a,45,48a] that some classes of diaryl compounds may assume either conformation, depending upon structural and electronic factors, the data do not in all cases permit an unequivocal decision.[45d,48a] In the case of diaryl ethers[46] and sulfides,[46f,g] diarylcarbonium ions,[47] substituted methanes,[48] boranes,[49] benzophenones,[50] and pyridinium ions,[51] nmr evidence, although in some cases ambiguous or even conflicting, seems to indicate that either conformation may be preferred, depending upon the structure of the molecule. In particular, diarylmethanes, ethers, and sulfides in which three of the four ortho positions are substituted by groups such as methyl or nitro have usually been discussed in terms of the perpendicular conformation.

Isomerism and isomerization in diaryl systems may be analyzed in a manner analogous to that employed for the triaryl systems. The helical Ar_2ZXY system possesses the elements of central, planar, and axial chirality and may be exemplified by the generalized structure **6**[4b](shown in one possible conformation), which is formally analogous to **1**.



6



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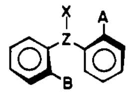

8

Replacing the Y group in **6** by X results in Ar_2ZX_2 (**7**). For the purposes of the present analysis, this is equivalent to Ar_2ZX', in which a single pseudo-ligand (X′) takes the place of the two X groups. In turn, Ar_2ZX' is topologically equivalent to Ar_2ZX (**8**), where X is a real ligand. It is therefore unnecessary to discuss Ar_2ZX_2 separately, both systems being subsumed under Ar_2ZX.[3] The number of isomers possible in diaryl systems is listed in Table VI.[54]

As a matter of convenience and clarity of exposition, we begin our discussion with an analysis of Ar_2ZX systems. The flip mechanisms in these systems are analogous to those described for the Ar_3Z case. The reference plane is now defined by the central atom Z and the two aryl carbons bonded to it. Thus, the two-ring flip of **8** involves rotation of both rings through case I orientations (conrotatory), a one-ring flip involves rotation of one ring through a case I orientation and the other through a case II orientation (disrotatory), and a zero-ring flip involves rotation of both rings through case II orientations (conrotatory). It follows that the perpendicular structure is the transition state (or a close approximation thereof) for a one-ring flip.[55]

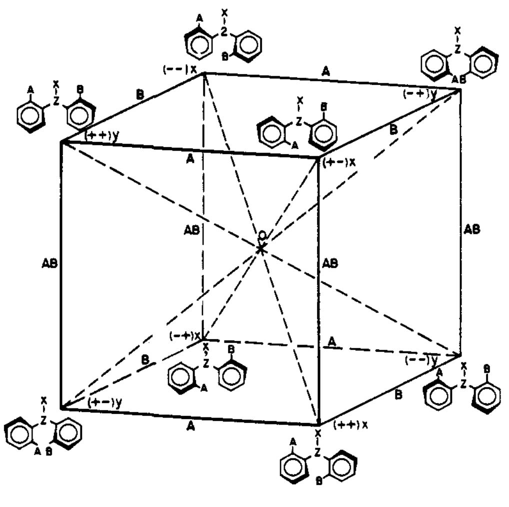

Figure 10. Graph depicting all possible interconversions for the Ar_2ZX system by the flip mechanisms. Each vertex is identified by the appropriate structural formula. In addition, each vertex is marked with a symbol. An x indicates that A and B are on the same side of the reference plane, while a y denotes a structure in which A and B are on opposite sides. The first and second signs within the parentheses denote configuration with respect to the plane and axis of chirality, respectively. The letters on the edges of the graph identify the rings which flip during the specified interconversion. The point of intersection in the center of the cube is not a vertex.

