CROATICA CHEMICA ACTA
CCACAA **76** (4) 357–363 (2003)

ISSN-0011-1643
CCA-2894
Original Scientific Paper

Ab initio and Semiempirical Modelling of Stereoselectivities of Diels-Alder Cycloadditions of Furan and Cyclopentadiene with Norbornenes

Davor Margetić[a,]* and Ronald N. Warrener[b]

[a]*Laboratory for Physical Organic Chemistry, Division of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, P. O. Box 180, 10002 Zagreb, Croatia*

[b]*Centre for Molecular Architecture, Central Queensland University, North Rockhampton, 4702, QLD, Australia*

RECEIVED JULY 5, 2003; ACCEPTED SEPTEMBER 30, 2003

Key words
ab initio calculations
semiempirical calculations
cycloadditions
Diels-Alder reaction
dienes

Ab initio (RHF/3-21G and RHF/6-31G* basis sets) and semiempirical (AM1 and PM3) quantum chemical calculations have been applied to a study of Diels-Alder reactions of furan and cyclopentadiene as 1,3-dienes, with norbornene and 7-oxanorbornene as dienophiles, in order to model π-facial selectivities and stereoselectivities of these reactions. To achieve this goal, transition states for these reactions are located and activation energies estimated. The exclusive *exo* π-facial selectivity exhibited in these cycloadditions are readily predicted using semiempirical or *ab initio* methods. To determine stereochemical outcomes following π-facial attack, *ab initio* calculations are required. *Exo,endo* stereoselectivities found experimentally, are successfully predicted by using RHF/6-31G*//3-21G or higher levels of calculations. Secondary orbital interactions are postulated to be responsible for the experimental stereoselectivities.

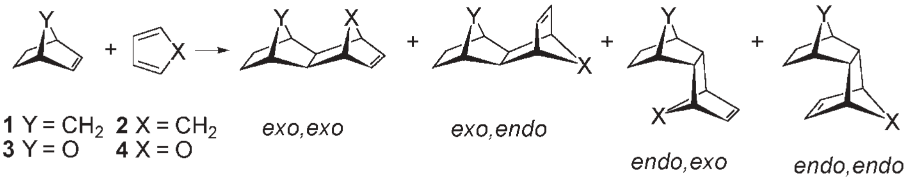
INTRODUCTION

Diels-Alder strategies have been used by us[1] and others[2] to produce rigid polyalicyclic structures. The shape of such systems depends on the specificity of the reaction used in each step of the construction. With the knowledge of stereoselectivity, for example, it is possible to introduce a bend into the framework or to extend the structure linearly. An elegant example of geometric control was reported some year ago by Stoddart who used the high diastereoselectivity associated with the reaction of alicyclic 1,3-dienes with oxanorbornenes to produce beltanes.[3] In another situation, we have employed the *exo*-selectivity of quadricyclane cycloaddition with cyclobutene-1,2-diesters to produce rigid rods.[4] More recently, our interest in the synthesis and functionalisation of cavity molecules has been predicated on knowledge of the selectivities attendant on the reaction of cyclic 1,3-dienes with rigid carbocyclic dienophiles.[5]

At the outset of our study, little work had been reported on the selectivities of cycloaddition reactions in rigid alicyclic systems using computational methods. It appeared that, without such information, it was extremely difficult to undertake rational design and so we have addressed this issue. In particular, we have set up the following goals: (i) To investigate the ability of computational methods to correctly predict the stereoselectivities of Diels-Alder reactions between alicyclic dienophiles

---

* Author to whom correspondence should be addressed. (E-mail: margetid@emma.irb.hr)



Scheme 1.

and cyclic 1,3-dienes; (ii) To work with large molecules (by computational standards) so that the outcomes can be applied to real systems; (iii) To determine computational levels of theory by which we can use these methods in a predictive way.

