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A Computational Study on Some Pyridine-Substituted-Bis-1,2,4-Triazole Derivatives and Investigation of Their Catalytic Activities

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Abstract

In this work were specified catalytic activity of pyridine-substituted-bis-1,2,4-triazole (PBTT) derivative ligands 5,5′-(pyridine-2,5-diyl)bis(4-ethyl-4H-1,2,4-triazole-3-thiol) (L_1) and 5,5′-(pyridine-2,5-diyl)bis(4-phenyl-4H-1,2,4-triazole-3-thiol) (L_2) in biaryl synthesis *in situ*-reaction condition. Catalytic activities are determined in terms of conversion percentages to derivatives of biaryl of aryl bromides by GC-MS. The highest catalytic effect for L_1 ligand was measured as 61% with 4-bromobenzaldehyde. Apart from catalytic activity studies, some structural properties of related ligands were discussed by computational methods. As a result, the ground state geometries, frontier molecular orbitals (FMOs) and also the maps of molecular electrostatic potential (MEP) of L_1 and L_2 ligands were obtained using DFT/B3LYP/6-31+G(d) calculations. Additionally, the global reactivity descriptors were reached using the FMOs calculations.

Keywords: Catalytic activity, density-functional theory, *in situ*-reaction condition, pyridine-substituted-bis-1,2,4-triazole derivatives

Bazı Piridin-Sübstitüe-Bis-1,2,4-Triazol Türevleri Üzerine Hesaplamalı Bir Çalışma ve Katalitik Aktivitelerinin İncelenmesi

Öz

Bu çalışmada piridin-sübstitüe-bis-1,2,4-triazol türevi (PBTT) ligandlarının (L_1: 5,5′-(piridin-2,5-diil)bis(4-etil-4H-1,2,4-triazol-3-tiyol) ve L_2: 5,5′-(piridin-2,5-diil)bis(4-fenil-4H-1,2,4-triazol-3-tiyol)) biaril sentezinde *in situ*-reaksiyon koşullarında katalitik aktiviteleri belirlendi. Katalitik aktiviteler, GC-MS ile aril bromürlerin biaril türevlerine dönüşüm yüzdeleri cinsinden belirlendi. L_1 ligandı için en yüksek katalitik etki 4-bromobenzaldehit ile %61 olarak ölçüldü. Katalitik aktivite çalışmalarının yanı sıra, ilgili ligandların bazı yapısal özellikleri hesaplama yöntemleriyle tartışıldı. Sonuç olarak, DFT/B3LYP/6-31+G(d) hesaplamaları kullanılarak L_1 ve L_2 ligandlarının temel durum geometrileri, sınır moleküler orbitalleri (FMOs) ve ayrıca moleküler elektrostatik potansiyel (MEP) haritaları elde edildi. Ek olarak, global reaktivite tanımlayıcıları FMOs hesaplamaları kullanılarak elde edildi.

Anahtar kelimeler: Katalitik aktivite, yoğunluk fonksiyonel teorisi, *in-situ* reaksiyon koşulları, piridin-sübstitüe-bis-1,2,4-triazol türevleri

INTRODUCTION

(PBTT) derivatives that contain triazole and pyridine ring have a significant place medically and pharmacologically (Ahirwar et al., 2017). Numerous studies have been reported about medical and pharmacological applications of these compounds include significant biological activities in the literature (Bulut et al., 2018). Besides the biological applications mentioned, mercapto-1,2,4-triazoles antibacterial and antioxidant activities, the using of 1,2,4-triazole derivatives in different therapeutical drug candidates as antimicrobial, anti-inflammatory and sedative agents can be exemplified to these application fields. Compounds in this class can give different heterocyclic compounds such as thiazolotriazoles, triazolothiadizoles, triazolothiazepines, and triazolothiadiazines via various reactions with numerous reagents in terms of synthetic organic chemistry. These compounds are preferred as easily accessible nucleophilic centers for

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the preparation of N-bridged heterocyclic compounds due to their amino and mercapto groups (Muthal et al., 2010; Muneer et al., 2014; Bulut et al., 2018). Moreover, catalytic activities of (PBTT) derivatives besides pyridine–substituted-1,2,4-triazole derivatives weren't investigated in detail (Turek et al., 2014).

