

Correlated Rotation of Aryl Substituents in Diarylmethyl-, Diarylphosphine- and Related Fragments An Empirical Force Field Study

W. Weissensteiner

Institut für Organische Chemie, Universität Wien, A-1090 Wien, Austria

Summary. Ground state structures and conformational interconversion mechanisms of 25 diaryl compounds Ar_2Z ($Z = CH_2, CHR, CH(OH), P-CH_3$) were analyzed. For tetra(ortho-alkyl)substituted diaryls the cogwheeling mechanism was found as the threshold mechanism. A shift from the cogwheeling mechanism to interconversions via 2-ring flips is found in di(ortho-alkyl)substituted compounds. The ground state structures and interconversion mechanisms of diarylmethylphosphines are very similar to those of the related 1,1-diarylethanes. The interconversion barrier for correlated conrotation of the aryl rings in di(*tert*-butylphenyl)methanol (**20**) was measured by low temperature NMR and is in excellent agreement with the calculated value for the 2-ring flip T_2'' (ΔG^\ddagger (exp.) = 48 kJ mol⁻¹; ΔG^\ddagger (calc.) = 54 kJ mol⁻¹).

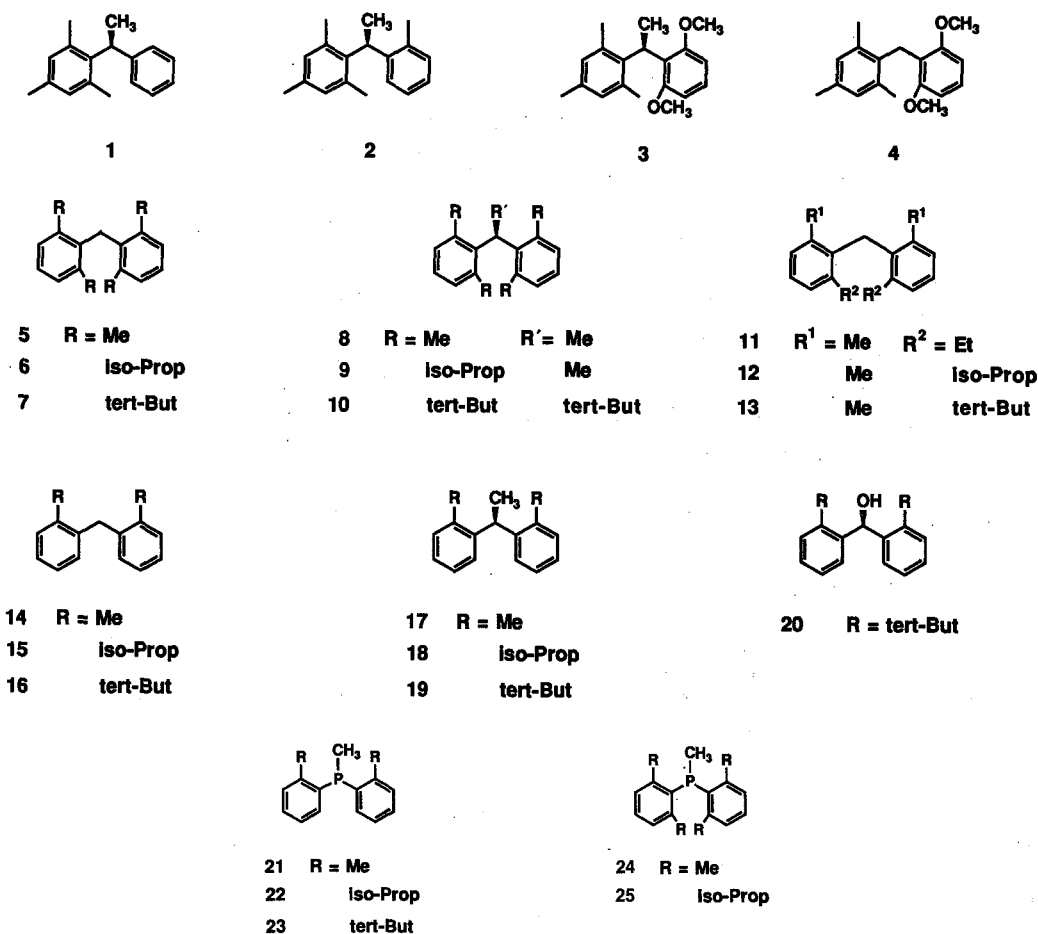
Keywords. Flip mechanisms; Threshold mechanism; Conformational interconversion.