Here, we report the results of *ab initio* and semiempirical calculations on reactions involving furan and cyclopentadiene as cyclic 1,3-dienes and norbornene and 7-oxanorbornene as dienophiles (Scheme 1). As shown in Scheme 1, there are four different orientations of the cyclic diene during attack onto the π-bond of the bicyclic dienophile, *e.g.* norbornene. Experimentally, these reactions exhibit exclusive *exo* π-facial selectivity, as well as high *exo,endo* stereoselectivities.

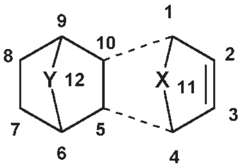
In order to explain the observed stereoselectivities, transition states for these reactions have been located and activation energies estimated at various levels of theory. Differences in activation energies were explained by estimating secondary orbital interactions between addends using Mulliken population analysis.

METHODS OF CALCULATION

Semiempirical calculations (AM1 (Ref. 6) and PM3 (Ref. 7) methods) were conducted using the SPARTAN program[8] on a Silicon Graphics R4600 workstation. These geometries have been used as the initial geometries for *ab initio* calculations with Gaussian 94.[9] All *ab initio* calculations were conducted using an IBM SP2 computer. Geometric optimizations were carried out without using symmetry or other structural restrictions. All calculations were performed at the restricted Hartree-Fock level[10] with 3-21G and 6-31G* basis sets.[11] For all structures vibrational analysis was performed with the same basis set used for optimization. Each transition structure was located using a standard routine within Gaussian 94 and verified by the possession of only one imaginary frequency of vibration, corresponding to the motion of forming new C–C bonds for concerted transition structures.[12] The activation energies were also estimated from 6-31G* and MP2/6-31G* single point calculations on the RHF/3-21G and RHF/6-31G* optimized geometries.

RESULTS AND DISCUSSION

We initially calculated the heats of formation of products for the reactions studied. The preliminary results suggest kinetic control of these reactions, as in the case of the 7-oxanorbornene/cyclopentadiene reaction leads to formation of products **9** and **10** (**P9** and **P10**).[13] RHF/3-21G, 6-31G*//3-21G and 6-31G* calculations predicted that **P9** was preferred over **P10** by 23.8, 14.1 and 14.0 kJ mol^{-1}, respectively. Similar results were obtained by estimating heats of formation of adducts of 7-oxanorbornene and furan (**P1** and **P2**). In this case 3-21G and 6-31G*//3-21G calculations predict that the *exo,exo* adduct is preferred over the *exo,endo* by 9.7 and 14.3 kJ mol^{-1}, respectively. These preliminary results led to the calculation of transition states.



Scheme 2. Numbering scheme used throughout this paper.

Energetics of the Transition Structures

The goals of this computational study were to determine the level of theory required to correctly model π-facial selectivity, and stereoselectivities.

π-Facial Selectivity

The *exo*-side preference in reactions on the norbornene and 7-oxanorbornene double bonds is a well-known fact, and has been studied theoretically and experimentally in detail.[14] Pyramidalization of olefinic hydrogens towards *endo* side is the most plausible explanation.[15] The reaction of 7-oxanorbornene and furan was used as a model reaction and only in this case were all four transition structures located (Figure 1). As the analysis of results collected in Tables I–III shows, all computational methods gave an excellent prediction of *exo* π-facial selectivity in the norbornene system. The differences in activation energies between **TS1** and **TS3** (23.4 and 27.3 kJ mol^{-1}, as estimated by AM1 and PM3, respectively) clearly indicate that *exo* attack is greatly favored over *endo* attack regardless of the diene mode of approach. As can be seen from data collected in Tables I–III, all *ab initio* levels employed in this study resulted in a similar trend – *i.e.* energetically very unfavorable *endo* additions. For instance, the differences in activation energies between **TS2** and **TS3** are 39.8, 91.3 and 60.7 kJ mol^{-1} as estimated at the

TABLE I. Heats of formation and total energies of molecules under studies[(a,b)]

