Conformational analysis of *ortho*-substituted diphenyl ethers and diphenylmethanes with linear substituents

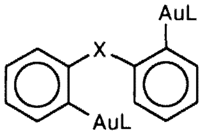
O. V. Shishkin[a] **and L. G. Kuz'mina**[b]*

[a]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: 007 (095) 135 5085
[b]N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117907 Moscow, Russian Federation.
Fax: 007 (095) 954 1279

Conformational analysis of di-*ortho*-substituted diphenylmethanes and diphenyl ethers containing I, CCH, and CCCCH substituents was carried out by the molecular mechanics method using the MM3 program. Several minima on the potential energy surface, which correspond to the *gg*, *gt*, *tg*, and *ort* conformations, were found. An increase in the length of the linear substituent results in a substantial decrease in the difference in the relative energies of conformers. Barriers to conformational transitions between the *gt*, *tg*, and *ort* conformers are less than 2 kcal mol^{-1}. The transition *ort*—*gg* requires expenditure of energy of up to 5 kcal mol^{-1}. Two valleys of centrosymmetric pairs of the *gt*, *tg*, and *ort* conformers are separated by a barrier of up to 6 kcal mol^{-1}.

Key words: *ortho*-substituted diphenylmethanes and diphenyl ethers; conformational analysis; molecular mechanics.

The characteristic feature of gold compounds with organic ligands is the participation of a gold atom in weak (secondary) interactions with various atoms and groups. Secondary Au...Au and Au...X bonds (X is a heteroatom) and agostic Au...H—C bonds with the participation of Au atoms are known. With the aim of studying the effect of secondary bonds on the structures of these compounds, we chose the following model polyaurated molecules, in which these bonds may compete with each other due to the conformational lability of the organic ligand.



X = O, S, CH_2, CH_2CH_2

L = PPh_3, dppe, dppm

As a result of rotation around the X—C(Ar) bonds, these molecules can adopt conformations in which the Au atoms are in spatial proximity either to each other or to the X group. A particular structure of the molecule can actually occur according to which interaction is preferred. Studies of these model molecules make it possible to elucidate how the changes in the geometry which occur as X changes affect the character of secondary bonds of Au atoms.

Previously, it was established by X-ray structural analysis that conformations favorable for Au...O and Au...H—C interactions, are typical of compounds with X = O [1] and CH_2 [2], respectively, whereas conformations with Au...Au bonds, which are typical of Au^{I} compounds, are uncommon for the above-mentioned compounds. It is not improbable that steric effects in the molecules prevent the formation of Au...Au bonds.

The simplest conformational calculations[1,2] demonstrated that the ligands are conformationally labile and that the Au...Au distances in the corresponding diaurated compounds change when the benzene rings rotate around the X—C(Ar) bonds in the region of sterically allowed conformations of the ligands. Therefore, the molecules under consideration can adopt conformations in which gold atoms are brought into proximity. The direct replacement of two PPh_3 ligands by one diphosphine (dppe) ligand in the diphenylmethane complex, which proceeds readily, makes the conformationally labile macrocyclic molecule with a staggered conformation favorable for an Au...Au interaction.[3] These data suggest that steric effects in these molecules exert virtually no effect on the occurrence of a particular secondary bond, and hence on the formation of a particular type of secondary bond. However, this suggestion needs a more severe test.

In this work, we carried out conformational analysis of di-*ortho*-substituted diphenylmethanes and diphenyl ethers (**1a—c** and **2a—c**).

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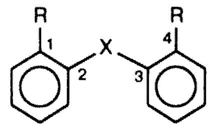


1a: X = CH_2, R = I

1b: X = CH_2, R = C≡CH

1c: X = CH_2, R = C≡C—C≡CH

2a: X = O, R = I

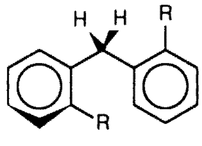
2b: X = O, R = C≡CH

2c: X = O, R = C≡C—C≡CH

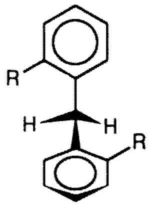
The spatial structures of molecules **1a—c** and **2a—c** were calculated by the molecular mechanics method[4] with the MM3 force field.[5] The potential energy surfaces were calculated by scanning the φ_1 and φ_2 torsion angles in the range of 0—350° with a step of 10° and with optimization of the other geometric parameters at each step.