Korrelierte Rotation von Arylringen in Diarylmethyl-, Diarylphosphin- und verwandten Fragmenten. Eine Untersuchung mit Hilfe der empirischen Kraftfeldmethode

Zusammenfassung. Die Grundzustandskonformationen und die konformativen Interkonversionsmechanismen von 25 Diarylverbindungen Ar_2Z ($Z = CH_2, CHR, CH(OH), P-CH_3$) wurden analysiert. Für tetra(ortho-alkyl)substituierte Diaryle wurde der cogwheeling-Mechanismus als der Interkonversionsmechanismus niedrigster Energie ermittelt. In di(ortho-alkyl)substituierten Verbindungen werden nicht der cogwheeling-Mechanismus sondern 2-ring flips als Interkonversionsmechanismen gefunden. Die Grundzustände und Interkonversionsmechanismen für Diarylmethylphosphine sind sehr ähnlich jenen der verwandten 1,1-Diarylethane. Die Interkonversionsbarriere für die korrelierte Bewegung der Arylringe von Di(*tert*-butylphenyl)methanol (**20**) wurde mittels Tieftemperatur-NMR-Spektroskopie ermittelt und ist in sehr guter Übereinstimmung mit dem berechneten Wert für den 2-Ring flip T_2'' (ΔG^\ddagger (exp.) = 48 kJ mol⁻¹; ΔG^\ddagger (calc.) = 54 kJ mol⁻¹).

Introduction

It is well established that when two suitably substituted aryl rings are attached to a common central unit their internal rotations are coupled, the rotation of one ring thus causing that of the other [1,2]. Coupled or correlated rotation may have



several stereo chemical consequences, such as residual stereoisomerism or symmetry changes, as has been shown for many di- and polyaryl compounds [3]. Examples are diarylmethanes, benzophenones [4–6], acetic acids [7, 8], sulfides [9], ethenols [10] (Ar_2Z), triarylmethanes, -amines (Ar_3Z) [3], tetraarylethanes, -ethylenes [11, 12], ditriptycylmethanes and others [13].

By analogy to classical mechanical systems this effect has been dubbed molecular cogwheeling [14] or gearing [15]. Figure 1 shows a graphical representation of such a dynamic process. According to early force field calculations bis(2,6-dimethylphenyl)-methanes (5) [16], adopts a chiral, C_2 symmetrical ground state conformation. The cogwheel effect has been calculated to be the conformational interconversion mechanism of lowest energy (threshold mechanism, Fig. 1). One helical conformation is interconverted into another helical conformation with opposite helicity via a perpendicular transition state by a correlated (concerted) disrotatory motion of both dimethylphenyl rings (if both rings are viewed from the common center Z , one ring moves clockwise the other one counterclockwise) [17]. Continuation of that correlated rotation closes the "cogwheeling circuit". In general, the interconversion possibilities of propeller like molecules are analyzed in terms of flip mechanisms [18], whereby a flip interconverts helical conformations under helicity reversal. Figure 2 shows the 3 types of idealized flip mechanisms. All flip mechanisms involve correlated rotations. The 0- and 2-ring flips involve correlated

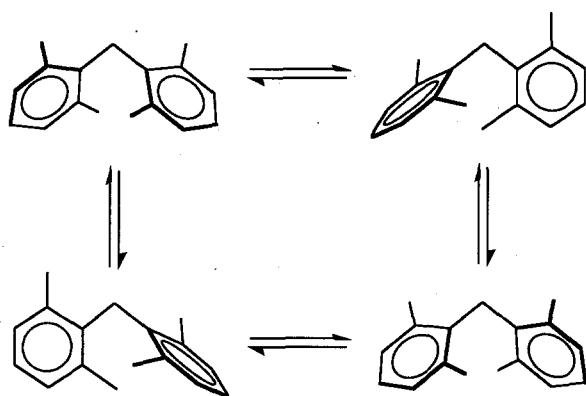


Fig. 1. Cogwheeling circuit of 1

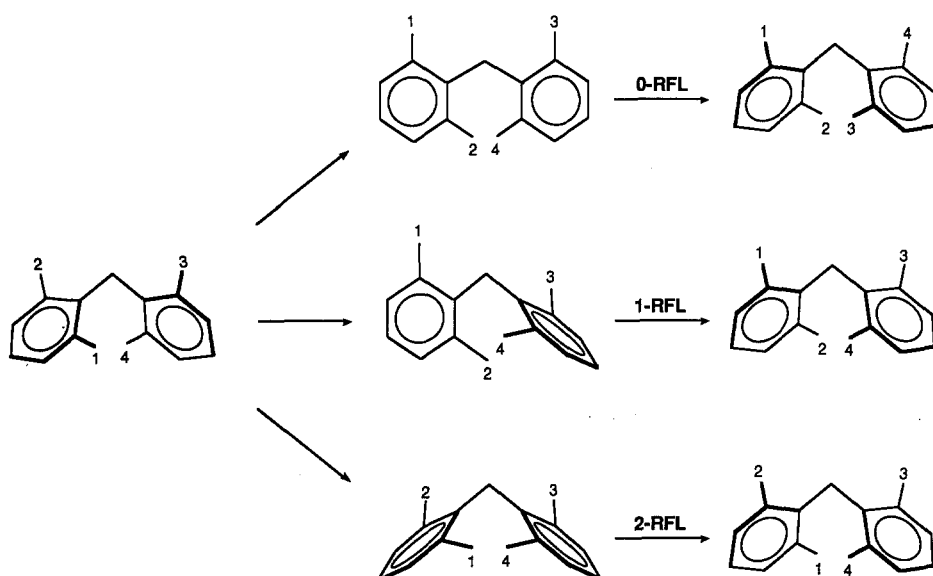


Fig. 2. The three types of flip mechanisms in propellerlike compounds Ar_2Z

conrotation of both aryl rings whereas the 1-ring flip involves correlated disrotation. The cogwheeling circuit shown in Fig. 1 includes two consecutive 1-ring flips. Non-flip mechanisms are usually ascribed as non correlated mechanisms.