Table VI. Number of Isomers for Diaryl Systems

No. of identical rings	No. of rings with C_2 axes: 0	1	2
	Ar_2ZXY		
0	16	8	4
2	8	0	2
	Ar_2ZX or Ar_2ZX_2		
0	8	4	2
2	6	0	2

Interconversions among the eight isomers of **8** (Table VI) by flip mechanisms are depicted by the graph shown in Figure 10. The corners of the cube represent the eight helical conformers (four *dl* pairs). The edges of the top and bottom faces of the cube (labeled A or B) correspond to one-ring flips; the label identifies the ring which flips. The four vertical edges (labeled AB) represent two-ring flips. The four lines connecting diagonally opposite corners of the cube and passing through its center depict zero-ring flips; note that the apparent intersection of these four lines at the center of

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(52) This arrangement has also been called a "skew" conformation.[48a,50b] However, we avoid use of this word to describe the conformation shown in **5a**, since the same term has also been applied to hypothetical nonhelical twisted conformations (see ref 11b and references cited therein) and to the perpendicular conformation.[39a,45b,c,46c,d]

(53) This generalization obtains for unsubstituted molecules, or for molecules in which one, two, or four ortho positions are substituted. X-Ray data are not available for triply ortho-substituted molecules.

(54) This number is the same for a given system whether the isomers assume the helical or the perpendicular conformation except for the last entry in the table, which reads 4-0-1 for the perpendicular conformation.

(55) Note that the planes of the two rings will be orthogonal only when one of them coincides with the reference plane.

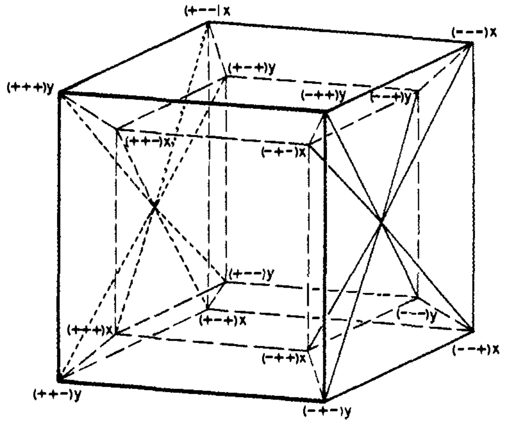

Figure 11. Graph depicting interconversions for the Ar_2ZXY system, as described in the text. The vertices are identified as described in Figure 10, with the addition of the initial sign within the parentheses, which denotes configuration at the center of chirality. Thus, the three signs denote configuration with respect to the center, plane, and axis of chirality, respectively. The two points where four edges intersect are not vertices (see Figure 10).

the cube is *not* a vertex of the graph. Diagonally opposite vertices represent enantiomers.

In the Ar_2ZXY system, the presence of a chiral center requires that inversion as well as torsional (flip) mechanisms be considered. The graph in Figure 11 represents all the possible interconversion mechanisms. If we imagine the deletion of the eight horizontal edges, which represent inversion pathways at the chiral center, the remaining subgraphs, which in appearance resemble truncated square pyramids, are nothing more than distorted images of the graph in Figure 10 and of its mirror image (left and right, respectively). The meaning of vertices and edges is the same as described for the graph in Figure 10

As was pointed out, the perpendicular structure **5b** is simply the transition state for a one-ring flip of the helical structure **5a**. Thus, all the data from nmr and dipole moment studies cited in favor of the perpendicular conformation are also consistent with a mixture of helical structures which, on the time scale of the measurement, are rapidly interconverting by one-ring flips. In other words, the perpendicular species may be interpreted as time average structures rather than energy minima.[56] Such an interpretation has several advantages. It is consistent with the available X-ray structural data,[53] and it permits the direct use of the graphical approach outlined above as an aid to the analysis of internal motions in compounds of this type. However, even in the case of molecules for which the lowest energy conformation should prove to be perpendicular, the same graphs (Figures 10 and 11) and their subgraphs are still fully applicable. For example, if the ground state conformation is taken to be perpendicular, the stable isomers may be represented by points along the edges of the top and bottom faces of the cube in Figure 10, and the graph may still be used to depict the consequences of interconversions by the various mechanisms for the Ar_2ZX system.