In addition, some studies reported on the electronic structures of heterocyclic thione derivatives and the thiol-thione tautomeric equilibrium (Coyanis et al., 2002; Cansiz et al., 2009). In the X-ray single crystallographic analysis of 1,2,4-triazole compounds, N-H…S hydrogen bonds forming dimers which are linked into a chain by N-H...N hydrogen bonds (Dege et al., 2004; Dege et al., 2005).

Actually, we aimed to investigate the catalytic activities of palladium complexes that include (PBTT) derivatives. By reason of solubility and purification problems during the synthesis of the complexes of related ligands came to light, for this reason, we decided to investigate the catalytic activities of these ligands *in situ*-reaction conditions. Information about the molecular geometry and electronic properties were obtained by DFT calculations.

MATERIAL AND METHOD

(PBTT) derivatives (L_1: 5,5′-(pyridine-2,5-diyl)bis(4-phenyl-4H-1,2,4-triazole-3-thiol) and L_2: 5,5′-(pyridine-2,5-diyl)bis(4-ethyl-4H-1,2,4-triazole-3-thiol) were synthesized according to the given procedure in the literature (Çetin and Dayan, 2009). The B3LYP/6-31+G(d) optimized structures of the L_1 and L_2 ligands are given in Figure 1.

According to Suzuki coupling reaction, the synthesis of biaryl between aryl bromide and phenylboronic acid was performed *in situ*-reaction conditions.

General Procedure for the Suzuki Coupling Reaction *in situ*-Reaction Conditions

(PBTT) derivatives L_1 and L_2 (2.0 mmol %), $PdCl_2$ (1.0 mmol %), aryl bromide (1.0 mmol %), phenylboronic acid (1.0 mmol %), K_2CO_3 (2 mmol %), and 2 mL *i*-PrOH/H_2O (1:3), were taken up to a small Schlenk tube and the temperature of the reaction mixture was raised to 80 °C for 15 h. The purification was completed via GC and the yield of the reaction was based on aryl bromide.

Computational Details

The ground-state geometries of the L_1 and L_2 ligands are obtained using the B3LYP method at a 6-31+G(d) basis set. The geometric parameters with atom numbering of the L_1 and L_2 ligands are given in Appendix 1. The vibrational frequencies are calculated to show that these structures did not have an imaginary frequency. Gaussian 09 program package is used for all calculations (Frisch et al., 2010).

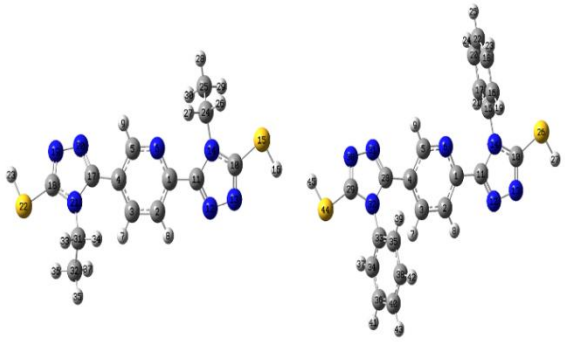

Figure 1. The optimized structures of the L_1(left) and L_2(right) ligands with atom numbering scheme (B3LYP/6-31+G(d))

RESULTS AND DISCUSSION

Catalytic Activity Results of the L_1 and L_2 Ligands

In the Suzuki coupling reaction known as the C-C coupling reaction in the biaryl synthesis, the bound groups in the selected substrates (-CH=O, -CH_3C=O and -OCH_3) are in the para-position and therefore, have no steric effect. However, if an electron-withdrawing group is bound to the aromatic ring in the substrate, the Ar-Br bond is weakened, whereas the electron donor group is bound, the electron density of the Ar-Br bond is increased and the C-Br bond becomes difficult to break (İnce, 2016).