It has been pointed out previously that in diaryl compounds Ar_2Z the threshold mechanism of isomerisation depends on the relative size of the aryl rings (aryl substituents) as well as on the central unit Z [6]. For example, from low temperature NMR studies it has been concluded that the lowest energy conformational interconversion of 1-mesityl-1-phenylethane (**1**) [19], takes place via nonflip mechanisms (the mesityl ring staying in a given conformation while the phenyl ring is spinning rapidly). In contrast, it has been reported that in 2,2-diarylethenols [10] the threshold mechanism of conformational interconversion is correlated conrotation (the 2-ring flip).

We recently investigated several diarylmethanes, ethanes, benzophenones and diarylmethanols as well as their chromium tricarbonyl complexes [4] and found

that for all tetra-*ortho*-alkyl substituted diaryl derivatives correlated disrotation (the cogwheeling mechanism) was the threshold mechanism. Other reported examples are diaryl sulfides, -sulfones [9] and acetic acids [7].

The aim of this study is to systematically analyze a variety of diaryl compounds of the type Ar_2Z and determine how the ground state conformations and the internal dynamics of the aryl rings depend on substitution patterns and on the central unit Z . This study includes diarylmethanes, -ethanes, methyl-diarylphosphines and a few additional compounds.

Results and Discussion

The minimum energy conformations and conformational interconversion pathways of compounds **1**–**25** were analyzed with use of the empirical force field method. All calculations were performed with Allinger's force field.

Compounds **1**–**25** are grouped together according to both their central unit and the substitution patterns of the aryl rings. Compounds **1**–**4** are representatives of diaryls with nonidentical aryl rings (different substitution patterns) whereas all other compounds **5**–**25** have identical rings. The aryl rings of the tetrasubstituted compounds **5**–**10** possess a local C_2 symmetry, those of **11**–**13** are desymmetrized by nonidentical substituents. From a symmetry viewpoint the disubstituted diaryls **14**–**16** are related to **11**–**13**, whereas the phosphines **21**–**23** are interconnected to **17**–**20**. The tetrasubstituted phosphines are analogous to the ethanes **8** and **9**.

Minimum Energy Conformations

The minimum energy conformations of diaryl compounds Ar_2Z are usually classified as helical (propellerlike) or perpendicular structures. With the exception of **7**, which adopts a perpendicular conformation, exclusively propellerlike ground state conformations were located for all tri-, **2**, and tetrasubstituted diaryls **3**–**13**, **24** and **25**. For all disubstituted diaryls, **14**–**23**, the situation is more complicated since propellerlike, perpendicular and other conformations are found. It has been pointed out previously [18] that under given symmetry considerations the maximum number of possible conformers can be calculated using a permutational approach, assuming a given molecular skeleton (e. g. a propellerlike diaryl skeleton) and conical symmetrical substituents.

Table 1 lists all diaryls for which more than one minimum energy conformation disregarding enantiomers is expected, their preferred conformations and relative energies and the calculated (under the assumptions mentioned above) number of diastereomeric conformers. Except for **1**, in each case more than one conformer was located. As far as minimum energy conformations are concerned, methoxy, ethyl and isopropyl groups cannot be considered as conical symmetrical. Ethyl groups adopt conformations with the methyl group either above or below the plane of the aryl ring [20] whereas isopropyl and methoxy groups prefer in plane conformations (the isopropyl methane or the methoxy-methyl group coplanar with the aryl ring) [21]. In all isopropyl substituted compounds, conformations with the isopropyl methane proton pointing towards the central unit Z are significantly lower in energy than other arrangements. In the methoxy substituted diaryls, the methoxy methyl group always points away from the central unit Z . Only those

Table 1. Calculated relative energies and preferred geometries of the minimum energy conformations of compounds **1–25**