Species	E_1	E_2	E_3	E_4	E_5	E_6	E_7
1	25.957	22.005	–269.369085	–270.861003	–271.766118	–270.861841	–271.767370
2	37.059	31.750	–191.717080	–192.791378	–193.422782	–192.791721	–193.423507
3	1.402	–2.938	–304.977357	–306.671852	–307.620403	–306.675564	–307.621146
4	2.959	–4.030	–227.350082	–228.622689	–229.307475	–228.625214	–229.307482
TS1	35.512	28.103	–532.274184	–535.227985	–536.910423	–535.235158	–536.910756
TS2	37.110	29.589	–532.277634	–535.229419	–536.912627	–535.236956	–536.912867
TS3	41.105	34.628	–532.259030	–535.194679	–536.889539	–535.217026	–536.895025
TS4	46.740	37.497	–532.251763	–535.192400	–536.886989	–535.212261	–536.890049
TS5	61.738	55.096	–496.663802	–499.411427	–501.052099	–499.416057	–501.053233
TS6	64.735	56.338	–496.658841	–499.409041	–501.049707	–499.413642	–501.050689
TS7	103.046	92.766	–461.024666	–463.576145	–465.169224	–463.577419	–465.171081
TS8	99.186	91.943	–461.032159	–463.583251	–465.177103	–463.584605	–465.179594
TS9	70.555	64.721	–496.653034	–499.401108	–501.036719	–499.406120	–501.039055
TS10	71.993	65.610	–496.650401	–499.402997	–501.039386	–499.407483	–501.040977

(a) $E_1 = E$(AM1); $E_2 = E$(PM3); $E_3 = E$(3-21G); $E_4 = E$(6-31G*//3-21G); $E_5 = E$(MP2/6-31G*//3-21G); $E_6 = E$(6-31G*); $E_7 = E$(MP2/6-31G*//6-31G*).

(b) For semiempirical methods heats of formation are given in kJ mol^{-1}.

3-21G, 6-31G*//3-21G and MP2/6-31G*//3-21G levels, respectively. This result is in accord with results obtained by Hehre *et al.* who recently showed that *ab initio* calculations using the 3-21G model correctly predicted the relative energies of the transition states for the two modes of attack to the diastereotopic faces of a diene.[16] Furthermore, Marchand has obtained good prediction for π-facial selectivity for the reaction of polychlorinated cyclopentadienes to norbornadiene using AM1 and 3-21G//AM1 methods.[17]

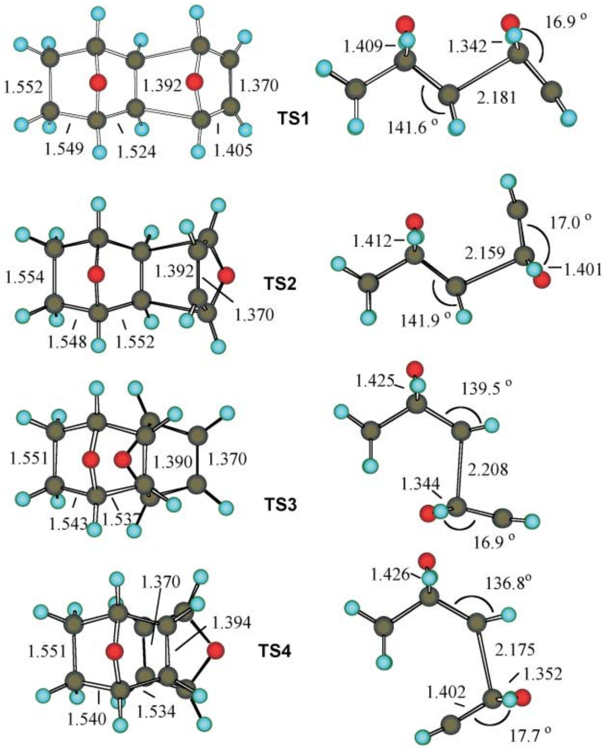


Figure 1. Structures of **TS1** – **TS4** located at the RHF/6-31G* level.