The catalytic activity of the L_1 ligand in the Suzuki coupling reaction that is performed in situ reaction conditions was determined 32%, 52%, and 61%, respectively, when used 4-bromo anisole, 4-bromo acetophenone, and 4-bromo benzaldehyde.

The bonded groups on aromatic ring of substrate lead to the increase in catalytic activity. This increase is compatible with electron-withdrawing group or electron donor group at the aromatic ring of a substrate (İnce, 2016). However, the obtained catalytic activity results are lower when compared to the catalytic activity of the benzimidazole derivatives (Özdemir et al., 2007; Yiğit et al., 2010).

When using the ligand of L_1 in the synthesis of biaryl, 52%, and 61% yield were achieved with 4-bromoacetophenone and 4-bromobenzaldehyde. The

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L_1 ligand includes bound ethyl group to either triazole nitrogen atom, otherwise, the ligand of L_2 has bound phenyl group to either nitrogen atom of triazole ring. The same experiments for either substrate were repeated by using L_2 ligand and was obtained 48% and 50% yield respectively with 4-bromobenzaldehyde and 4-bromoacetophenone. A control experiment with $PbCl_2$ indicated that the Suzuki coupling reaction resulted in lower yield in the absence of L_1 ligand (See experiment number 6 Table 1).

Computational Study Results

Potential energy surface (PES) scans are done around the six single bonds to find the most stable conformers of L_1 and L_2 at HF/6-31G(d) level of theory. The mentioned dihedral angles are τ_1=N6-C1-C11-N12, τ_2=C5-C4-C17-N21, τ_3=N21-C18-S22-H23, τ_4=C17-N21-C31-C32, τ_5=C11-N14-C24-C25 and τ_6=N6-C1-C11-N12 for L_1. The scan runs are performed by varying the dihedral angles at a step of 10^o in the range 0–360◦. Then the most stable conformers of $L_1$and L_2 are optimized on the B3LYP method at 6-31+G(d) basis set to give the ground-state geometries of L_1 and L_2 as seen in Figure 1. Comparison of the Hartree-Fock (HF) and DFT methods, the DFT calculations based on the B3LYP level give much more sensitive results in predicting structural and electronic properties than HF methods. Therefore, we used DFT/ B3LYP method in our all other calculations. C3-C4-C28-N31 and N6-C1-C11-N14 dihedral angles of L_2 are calculated as -149.13^o and -6.98^o, respectively. Phenyl rings twisted triazole rings with angels of 86.04^o (C11-N14-C15-C17) and 69.46^o (C28-N32-C33-C35). The bond lengths C10-S26 and C29-S44 are found as 1.764^o. The dihedral angles of N32-C29-S44-H45 and N14-C10-S26-H27 are calculated as 177.81^o and -179.65^o, respectively. The corresponding dihedral angles of L_1 are found as 171.07 ^{o} and 176.07 ^{o}. As seen in Figure 1, the molecular shape of L_2 is almost similar to L_1.

HOMO-LUMO Gaps and Reactivity Descriptors

Molecular orbital theory is widely used to understand important properties of organic molecules such as their electronic, biological, optical and chemical reactivity. According to frontier molecular orbital theory, the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) provide information about the chemical reactivity of the species (Özdemir Özmen et al., 2014; Gündüzalp et al., 2016; Özdemir Özmen et al., 2017). Furthermore, the difference between the HOMO and LUMO energy, so HOMO-LUMO energy gap, will helpful in measuring the optical polarizability, chemical softness-hardness, biological activity and kinetic stability of the molecules. The shapes of HOMO and LUMO of L_1 and L_2 are determined using the DFT/B3LYP method with 6-31G+(d) (Figure 2).