The choice of the above-mentioned linear substituents is determined by the necessity of simulating an extended linear —Au—P fragment, which cannot be included in the molecular mechanics calculations because the parameters of the potential for the gold atom are unavailable. Computer simulations of the corresponding diaurated compounds demonstrated that phenyl substituents at the phosphorus atom are rather far removed from an organic ligand and do not impose additional conformational restrictions at least in the range of conformations of interest.

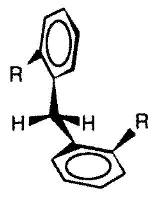
The molecules of diphenylmethane and diphenyl ether have two rotational degrees of freedom associated with rotations around the C(Ar)—X bonds. Therefore, we chose the C(1)C(2)XC(3) and C(4)C(3)XC(2) torsion angles (φ_1 and φ_2 angles) as the geometric characteristics of possible conformers of **1a—c** and **2a—c**. According to the results of the calculations (Table 1), four pairs of centrosymmetric conformers with *gauche—gauche-* (*gg*), *gauche—trans-* (*gt*), *trans—gauche-* (*tg*), and perpendicular (*ort*) mutual arrangements of benzene rings occur for these molecules.



gt



ort



gg

The *gt* and *tg* conformers are equivalent because they have a twofold rotation axis passing through the bridging atom.

The conformer with a virtually perpendicular orientation of the aromatic rings with respect to the C—X bonds is the most stable for the compounds under consideration (see Table 1), unlike diphenylmethane, which adopts the *gg* conformation.[6] In all cases, the *gg* conformer has the highest energy, which is due to the proximity of the *ortho* substituents. This effect is particularly pronounced in the case of the diiodo derivative of diphenyl ether **2a** (see Table 1).

Table 1. Torsion angles φ_1 and φ_2 and relative energies (ΔE) of conformers

Compound	X	R	Conformer	φ_1	φ_2	ΔE /kcal mol^{-1}
				deg		
1a	CH_2	I	*gg*	62.1	62.1	0.81
			gt	73.3	146.5	0.0
			tg	−146.6	73.2	0.0
			ort	110.0	110.0	0.03
1b	CH_2	CCH	*gg*	72.0	72.0	0.74
			gt	73.2	−128.1	0.54
			tg	−128.0	73.0	0.54
			ort	101.1	101.1	0.0
1c	CH_2	CCCCH	*gg*	72.4	72.4	0.17
			gt	73.4	−127.0	0.04
			tg	−127.0	73.4	0.04
			ort	98.9	98.9	0.0
2a	O	I	*gg*	58.7	58.7	4.05
			gt	78.6	−149.1	1.41
			tg	−149.0	78.7	1.41
			ort	118.4	118.4	0.0
2b	O	CCH	*gg*	63.4	63.4	1.69
			gt	72.9	−130.9	0.83
			tg	−130.9	72.9	0.83
			ort	110.9	110.9	0.0
2c	O	CCCCH	*gg*	61.7	61.7	0.91
			gt	73.4	−129.7	0.26
			tg	−129.6	73.4	0.26
			ort	110.1	110.1	0.0

The distance between the carbon atom at the *ortho* position of the benzene ring and the terminal atom of the R substituent is 2.1, 3.62, and 6.02 Å for I, CCH, and CCCCH, respectively. An increase in the length of the linear substituent R causes the difference in the relative energies of the conformers to decrease. The exception is compound **1a**, for which the *gt* and *ort* orientations are almost equally stable. Apparently, the decrease in the above-mentioned differences is associated with destabilization of the *ort* conformer caused by an increase in unfavorable nonbonded interactions between substituents and hydrogen atoms at the *ortho* positions of adjacent rings. The decrease in the angles of rotation of the rings with respect to each other in the *ort* conformation (see Table 1) is also indicative of this fact.