TABLE II. Calculated activation energies /kJ mol^{-1} for the Diels-Alder reactions of cyclopentadiene and furan to norbornene and oxanorbornene[(a)]

	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5	ΔE_6	ΔE_7
TS1	130.429	146.842	139.919	174.865	46.860	172.406	46.956
TS2	137.120	153.064	130.855	171.098	40.070	167.682	41.410
TS3	153.847	174.162	179.739	262.372	100.730	220.045	88.287
TS4	177.441	194.549	198.827	268.359	107.429	232.564	101.360
TS5	137.426	155.426	145.463	189.865	56.472	186.536	56.801
TS6	149.974	160.626	158.497	196.134	62.757	192.881	63.484
TS7	167.606	163.330	161.579	200.290	51.890	200.050	52.011
TS8	151.440	159.890	141.892	181.628	30.990	181.130	29.630
TS9	134.378	150.351	108.780	163.216	16.988	175.123	14.709
TS10	140.398	154.073	115.698	158.253	9.981	171.542	9.658

(a) $\Delta E_1 = \Delta E$(AM1); $\Delta E_2 = \Delta E$(PM3); $\Delta E_3 = \Delta E$(3-21G); $\Delta E_4 = \Delta E$(6-31G*//3-21G); $\Delta E_5 = \Delta E$(MP2/6-31G*//3-21G); $\Delta E_6 = \Delta E$(6-31G*); $\Delta E_7 = \Delta E$(MP2/6-31G*//6-31G*).

TABLE III. Relative energies /kJ mol^{-1} for the studied Diels-Alder reactions[(a)]

	ΔE_1	ΔE_2	ΔE_3	ΔE_4	ΔE_5	ΔE_6	ΔE_7
TS1	0	0	9.064	3.768	5.791	4.724	5.546
TS2	6.691	6.222	0	0	0	0	0
TS3	23.418	27.320	39.820	91.274	60.660	52.363	46.877
TS4	47.012	47.710	58.972	97.261	67.359	64.882	59.950
TS5	0	0	0	0	0	0	0
TS6	12.548	5.200	13.034	6.269	6.285	6.345	6.684
TS7	16.162	3.446	19.687	18.670	20.701	18.924	22.374
TS8	0	0	0	0	0	0	0
TS9	0	0	0	4.962	7.007	3.581	5.050
TS10	6.021	3.772	6.918	0	0	0	0

(a) $\Delta E_1 = \Delta E$(AM1); $\Delta E_2 = \Delta E$(PM3); $\Delta E_3 = \Delta E$(3-21G); $\Delta E_4 = \Delta E$(6-31G*//3-21G); $\Delta E_5 = \Delta E$(MP2/6-31G*//3-21G); $\Delta E_6 = \Delta E$(6-31G*); $\Delta E_7 = \Delta E$(MP2/6-31G*//6-31G*).

Stereoselectivities, exo,exo vs. exo,endo *Approach.*

The second problem we wanted to address in this paper was the determination of the lowest level of theory that was required to correctly predict stereoselectivities in these reactions. The initial study, carried out using semiempirical AM1 and PM3 methods, revealed a total lack of ability of these methods to correctly predict the stereoselectivities of reactions outlined in Scheme 1. For instance, the AM1 method predicted that for the reaction of cyclopentadiene with 7-oxanorbornene, the linear **TS5** was preferred over the bent **TS6** by 12.5 kJ mol^{-1}, a result totally opposite to that observed experimentally.[18] These predictions are opposite than published results, where AM1 calculations gave an excellent agreement with experiment.[17] It is obvious that the lack of sterically congested chlorine substituents diminishes energy differences between two modes of diene approach. In light of these results, *ab initio* methods were employed in successive calculations, starting with the 3-21G level. The four pairs of addends modeled in this study will be discussed separately.