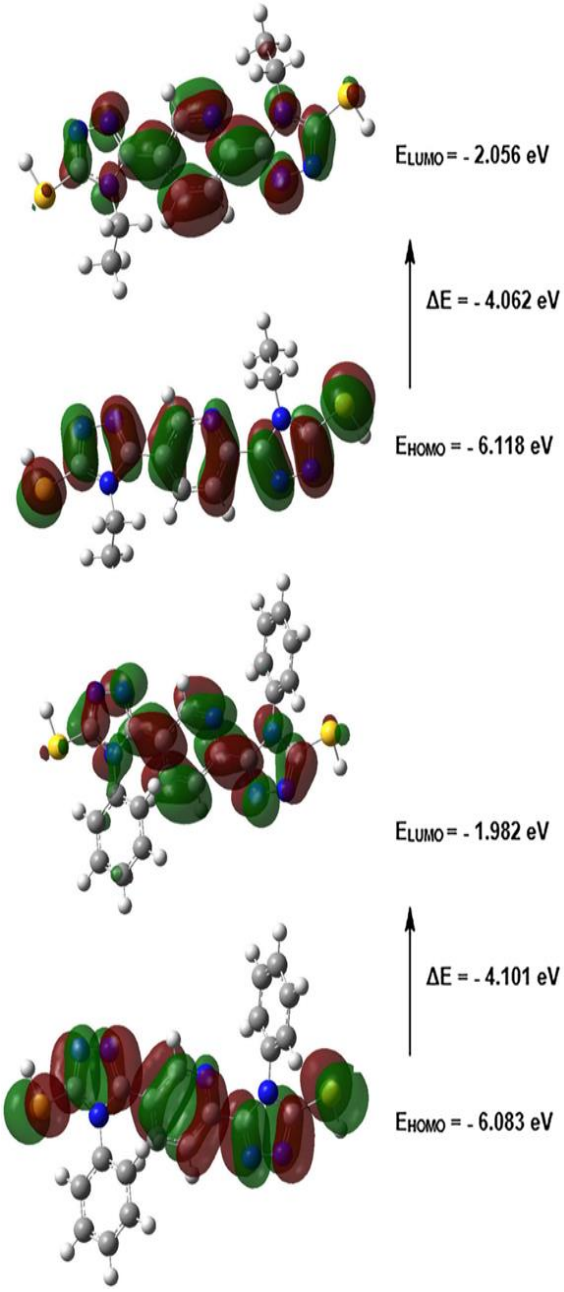

Figure 2. FMOs of the L_1 (top) and L_2 (bottom) ligands

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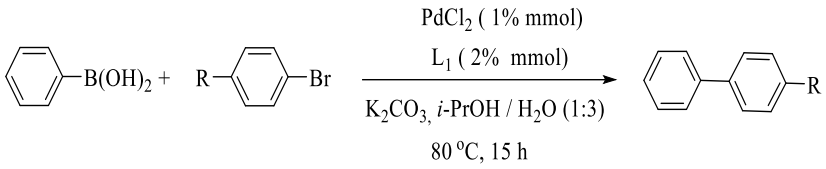
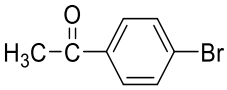
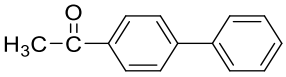
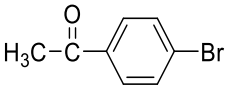
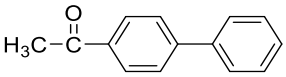
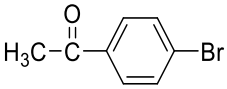
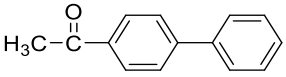
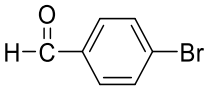
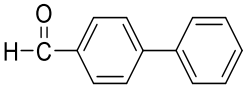
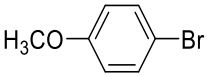
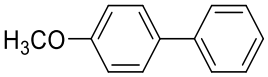
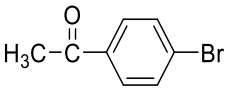
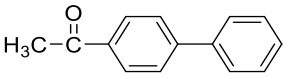
Table 1. The Suzuki coupling reaction of aryl bromides with phenylboronic acid *in situ*-reaction conditions ($PdCl_2/L_1$)[a]