Number of conformers ^a	Aryl substituents ^b					Conformation ^b	Relative energy (kJ/mol)	
	<i>R</i> ¹	<i>R</i> ^{1'}	<i>R</i> ²	<i>R</i> ^{2'}	<i>X</i>			
1 a	2	<i>Me</i>	H	<i>Me</i>	H	<i>Me</i>	A	0
2 a	4	<i>Me</i>	<i>Me</i>	<i>Me</i>	H	<i>Me</i>	B	0
b		<i>Me</i>	<i>Me</i>	H	<i>Me</i>	<i>Me</i>	A	12.4
c		<i>Me</i>	<i>Me</i>	<i>Me</i>	H	<i>Me</i>	A	16.6
d		<i>Me</i>	<i>Me</i>	H	<i>Me</i>	<i>Me</i>	C	20.7
3 a	2	<i>Me</i>	<i>OMe</i>	<i>Me</i>	<i>OMe</i>	<i>Me</i>	A	0
b		<i>OMe</i>	<i>Me</i>	<i>OMe</i>	<i>Me</i>	<i>Me</i>	A	7.4
11 a^c	3	<i>Et</i>	<i>Et</i>	<i>Me</i>	<i>Me</i>	H	D	0
b							B	0.9
c							A	1.3
12 a	3	<i>i-Prop i-Prop</i>		<i>Me</i>	<i>Me</i>	H	D	0
b							B	5.1
c							A	11.1
13 a	3	<i>t-But</i>	<i>t-But</i>	<i>Me</i>	<i>Me</i>	H	A	0
b							B ^d	13.6
c							C	33.9
		<i>R</i> ¹ = <i>R</i> ^{1'}			<i>X</i>			
14 a	3	<i>Me</i>			H		B'	0
b							D	0
c							A	1.5
15 a	3	<i>i-Prop</i>			H		D	0
b							B''	1.7
c							A	10.8
16 a	3	<i>t-But</i>			H		A	0
b							B''	1.7
c							D	45.0
17 a	4	<i>Me</i>			<i>Me</i>		B'	0
b							D	4.5
c							A	15.5
d							C	21.2
18 a	4	<i>i-Prop</i>			<i>Me</i>		B'	0
b							D	1.6
c							C	23.2
d							A	30.4
19 a	4	<i>t-But</i>			<i>Me</i>		B'	0
b							D	31.6
c							C ^e	47.2
d							A'	48.0

Table 1. (continued)

Number of conformers ^a	Aryl substituents ^b					Conformation ^b	Relative energy (kJ/mol)
	<i>R</i> ¹	<i>R</i> ^{1'}	<i>R</i> ²	<i>R</i> ^{2'}	<i>X</i>		
20 a	4	<i>t-But</i>			OH	B''	0
b						A'	24.2
c						D	37.8
21 a	4	<i>Me</i>			<i>P-Me</i>	B	0
b						A	5.8
c						D	10.5
d						C^e	15.0
22 a	4	<i>i-Prop</i>			<i>P-Me</i>	B	0
b						D	8.7
c						A	11.6
d						C	35.9
23 a	4	<i>t-But</i>			<i>P-Me</i>	B''	0
b						D	45.9
c						A'	56.5
d						C^e	59.9

^a Calculated under the assumption of a propellerlike diaryl skeleton and conical symmetrical aryl substituents

^b See Fig. 3

^c From each set of conformers belonging to conformations **A**, **B**, and **D** (Fig. 3) only the conformer of lowest energy is given

^d Perpendicular

^e Distorted

conformers with the above characteristics are listed in Table 1. Moreover, the ethyl groups in **11** may be arranged above or below the plane of the aryl rings resulting into a maximum of 10 conformers (instead of 3 calculated for conical substituents). All conformers were located and lie within an energy range of $\pm 3.2 \text{ kJ mol}^{-1}$. Unlike the case of the isopropyl substituted diaryls, all 10 conformers of **11** are expected to take part in a conformer equilibrium.

Like the ground state conformers of **1–13**, except the *tert*-butyl substituted conformer **13 b**, all higher energy conformers show propellerlike aryl arrangements. This situation changes significantly in the disubstituted compounds **14–23**. The ground state conformations are either propellerlike, **14**, **15**, **16**, perpendicular, **19**, **20**, **23**, or significantly distorted from a propellerlike (or perpendicular) conformation, **7**, **18**, **21**, **22**; (conformers **B'** and **B''**, Fig. 3). The higher energy conformers similarly show varying diaryl arrangements. Nevertheless the number of located minimum energy conformations corresponds to the number of conformers expected for a helical diaryl arrangement (for **20**, 3 out of 4 isomers were found) allowing a conventional analysis of the interconversion pathways in terms of flip mechanisms (see below).

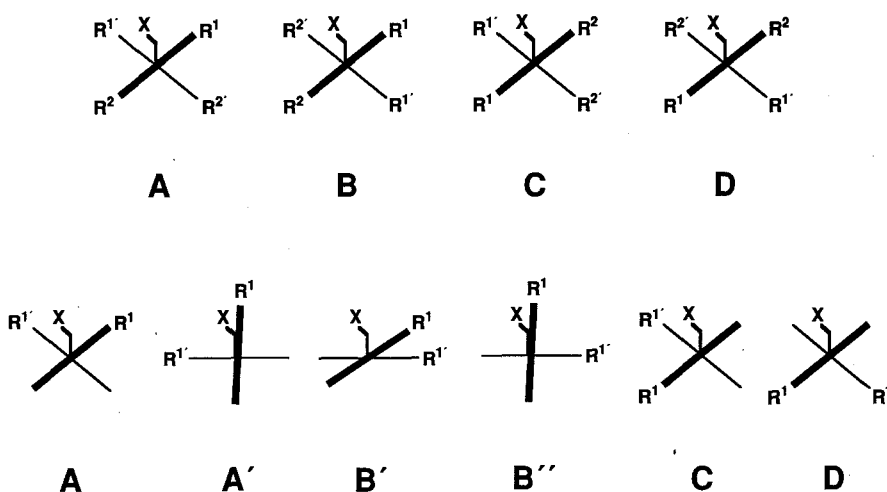


Fig. 3. Top: Possible propellerlike conformations of tetrasubstituted diaryls Ar_2Z ($Z=CH-CH_3$, $P-CH_3$; $X=CH_3$). Note: for $Z=CH_2$ ($X=H$) conformations **C** and **D** become equivalent. Bottom: Conformations of disubstituted diaryls Ar_2Z ($Z=CH-CH_3$, $CH-OH$, $P-CH_3$; $X=CH_3$, OH)