The mechanisms for interconversion of conformers in the diaryl systems which have been proposed by various authors may be interpreted in terms of Figure 10 or 11. Several such mechanisms which have been postulated for the perpendicular conformation need be modified slightly to include rapid one-ring flips between at least one set of helical isomers as discussed above. In these cases, the lowest energy conformation is now taken to be helical, and the perpendicular arrangement becomes a time average structure.

The one-ring flip is topologically equivalent to the "concerted rotation" or "cogwheel" mechanism suggested for hindered diaryl ethers by Allen and Moir,[57] and later discussed by Lehmann F.[46d] and by Bergman and Chandler,[46b] and suggested for diarylcarbonium ions by Kwart and Alekman.[47] This mechanism is also analogous to the "conversion 2" discussed by Akkerman and Coops in their study of substituted acetic acids,[58] to the mechanism proposed by Adam and Falle[59] for diarylmethyl radicals, and to one of the mechanisms discussed by Fong for a variety of diaryl compounds.[60]

The two-ring flip transition state is identical with that of "conversion 1" of Akkerman and Coops,[58] with that of one of the mechanisms discussed by Bergman and Chandler,[46b] and with that of a mechanism proposed by Fong.[60]

The zero-ring flip transition state is identical with that of one of the mechanisms discussed by Bergman and Chandler[46b] for ethers, and with that of a mechanism suggested by Kessler, *et al.*,[46f] for ethers and sulfides. Although not discussed separately by Akkerman and Coops,[58] the zero-ring flip is an alternative to the "conversion 1" illustrated by these authors.

The two "butterfly" mechanisms of Bergman and Chandler[46b] are topologically analogous to, and equivalent in their results to a one-ring flip plus a two-ring flip, and to a one-ring flip, respectively. Hoffmann, *et al.*,[25s] have discussed all three mechanisms for phenyl-substituted carbonium ions, radicals, and carbanions, and have calculated potential energy curves for these motions.

All the classes of diaryl compounds discussed above[36–51,57] are topologically related, and isomerism in such systems may be analyzed completely using Figure 10 or 11, in conjunction with Table VI. It is only necessary to recognize the appropriate degeneracies and constraints. This unified approach avoids needless duplication of terminology and clearly illustrates the basic stereochemical features which are common to all of these chemical systems.

Conclusions

In this paper, an attempt has been made to develop a general and systematic scheme designed to facilitate the study of isomerism resulting from restricted in-

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(56) In our view, the oft-stated dichotomy between perpendicular and helical conformations is thus more apparent than real. The helical structures represent a continuum of conformations, each of which may be defined by the magnitude of the torsional angles of the aryl rings with respect to some reference structure. In particular, instead of discussing the structure of a given molecule in terms of a "preference" for either the perpendicular or the helical conformation, it would seem desirable to describe the system in terms of the magnitude of the angular deviation of the helical conformers from the perpendicular reference structure. In the case of rapid one-ring flips, one could then speak of the amplitude of torsional oscillation (*i.e.*, of the degree of helicity) with respect to the time average perpendicular structure. This amplitude, or an upper limit thereof, could be related to physically measurable quantities, such as dipole moment or chemical shift. The degree of helicity will clearly be a function of the substitution pattern.

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ternal motions in a wide variety of compounds containing two or three aromatic rings attached to a central atom. This systematic approach has disclosed that some of the data reported in the literature are consistent with several interconversion mechanisms not previously considered.

We are of the opinion that only a complete and exhaustive analysis is capable of disentangling the often complex web of mechanistic alternatives, and that any approach other than a systematic one is bound to be superficial by comparison, and therefore prone to error. What might be a formidable task is however rendered less arduous through the use of graphical representations.