The φ_1 and φ_2 torsion angles in acetylene derivatives **1b,c** and **2b,c** are virtually identical (see Table 1). The substantial differences in these angles in compounds **1a** and **1b**, **2a** and **2b** are apparently determined by the difference in the van der Waals radii of the carbon and iodine atoms and, as a result, by stronger repulsion between iodine atoms and the other atoms in the molecule.

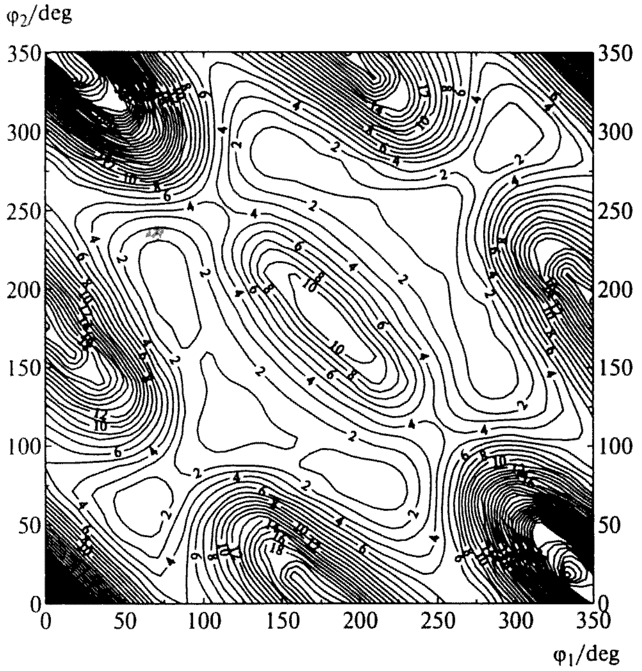


Fig. 1. Potential energy surface as a function of the φ_1 and φ_2 torsion angles of molecule **1a**.

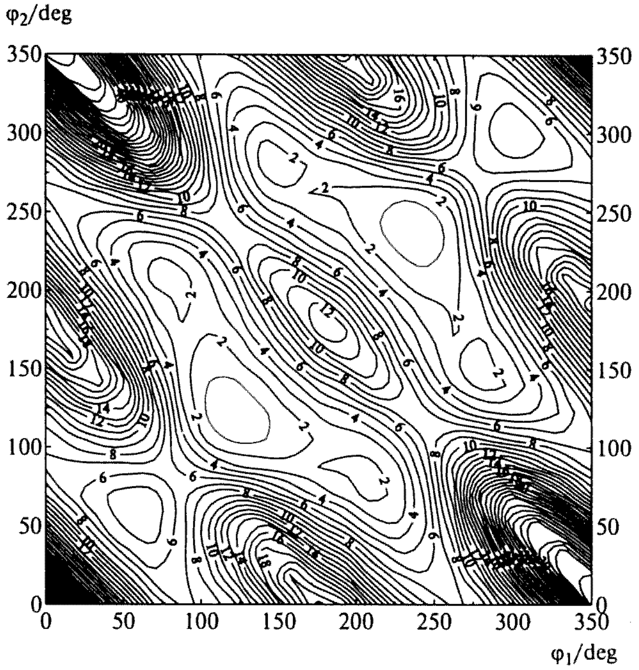


Fig. 2. Potential energy surface as a function of the φ_1 and φ_2 torsion angles of molecule **2a**.