Inspection of Table 1 together with Fig. 3 shows that the ground state conformations strongly depend on the type and on the combination of substituents. While the isopropyl groups in **12 a** point below the central unit Z (Fig. 3, conformer **D**; $R^1=R^{1'}=iso\text{-propyl}$), the *tert*-butyl groups of **13 a** are located above that unit (Fig. 3, conformer **D**; $R^1=R^{1'}=tert\text{-butyl}$). A similar behavior is found for **15 a** and **16 a**. An interesting structural change is also seen in the disubstituted diaryls **14–23**. In the diaryl methanes **14–16** the ground state conformations are propellerlike although conformations **B** or **B'** (Fig. 3) are of comparable energy. For the ethanes **17–20** as well as for the methylphosphines **21–23** conformations **B** or **B'** are of lowest energy. This shift in the ground state conformation while partly induced by the central unit (CH_3-CH or $HO-CH$), is also related to a shift in the threshold mechanism as will be outlined in the next paragraphs. The main structural differences between the phosphines **21–25** and the ethanes **17–19**, **8** and **9** are found at the central unit: the $C_{\text{aryl}}-P(CH_3)$ bonds are about 0.3 \AA longer than the $C_{\text{aryl}}-CH(CH_3)$ bonds while the bond angles $C_{\text{aryl}}-P-C_{\text{aryl}}$ are smaller than those of the corresponding ethanes by about 13° . An extreme bond angle $C_{\text{aryl}}-CH_2-C_{\text{aryl}}$ is found for the very crowded molecule **7**.

Conformational Interconversion Pathways

Conformational interconversions in diaryl fragments can take place via correlated or via noncorrelated rotation of both aryl rings. As for **1**, noncorrelated rotation has been established as the threshold mechanism for many aryl-phenyl fragments [6, 19]. Structural similarities of all these compounds are one *o,o*-disubstituted and one (unsubstituted) phenyl ring with a central unit of the type $CH-X$ with a variety of substituents X . The reported experimental data for **1**, [19], together with the results of our calculations clearly indicate a threshold mechanism of uncorrelated

rotation with barriers of aryl ring rotations of $\Delta G^{\ddagger}_{228}$ (exp.) = 47 kJ mol⁻¹ for the mesityl ring rotation [19], and 26 kJ mol⁻¹ for the phenyl rotation.

For *o,o,o',o'*-tetra(alkyl)substituted methanes [8], ethanes [6, 8], sulfides [9], acetic acids [7, 8], and benzophenones [5, 8] the experimental data indicate correlated conrotation as the threshold mechanism of conformational interconversion. As mentioned above, correlated rotations are usually analyzed in terms of flip mechanisms. However, as a basic requirement for such an analysis all interconverting conformers must adopt the same diaryl skeletal geometry (for example propellerlike or perpendicular). According to our calculations this is the case for compounds **2**–**12**, **24**–**25** where all found conformers show propellerlike conformations. Propellerlike together with perpendicular or other conformations were located for all other compounds. However as pointed out in the previous section, the number of located conformers is exactly the same (with the exception of one missing conformer of **20**) as expected for a propellerlike skeleton. Hence, for analytical purposes the conformations **A'**, **B'**, and **B''** can be considered as being distorted from the propellerlike conformations **A** and **B**, respectively.