Experiment number	Aryl bromide	$PdCl_2$/ L_1	Product	Conversion percentage
1		**L_1**		18[b]
2		**L_1**		33[c]
3		**L_1**		52
4		**L_1**		61
5		**L_1**		32
6		**$PdCl_2$**		25

[a]*Reaction conditions*:1 mmol phenylboronic acid, 1 mmol aryl bromide, 2 mmol K_2CO_3, 2 mmol L_1, 2 mL *i*-PrOH/H_2O (1:3), temperature 80 °C, 15 h. [b]Solvent: 1,4-dioxane, [c]Reaction time: 8 h

Table 2. Calculated global reactivity descriptors for ligands in eV

Compound	I	A	ΔE	X	μ	η	S	ω
L_1	6.118	2.056	4.062	4.087	-4.087	2.031	0.246	4.112
L_2	6.083	1.982	4.101	4.033	-4.033	2.051	0.244	3.965

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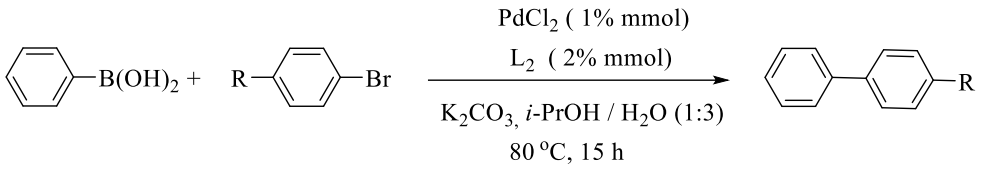
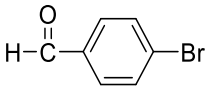
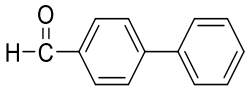
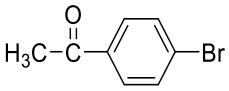
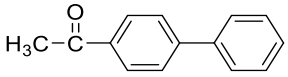
Table 3. The Suzuki coupling reaction of aryl bromides with phenylboronic acid *in situ*-reaction conditions ($PdCl_2/L_2$)[a]



Experiment number	Aryl bromide	$PdCl_2$/ L_1	Product	Conversion percentage
1		L_2		48
2		L_2		50

[a]*Reaction conditions*:1 mmol phenylboronic acid, 1 mmol aryl bromide, 2 mmol K_2CO_3, 2 mmol L_2, 2 mL *i*-PrOH/H_2O (1:3), temperature 80 °C, 15 h