7-Oxanorbornene + Furan (Figure 1)

7-Oxanorbornenes generally react with furan to yield mixtures of isomers.[19] *Exo,exo* and *exo,endo* isomers are found to be formed, in various reactions with the *exo,endo* isomer being always preferred. As can be seen from inspection of results collected in Tables II and III, all *ab initio* levels correctly predict the preference for the *exo,endo* approach. The computed energetic order of the transition states is the same at all computational levels, and the relative energies are very similar at all levels above 3-21G//3-21G. The minimal relative energy was estimated by the 6-31G*//3-21G method to be 3.8 kJ mol^{-1}, while the largest was at the 3-21G level (9.1 kJ mol^{-1}). As mentioned above, semiempirical methods in this case give opposite predictions. These results are in accord with our calculations on cycloadditions of 7-azanorbornenes and 5,6-benzo-2-azabicyclo[2.2.2]oct-7-ene-3-ones.[20]

The origin of the stereoselectivity may be rationalized by unfavorable steric and electronic interactions for *exo,exo* furan approach. One may assume that repulsive interactions between two oxygen lone pairs destabilize **TS1** to a greater extent than electron interactions involving an oxygen lone pair and the π-system in **TS2** because the lone pair in **TS2** bisects the double bond. This assumption is supported by an analysis of inter-atomic distances in the transition states *e.g.* the distance between the two oxygen atoms in **TS1** is 2.8 Å, close enough to have some through-space interaction. On the other hand, the distance between the oxygen atom and the carbon double bond of diene fragment in **TS2** is larger (3.0 Å), suggesting a lesser destabilizing interaction.

Mulliken population analysis, which gives a qualitative indication of the amount of electron density shared by two atoms, provides some evidence for secondary orbital interaction between two reactants and has been successfully employed by Houk *et al.* to explain stereoselectivities in Diels-Alder reaction of butadiene with acrolein.[21] In **TS1** the $O_{11}O_{12}$ overlap density has a negative value of –0.004, indicating a repulsive interaction, while in **TS2** the C_2O_{12} overlap population has the value –0.002, indicating larger destabilizing secondary orbital interactions in **TS1**.

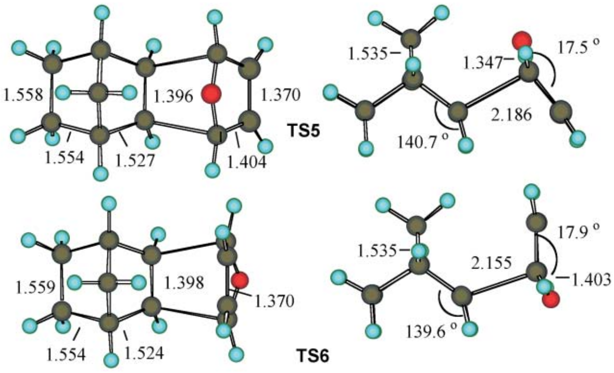


Figure 2. Structures of **TS5** and **TS6** located at the RHF/6-31G* level.

Norbornene + Furan (Figure 2)

As far as we aware, there is no published information on this reaction (or with other related norbornenes). However, there is experimental work reported by Bartlett[22] on cycloadditions of furan to the highly strained anhydride of norbornadiene dicarboxylic acid, but this will not be addressed here. Our own experience is that this reaction requires drastic conditions (such high temperatures and pressures) where furan adducts easily undergo retro-Diels-Alder reaction or polymerization. These experimental data are in good accord with theoretical predictions at all levels of theory which estimate an approximate 16 kJ mol^{-1} higher energy barrier for this reaction than for reaction of 7-oxanorbornene with furan. As can be seen from Table III, all theoretical levels employed in this study predict the *exo,exo* approach in **TS5** to be preferred over *exo,endo* **TS6**.