The conformational interconversion pathways are best visualized by intercon-

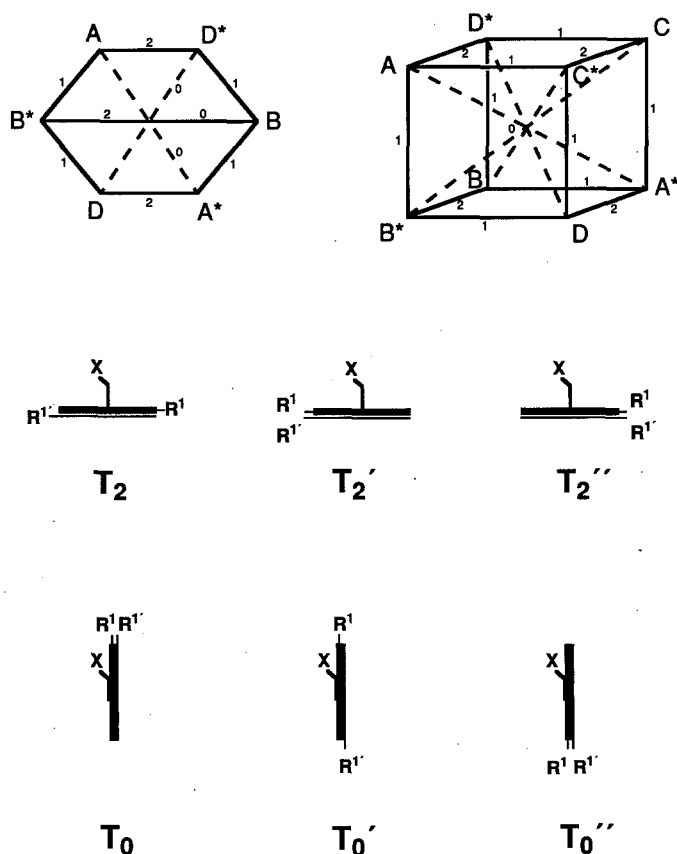


Fig. 4. Interconversion scheme of **11**–**16** (top left) and **17**–**23** (top right). Bottom: idealized transition states of possible 2-ring flips, T_2 , T_2' , T_2'' and 0-ring flips T_0 , T_0' , T_0'' ($X = \text{CH}_3$, OH). **A**, **B**, **C**, **D** are conformers defined in Fig. 3. **A'**, **B'**, **C'**, **D'** their enantiomers (for $X = \text{H}$: **B** and **C** as well as T_2' and T_2'' become equivalent)

version graphs where the vertices represent conformers and the edges interconversion pathways. Figure 4 shows the interconversion graphs of compounds **11–16** (top left), **17–23** (top right) and the different types of idealized transition states for all possible 2-ring and 0-ring flips. For **11–16**, with a central unit $-\text{CH}_2-$ conformers **B** and **C** and their enantiomers **B*** and **C*** (Fig. 3), as well as the transition states T_2' and T_2'' (Fig. 4), become identical.

With this type of analysis in mind, all 1-, 2- and selected 0-ring flips were calculated and the results are listed in Table 2. The barriers given for the 1-ring flips are those for a whole cogwheeling circuit. As can be seen from the interconversion graphs, a whole cogwheeling circuit consists either of two consecutive 1-ring flips (Fig. 1) as with compounds **3–10**, or four steps as with **11–23**. The

Table 2. Calculated interconversion barriers for diaryls **1–25**^a

	1-Ring	Activation energy (kJ/mol ⁻¹)			0-Ring flip ^b T_0
		2-Ring ^b T_2	T_2'	T_2''	
1	34 ^c , <u>26</u> ^d				
2	<u>43</u>	49	65		
3	<u>32</u>	49			
4	<u>18</u>	29			
5	<u>10</u>	54			> 165
6	<u>14</u>	91			
7	<u>15</u> ^e	> 150			
8	<u>18</u>	70			> 152
9	<u>46</u>	95			> 165
10	<u>21</u>	35			
11	<u>21</u>	60	70		69
12	<u>21</u>	65	82		
13	<u>57</u>	138			
14	16	<u>9</u>	13		62
15	29	<u>15</u>	23		44
16	<u>71</u>		100		90 ^e
17	22	25	52	<u>14</u>	91
18	49	34	57	<u>21</u>	88
19	122	82	145	<u>45</u>	116
20	109	75	100	<u>54</u>	148 ^e
21	22	36	53	<u>8</u>	70
22	33	49	58	<u>13</u>	62
23	84	80	> 150	<u>25</u>	73
24	<u>21</u>	58			152
25	<u>57</u>	71			> 165

^a Underlined numbers: flip mechanism of lowest energy

^b See Fig. 4

^c Mesityl rotation

^d Phenyl ring rotation

^e Results from BIGSTRN 3 (see Exp. Part)

cogwheeling circuit of **17–23** (Fig. 4, top right) interconverts conformers **A–B*–D–C*–A** via four diastereomeric pathways. Table 2 lists only the 1-ring flip of a cogwheeling circuit with the highest energy (usually step **B*–D**).

Inspection of Table 2 shows that for all tetraalkylsubstituted diarylmethanes, -ethanes and -phosphines, **5–13, 24–25**, the cogwheeling mechanism (1-ring flips) is by far the interconversion mechanism of lowest energy. Even for the trisubstituted diarylethane as well as the methoxy substituted compounds **3** and **4**, the 1-ring flip is calculated to be the threshold mechanism, although the 2-ring flips are in these cases only slightly higher in energy.

Except for **16**, a definitive shift towards the 2-ring flip as the mechanism of lowest energy is seen for all *o,o'*-disubstituted diarylmethanes, -ethanes and phosphines **14–23**. It is especially striking that for the ethanes and phosphines **17–23** exclusively the 2-ring flip T_2'' is significantly lower in energy than all other mechanisms.

A comparison of the calculated structural data and the interconversion barriers suggests some general trends. As one would expect, the barriers to 1-ring flips depend on the *ortho* (aryl)substituents although here their actual size has a less pronounced influence than has the substitution pattern. A comparison of the *tert*-butyl substituted diaryls **7, 13, 16, 19**, and **20** shows that the difference in the size of the *ortho* substituents is the predominant factor. The activation energy for the cogwheeling process increases in the order of $7 < 13 < 16 < 20 < 19$, with the 1-ring flip of the tetra *tert*-butyl substituted methane **7** actually being of lowest energy.