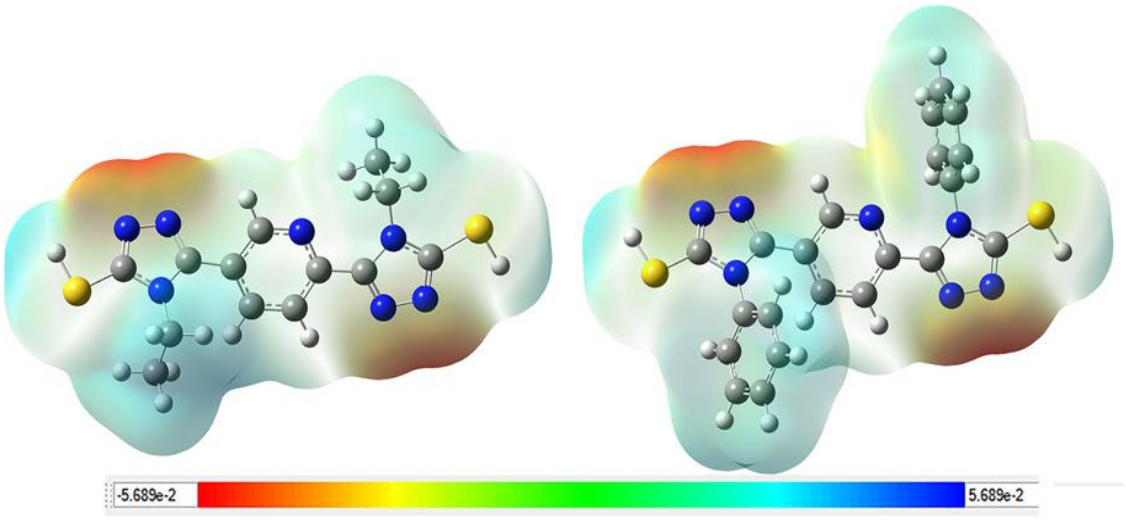


Figure 3. The molecular electrostatic potential (MEP) map of the L_1 (left) and L_2 (right) ligands

Global reactivity descriptors such as ionization potential ($I = -E_{HOMO}$), electron affinity ($A = -E_{LUMO}$), energy band gap ($\Delta E = E_{LUMO}–E_{HOMO}$), electronegativity ($\chi=I+A /2$), chemical potential ($\mu = - \chi$), global hardness ($\eta = I-A/2$), global softness ($S= 1/2\eta$) and global electrophilicity index ($\omega = \mu^2 /2\eta$) were identified to predict global chemical reactivity trends of L_1 and L_2 ligands (Table 2). Global chemical reactivity trends can be predicted with global chemical reactivity descriptors.

The energies of HOMO and LUMO are calculated as -6,118 eV and -2.056 eV for L_1, respectively. The electron densities of FMOs were located on the whole molecule except ethyl groups for

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L_1. The energy of HOMO is calculated as -6.083 eV and the energy of LUMO is calculated 1.982 eV for L_2, respectively. Both of the FMOs consist of the whole molecular moiety except phenyl rings. The energy gap for ligands L_1 and L_2 are obtained as 4.062 eV and 4.101 eV, respectively. A soft molecule has a low energy gap. The energy band gap of L_1 is lower than the energy band gap of L_2, also L_1 is a bit more polarizable than L_2 and more reactive towards any chemical reactions than L_2. The chemical hardness is expressed as the resistance of a molecule to changing its electron density with its environment. The less stable molecule is softer and hence more reactive. L_1 also shows a bit lower chemical stability than L_2 and the hardness of L_1 (η=2.031) is lower than L_2 (η=2.051). As a result, both calculation and experimental results show that the catalytic activity of the L_1 ligand is higher than the L_2 ligand.

Molecular Electrostatic Potential (MEP)

The molecular electrostatic potential (MEP) surface of the L_1 and L_2 ligands are given in Figure 3. The molecular electrostatic potential (MEP) surfaces shows the reactive sites for electrophilic and nucleophilic reactions of the molecules (Tomasi et al., 2005; Grabowski and Leszczynski, 2006). As seen in Figure 3, the most positive regions (blue in color) are localized on hydrogen atoms. The most negative regions (red in color) are associated with the adjacent N atoms in the triazole ring and these N atoms are the most probable active sites to react with metal ions.

CONCLUSIONS

As a result of experiments, catalytic activity of L_1 ligand was found higher than L_2 ligand. While the phenyl group has conjugation effect, in ethyl group hyperconjugation is important. The obtained result for L_1 ligand can be explained with the hyperconjugation effect of ethyl group. However, the obtained catalytic activity results of L_1 and L_2 ligand are lower when compared to the catalytic activity of the benzimidazole derivatives.

In addition to this, palladium, platinum and ruthenium complexes of smaller bulky (PBTT) derivatives can be synthesized, and then their applications in many fields, especially in the medical field, can be examined. It is expected palladium, platinum and ruthenium complexes that include (PBTT) derivatives may have more dominant properties than free ligands. The MEP surfaces of the nitrogen atoms in the triazole ring are red in color, ie, negative potential regions.

Acknowledgements

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CONFLICTS OF INTEREST STATEMENT

The authors declare that there is no conflict of interest in this study.

RESEARCH AND PUBLICATION ETHICS STATEMENT

The authors declare that they comply with research and publication ethics in this study.