In order to provide a rigorous treatment, the scope of this study has necessarily been restricted to include a somewhat limited set of compounds. For example, this analysis requires that the aryl rings of the compound under study assume a case III orientation so as to generate a propeller-shaped molecule and that the X and Y ligands have local conical symmetry as described above. In addition, the only allowable torsional mechanisms for interconversions are the flip mechanisms wherein the rotation of one aryl group is concurrent with that of the others. Thus, for any proposed study it must be demonstrated that the class of compounds being investigated actually fulfills the above conditions before the analysis presented here may properly be utilized.

There are many classes of compounds which are obviously similar to those belonging to systems described in this work, but which lack one or more of the attributes required for inclusion within the present framework of analysis.[61] Some examples are certain di- and triaryl compounds with bridged ring systems (*e.g.*, 9-arylfluorenes), and various monoaryl systems such as substituted acetophenones and substituted toluenes. Although these classes of compounds do not strictly fall within the scope of the formal analysis presented here, isomerism and isomerization of such compounds may nevertheless be analyzed in a similar manner. In some cases, only a slight modification of the scheme presented here may be needed, whereas in others, more extensive changes may be required. It must be stressed, however, that the matter of basic importance is not so much the formal analysis as it is the methodology, *i.e.*, the general, systematic, and exhaustive procedure which employs graphical representations where necessary for purposes of clarity and convenience.

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(61) Two classes especially closely related to the systems discussed here are compounds of the type Ar_2 (the biaryls) and Ar_4Z. Biaryls may be readily analyzed using the general procedures outlined in this paper. The maximum number of isomers for the Ar_2 system is four, and the only mechanisms for isomerization are analogous to the zero-ring flip (with a planar transition state), and the one-ring flip (with the two aryl groups perpendicular in the transition state.)[10] Analysis of Ar_4Z systems is considerably more complicated and will be the subject of a later report.

Deoxygenation and Desulfurization of Cyclic Ethers and Thioethers by Carbon Atoms. Intermediates with Excess Energy in a Low-Temperature Matrix[1]

P. S. Skell,* K. J. Klabunde,*[2] J. H. Plonka,[3] J. S. Roberts,[2] and D. L. Williams-Smith

Contribution from the Departments of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and University of North Dakota, Grand Forks, North Dakota 58201. *Received September 9, 1972*

Abstract: Singlet carbon atoms react with cyclic ethers to give carbon monoxide and diradical species. Cyclic thioethers react with singlet carbon atoms to give carbon monosulfide (CS) and diradicals. While both deoxygenation and desulfurization are facile processes, the deoxygenation reaction is more exothermic; this exothermicity difference is manifest in the more frequent occurrence in deoxygenations of fragmentations and hydrogen expulsion. These energetic reactions take place in a frozen matrix.

Many interesting reactive intermediates have been generated at low temperature by the reaction of carbon atoms with various organic compounds. The removal of oxygen or sulfur from organic compounds by carbon atoms has been a useful reaction in this respect,[1] and both reactions occur with about equal efficiencies.[1a] Deoxygenation is a highly exothermic process (ΔH = 85–100 kcal/mol) on the basis of bond energies. Desulfurization of thioethers is also an exothermic reaction (ΔH = 45 kcal/mol) on the basis of bond energies, but not to the extent of deoxygenation.[1] When dealing with such exothermicities, a pivotal consideration is the fate of the excess energy. In most chemical reactions, the exothermicity is manifest as vibrational excitation of the intermediate species and products. In previously investigated reactions of atomic carbon with carbonyl compounds,[4] no evidence

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(1) Preliminary communications concerning this and related work have appeared; see (a) K. J. Klabunde and P. S. Skell, *J. Amer. Chem. Soc.*, **93**, 3807 (1971); (b) P. S. Skell, J. H. Plonka, and R. R. Engel, *ibid.*, **89**, 1748 (1967); (c) J. H. Plonka and P. S. Skell, *Chem. Commun.*, 1108 (1970); (d) P. S. Skell, K. J. Klabunde, and J. H. Plonka, *ibid.*, 1109 (1970).

(2) University of North Dakota.

(3) National Institutes of Health Predoctoral Fellow, 1967-1970.

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