A comparison of the methanes **5** and **6** with ethanes **8** and **9** or of **14–16** with **17–20** shows that substituents at the central unit also raise the energy of the cogwheeling process. One plausible explanation could be that in the transition state the steric energy can be better released in the methanes than in ethanes by enlarging the $C_{\text{aryl}}\text{-CH}_2\text{-C}_{\text{aryl}}$ bond angle. A similar effect is also seen in the ground state structures where the bond angle at the central unit is larger in the methanes **5** and **6** than in the ethanes **8** and **9**, respectively. Finally, the 1-ring flip of phosphines **24** and **25** are almost like those of the ethanes **8** and **9**. The effect of the larger P-C bond which should cause a decrease in the 1-ring flip energy is obviously counterbalanced by the effect of the significantly smaller $C_{\text{aryl}}\text{-P-C}_{\text{aryl}}$ bond angle.

The 2-ring flips depend on the size of the *ortho* substituents and in all related compounds larger substituents cause larger energy barriers. However, very large substituents at the central unit, e.g. the *tert*-butyl group in **10**, cause a *decrease* in the energy of the 2-ring flip. A similar effect has been reported for tetraalkyl substituted 2,2-diarylethenols [10], where the 2-ring flip was found to be the interconversion mechanism of lowest energy. The difference in the 2-ring flip energy of **8** and **10** is most probably caused by a significant increase in the ground state energy of **10**. In the ground state structure of **10** the dihedral angles of the best planes of the aryl rings with the plane defined by carbons $C_{\text{aryl}}\text{-CH(CH}_3\text{)-C}_{\text{aryl}}$ are 69° and 60° as compared to 53° and 46° in **8**. Thus the *tert*-butyl group of the central unit of **10** forces the aryl rings and their substituents closer together than occurs in **8**, resulting in an increase of the ground state energy.

As pointed out above, the most striking effect caused by substrates is seen in compounds **17–23**, where the 2-ring flip T_2'' becomes the conformational interconversion pathway of lowest energy. This interconversion is shown schematically

in Fig. 5. As an example, the di-*tert*-butyldiphenylmethanol **20** was investigated by low temperature nmr.

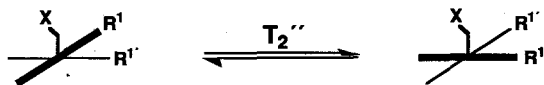


Fig. 5. Threshold mechanism of 17–23

NMR-Results

At room temperature, the proton nmr spectrum shows a single singlet for the *tert*-butyl groups which at 260 K starts to decoalesce into 2 signals (the aromatic signals also decoalesce with the limiting spectrum being reached at about 180 K). The observed exchange phenomenon is related to a change of the overall molecular symmetry. The fact that the proton signals of the central unit do not decoalesce as well as the fact that the highest overall molecular symmetry is a C_s symmetry shows that the exchange phenomenon is not caused by exchanging diastereomeric conformations but is the result of interchanging enantiomeric conformations. This indicates that the process is caused by a conrotatory motion of both aryl rings. While the experimental data do not unambiguously distinguish a single rigid asymmetric ground state conformer from a conformer interchanged by a cogwheeling process the excellent agreement between the experimental and calculated activation barriers ($\Delta G^\ddagger(\text{exp.}) = 48 \text{ kJ mol}^{-1}$ (238 K); $\Delta G^\ddagger(\text{calc.}) = 54 \text{ kJ mol}^{-1}$) strongly supports the conclusion that the two ring flip T_2' is the threshold mechanism of conformational interconversion in **20**, and, by analogy, in **17–19** and **21–23**.

Final Remarks

From our calculations and from previously reported results some general conclusions can be drawn about the expected threshold mechanisms:

(i) the expected threshold mechanism of conformational interconversion of aryl rings in aryl-phenyl fragments of the type $Ar-X-Ph$ ($X = CHR$) is noncorrected rotation but correlated rotation for benzophenones ($X = CO$) [22];

(ii) tetra (*ortho*-alkyl) substituted diaryls Ar_2X ($X = CH_2, CHR, C = O, S, P-R$) and related compounds interconvert via the cogwheeling mechanism (correlated disrotation, consecutive 1-ring flips) as the threshold mechanism;

(iii) for tri(*ortho*-methyl)substituted and tetrasubstituted diaryls with substituents less demanding than a methyl group, the activation energies of the cogwheeling mechanism and that of the 2-ring flip become comparable;

(iv) the threshold mechanism in di(*ortho*-alkyl)substituted diaryls Ar_2X ($X = CHR, PR$) is expected to be the 2-ring flip;

(v) very bulky substituents at the central unit in tetra *ortho* substituted diaryl Ar_2X ($X = CH-tert\text{-butyl}$) lower the 2-ring flip activation energy and can lead to a shift in the threshold mechanism from the 1-ring to 2-ring flip mechanism.

Experimental Part

Di(*tert*-butylphenyl)methanol (**20**) was prepared according to reference [23]. Variable temperature proton nmr spectra were recorded with a Bruker WM-250 spectrometer operating at 250.13 MHz. Temperatures were considered to be accurate to $\pm 2^\circ\text{C}$. CD_2Cl_2 was used as solvent. At 183 K two equally intense signals for the *tert*-butyl groups were observed at 1.27 and 1.60 ppm ($\Delta\nu = 82.0$ Hz). These signals coalesced at 238 K. The value of $\Delta G^\ddagger = 48$ kJ mol $^{-1}$ was calculated using the Gutowsky Holm approximation in combination with the Eyring equation.