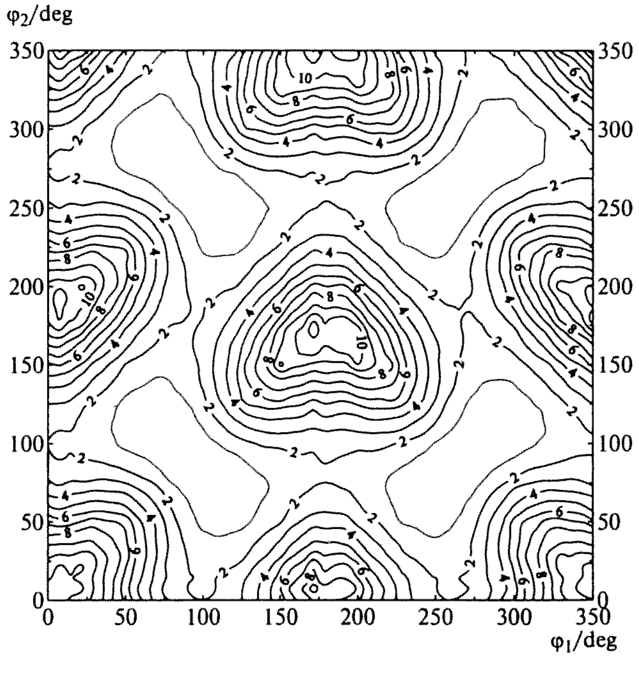


Fig. 3. Potential energy surface as a function of the φ_1 and φ_2 torsion angles of the diphenyl ether molecule.

The analysis of the potential energy surfaces as a function of the φ_1 and φ_2 torsion angles in compounds **1a** and **2a** (Figs. 1 and 2) demonstrated that a rather wide valley with shallow minima corresponds to the *gt*, *tg*, and *ort* conformers. The barriers to transitions between these conformers are no more than 2 kcal mol^{-1}. The local minima separated by low barriers belong to *gauche—gauche* conformations. The transition from the *ort* conformer to the *gg* conformer requires substantial expenditure of energy (up to 5 kcal mol^{-1}).

The two valleys of the centrosymmetric pairs of the *gg*, *tg*, and *ort* conformers are also separated by a high barrier (up to 6 kcal mol^{-1}). The conformational transitions *gt—gg* and *gt—tg* can occur only through the *ort* conformation, whereas the *ort—ort* transition can occur only through the *gt* or *tg* conformation. Barriers to the conformational transitions *gt*—*g*–*t* and *gt*—*t*–*g* are virtually identical, and these processes occur without formation of intermediate conformers.

The experimental structures of diaurated molecules (in diaurated diphenylmethane, φ_1 = 179°, φ_2 = −73°; in diaurated diphenyl ether, φ_1 = −175°, φ_2 = 80°) correspond to the *gt* conformer. An aurophilic interaction is possible in the range of *gg* conformations on moving along the potential energy surface either toward decreased or increased values of the φ angles. The increase in the steric energy in this region for diiodo-substituted compounds is caused primarily by the mutual repulsion between bulky iodine atoms. The repulsion between these atoms and the carbon atoms of adjacent rings is less substantial because of the larger covalent radius of the iodine atom. The gold atom has a substantially smaller van der Waals radius (1.66 Å compared to 2.20 Å for iodine) and, therefore, for digold-substituted derivatives, the increase in the energy in this region is considerably smaller. Besides, because mutual attraction between gold atoms should occur due to the aurophilic interaction, primarily steric hindrance in the ligand can be essential in this region.

To take into account only the steric repulsion between benzene rings and bridging groups, we calculated the conformational energies of molecules without *ortho* substituents. The conformational maps for diphenyl ether and diphenylmethane are basically identical. Hence, the data on the diphenyl ether alone are shown in Fig. 3. In the absence of *ortho* substituents, the transition between all conformations (the energy barriers are less than 2 kcal mol^{-1}) is virtually unhindered. Movements in the region of *gg* conformers, in which aurophilic interactions can occur in the di-*ortho*-aurated molecule, do not encounter steric hindrances in the ligands.

Note that as the φ_1 and φ_2 angles change by 10° with respect to the *gg* conformations of molecules **1a** and **2a**, the Au...Au distance in the diaurated derivatives becomes close to 3.3 Å, which corresponds to the aurophilic interaction. Generally, these interactions occur at distances which vary in a wide range (from 2.6 to 3.4 Å).[7] Therefore, the results of the conformational analysis confirm the fact that the diaurated molecules can adopt conformations with adjacent gold atoms.

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