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Appendix 1. Some optimized geometries for L_1 and L_2 ligands

L_1					
Bond lengths(Å)		Angles(º)		Dihedral angles(º)	
R(1,2)	1.406	A(2,1,6)	122.02	D(6,1,2,3)	-0.06
R(3,4)	1.406	A(5,4,17)	118.53	D(6,1,2,8)	178.99
R(3,7)	1.086	A(4,5,6)	124.00	D(11,1,6,5)	-179.64
R(4,5)	1.406	A(6,5,9)	116.60	D(2,1,11,12)	0.41
R(4,17)	1.466	A(1,6,5)	118.56	D(2,1,11,14)	-179.24
R(5,6)	1.334	A(13,10,14)	111.59	D(2,3,4,5)	0.84
R(10,14)	1.368	A(13,10,15)	125.09	D(2,3,4,17)	178.49
R(11,14)	1.386	A(14,10,15)	123.33	D(7,3,4,5)	-177.34
R(14,24)	1.474	A(1,11,12)	122.56	D(17,4,5,9)	157.49
R(18,19)	1.315	A(11,12,13)	108.47	D(5,4,17,21)	-143.59
R(18,22)	1.766	A(10,14,24)	125.70	D(1,11,14,24)	-158.74
R(19,20)	1.374	A(10,15,16)	92.44	D(12,11,1,6)	-179.33
R(21,31)	1.468	A(4,17,20)	123.41	D(12,11,14,24)	178.73
R(24,26)	1.095	A(20,17,21)	109.80	D(18,21,31,32)	81.99
R(24,27)	1.089	A(19,18,21)	111.40	D(27,24,25,28)	62.12
R(25,30)	1.094	A(21,18,22)	123.07	D(27,24,25,29)	-178.20
R(31,32)	1.531	A(18,22,23)	92.70	D(32,29,44,45)	177.81
R(31,33)	1.096	A(14,24,25)	112.62	D(14,10,26,27)	-179.65
R(32,36)	1.095	A(21,31,34)	107.17	D(3,4,17,20)	-142.90
L_2					
R(1,2)	1.406	A(2,1,6)	122.35	D(6,1,2,3)	-0.27
R(3,4)	1.406	A(5,4,28)	118.54	D(6,1,2,8)	179.36
R(3,7)	1.085	A(4,5,6)	123.91	D(11,1,6,5)	-179.25
R(4,5)	1.407	A(6,5,9)	116.57	D(2,1,11,12)	-50.29
R(4,28)	1.466	A(1,6,5)	118.39	D(2,1,11,14)	175.58
R(5,6)	1.333	A(13,10,14)	111.28	D(2,3,4,5)	0.45
R(10,26)	1.764	A(13,10,26)	125.97	D(2,3,4,28)	178.37
R(11,14)	1.390	A(14,10,26)	122.75	D(7,3,4,5)	-178.66
R(14,15)	1.440	A(1,11,12)	123.42	D(28,32,33,35)	69.46
R(29,30)	1.314	A(1,11,14)	127.08	D(5,4,28,31)	28.76
R(29,44)	1.764	A(10,14,15)	124.97	D(1,11,14,15)	-21.28
R(30,31)	1.375	A(10,26,27)	92.13	D(12,11,1,6)	174.71
R(32,33)	1.435	A(4,28,31)	123.91	D(11,14,15,17)	86.04
R(33,35)	1.398	A(31,28,32)	109.43	D(21,18,22,31)	171.07
R(26,27)	1.350	A(29,44,45)	92.21	D(14,10,15,16)	176.07
R(38,42)	1.086	A(34,36,41)	119.60	D(4,28,31,30)	179.99
R(40,43)	1.087	A(40,36,41)	120.23	D(32,28,31,30)	0.30
R(44,45)	1.349	A(35,38,40)	120.22	D(4,28,32,29)	179.93
R(34,37)	1.086	A(38,40,43)	119.98	D(3,4,28,31)	-149.13