Employing a similar analysis of transition state structures as described for the previous reaction, we found that the distance between methylene hydrogen and oxygen bridging atoms in **TS5** is 2.3 Å, while in **TS6** the distance between hydrogen and the carbon double bond is 2.6 Å suggesting closer proximity. This may cause greater destabilizing secondary orbital interactions in **TS5** than in **TS6**. Furthermore, Mulliken population analysis estimates in **TS5**, the $O_{11}C_{12}$ negative overlap density has a value of –0.011, indicating a repulsive interaction. Similarly in **TS6**, the C_2C_{12} overlap population is repulsive with a value of –0.009. These values are small but estimate almost identical repulsive secondary orbital interactions in both modes of furan approach.

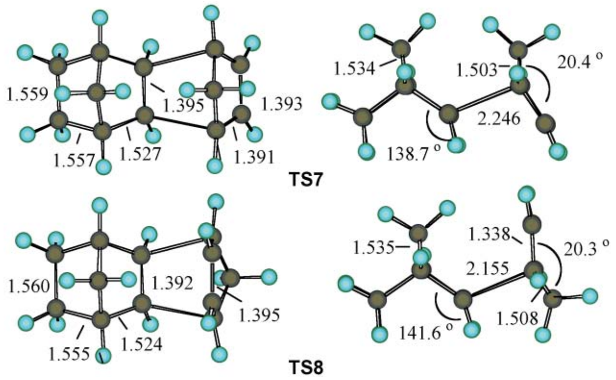


Figure 3. Structures of **TS7** and **TS8** located at the RHF/6-31G* level.

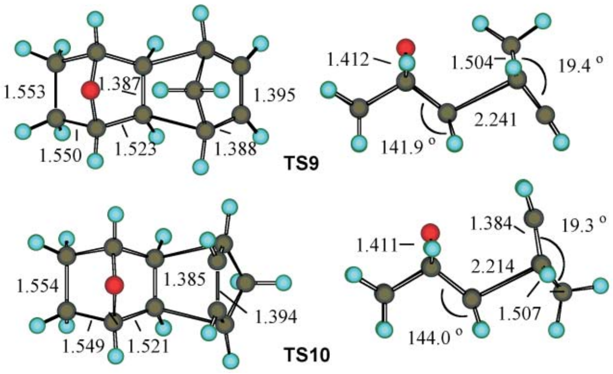


Figure 4. Structures of **TS9** and **TS10** located at the RHF/6-31G* level.

Norbornene + cyclopentadiene (Figure 3)

The reaction of norbornene with cyclopentadiene, gives only one isomer, possessing *exo,endo* geometry.[23] A comparison of the data collected in Table III reveals that activation barriers estimated at all *ab initio* levels, as well as semiempirical methods, correctly predict the *exo,endo* **TS8** to be preferred over *exo,exo* isomer **TS7**. The smallest energy difference is predicted by the 6-31G*//3-21G method (18.7 kJ mol^{-1}), the largest by MP2/6-31G*//6-31G* (22.4 kJ mol^{-1}), suggesting a high stereoselectivity for this reaction. At the semiempirical level, the AM1 method gives an essentially similar value (16.1 kJ mol^{-1}) to the *ab initio* methods, but PM3 method underestimates. The difference between these two transition states is calculated to be only 3.4 kJ mol^{-1}.

One may assume that steric repulsion between the methylene hydrogens is the major destabilizing interaction in the *exo,exo* attack. Supporting evidence for this assumption can be found in the inter-atomic distances within these transition states. The two methylene hydrogen atoms in **TS7** are separated by only 1.8 Å, while in **TS8**, the methylene hydrogen atoms and double bond carbons from diene moiety are significantly further apart (2.6 Å), suggesting larger steric repulsions in **TS7**.

For **TS7**, Mulliken population analysis estimates the $C_{11}C_{12}$ overlap density to have negative value of –0.008, indicating a repulsive interaction. In **TS8**, the C_2C_{12} overlap population is repulsive with an almost identical value of –0.009. Furthermore, the $C_{11}H_{12}$ overlap density in **TS7** is –0.007, while in **TS8** all other overlap populations between non-bonded atoms of the two addends (in two transition states) are significantly smaller, indicating reduced repulsive interactions is **TS8**.