All force field calculations were performed with Allinger's program MM2(87) [24]. In a few cases, such as **7**, extreme out of plane deformations were detected which led to very unreliable results. In those cases barriers were calculated with the Allinger force field (without π -system routines) implemented in the program BIGSTRN3 [25]. The results of these calculations are considered to be upper limits. Except otherwise indicated the MM2(87) results are listed in Tables 1 and 2. The activation barriers were calculated using Wiberg's torsion angle driving technique. 1-ring flips were calculated in the following way: the torsion angle $\text{C}_{ortho}\text{-C}_{ipso}\text{-C(P)}_{center}\text{-C}'_{ipso}$ was driven clockwise and counterclockwise over a range of 400° in steps of 10° (1° near the energy maximum). 2-ring and 0-ring flips were calculated by fixing 1 ring (torsion angle 1: $\text{C}_{ortho}\text{-C}_{ipso}\text{-C(P)}_{center}\text{-C}'_{ipso}$) at a given angle while the second ring was driven so as to pass the first ring. To search for the transition state, torsion angle 1 was varied over a wide angle range (usually $\pm 30^\circ$ away from the transition states of the idealized 1- and 0-ring flips). For the phosphine calculations a torsional parameter was added. P-C(sp 2)-C(sp 2)-C(sp 3) (atom types 25-2-2-1): $V_1 = -1.2$, $V_2 = 16.25$.

References

- [1] Mislow K. (1989) *Chemtracts-Org. Chem.* **2**: 151
- [2] Willem R., Gielen M., Hoogzand C., Pepermans H. (1985) In: Gielen M. F. (ed.) *Advances in Dynamic Stereochemistry*, Vol. 1, ch. 5. Freud Publishing House, London
- [3] Mislow K. (1976) *Acc. Chem. Res.* **9**: 26
- [4] Weissensteiner W., Scharf J., Schlögl K. (1987) *J. Org. Chem.* **52**: 1210
- [5] Lauer D., Staab K. A. (1969) *Chem. Ber.* **102**: 1631
- [6] Finnochiario P. (1975) *Gazz. Chim. Ital.* **105**: 149
- [7] Ackerman O. S., Coops J. (1967) *Rec. Trav. Chim. Pays-Bas* **86**: 55
- [8] Akkerman O. S. (1970) *Rec. Trav. Chim. Pays-Bas* **89**: 673
- [9] Lam W. Y., Martin J. C. (1981) *J. Org. Chem.* **46**: 4458, 4462
- [10] Biali S. E., Nugiel D. A., Rappoport Z. (1989) *J. Am. Chem. Soc.* **111**: 846
- [11] Schlögl K., Weissensteiner W., Widhalm M. (1982) *J. Org. Chem.* **47**: 5025
- [12] Finnochiario O., Gust D., Hounshell W. D., Hummel J. P., Paravina P., Mislow K. (1976) *J. Am. Chem. Soc.* **98**: 4945
- [13] Iwamura H., Mislow K. (1988) *Acc. Chem. Res.* **21**: 175
- [14] Bergman J. J., Chandler W. D. (1972) *Can. J. Chem.* **50**: 353
- [15] Hounshell W. D., Iroff L. D., Iverson D. J., Wroczyński R. J., Mislow K. (1980) *Isr. J. Chem.* **20**: 65
- [16] Iroff L. D., (1979) Ph. D. Thesis, Princeton University
- [17] In a previous paper [4] we have used the term conrotatory for the cogwheeling effect (1-ring flips) and disrotatory for 2-ring and 0-ring flips. To avoid difficulties with triarylsystems Ar_3X the terms correlated disrotation (associated with the 1-ring flip) and correlated conrotation (2-ring flip and 0-ring flips) are used in this paper [1].
- [18] Gust D., Mislow K. (1973) *J. Am. Chem. Soc.* **95**: 1535
- [19] Mannschreck A., Ernst L. (1971) *Chem. Ber.* **104**: 228
- [20] Hunter G., McKay R. L., Kremminger P., Weissensteiner W. (1991) *J. Chem. Soc., Dalton Trans.*: 3349

- [21] Siegel J., Gutiérrez A., Schweizer W. B., Ermer O., Mislow K. (1986) *J. Am. Chem. Soc.* **108**: 1569
- [22] Rapport Z., Biali S. E., Kaftory M. (1990) *J. Am. Chem. Soc.* **112**: 7742
- [23] Akkerman O. S. (1967) *Rec. Trav. Chim. Pays-Bas* **86**: 1018
- [24] Allinger N. L. Quantum Chemistry Program Exchange No MM2 (87), Indiana University, Bloomington, Indiana, IN 47405, U. S. A.
- [25] Nachbar R. B., Mislow K. Quantum Chemistry Program Exchange No 514, Indiana University, Bloomington, Indiana, IN 47405, U. S. A.

Received December 4, 1991. Accepted December 20, 1991