7-Oxanorbornene + Cyclopentadiene (Figure 4)

In contrast to the three previously described reactions, the stereoselectivity for this combination is not predicted correctly either at semiempirical or at the lowest level *ab initio* (3-21G), where **TS9** is predicted to be preferred by 6.9 kJ mol^{-1}.[24] However, the energy estimations at higher theoretical levels, using the 3-21G transition state geometry correctly favor *exo,endo* **TS10**, with the smallest differences in energies between the two modes of cyclopentadiene approach at the 6-31G* level and largest for MP2/6-31G*//6-31G* (3.6 and 7.0 kJ mol^{-1}, respectively). The activation energies for this reaction are predicted to be the smallest, when compared to other three reactions investigated herein. This is in good accord with experiment, which in this case requires mild reaction conditions.

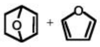
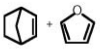
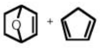
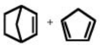
The origin of this selectivity can be found in the interatomic distances of the two approaches of addends in the TS. The distance between the methylene hydrogen and the oxygen atom in **TS9** is 2.2 Å, while in **TS10** the distance between the oxygen atom and the carbon double bond of the diene is much longer (3.0 Å), suggesting higher destabilizing steric repulsions in the *exo,exo* approach.

Mulliken population analysis provides some evidence for a larger secondary orbital interaction in **TS9** than **TS10**. The $C_{11}O_{12}$ overlap density in **TS9** has a negative value of –0.013, indicating a repulsive interaction, while in **TS10** the C_2O_{12} overlap population is repulsive but with a value of only –0.001. Differences in values suggest that repulsive secondary orbital interactions favor **TS10**.

CONCLUSION

The present results demonstrate the ability of *ab initio* calculations to accurately predict relative reactivities and stereoselectivities for Diels-Alder reactions (normal electron-demand) in alicyclic systems with cyclic 1,3-dienes. Transition states were located and activation barriers estimated at different levels of theory by semiempirical, Hartree-Fock and post-Hartree-Fock methods. As shown for the reaction of 7-oxanorbornene with furan, these reactions are under kinetic control. The exclusive *exo* π-facial selectivity exhibited in these cycloadditions were readily predicted using semiempirical and RHF/3-21G or higher *ab initio* levels. In order to determine the stereochemical outcomes following π-facial attack, higher level

TABLE IV. The comparison of relative energies /kJ mol^{-1} with experimentally observed stereoselectivities of theoretically modelled Diels-Alder reactions$^{(a,b)}$

Reaction	$\Delta\Delta E_1$	$\Delta\Delta E_2$	$\Delta\Delta E_3$	$\Delta\Delta E_4$	$\Delta\Delta E_5$	$\Delta\Delta E_6$	$\Delta\Delta E_7$	Exper. ratio$^{(c)}$
	–6.7	–6.2	9.1	3.8	5.8	4.7	5.5	30:70$^{(d)}$
	12.5	5.2	13.0	6.3	6.3	6.3	6.7	–$^{(e)}$
	16.2	3.4	19.7	18.7	20.7	18.9	22.4	0:100
	–6.0	–3.8	–6.9	5.0	7.0	3.6	5.1	0:100

(a) $\Delta\Delta E = \Delta E_{exo,exo} – \Delta E_{exo,endo}$; positive value means the preference of *exo,endo* isomer;

(b) $\Delta E_1 = \Delta E$(AM1); $\Delta E_2 = \Delta E$(PM3); $\Delta E_3 = \Delta E$(3-21G);
$\Delta E_4 = \Delta E$(6-31G*//3-21G); $\Delta E_5 = \Delta E$(MP2/6-31G*//3-21G);
$\Delta E_6 = \Delta E$(6-31G*); ΔE_7 = DE(MP2/6-31G*//6-31G*);

(c) *exo,exo*:*exo,endo* ratio;

(d) in various reactions the *exo,endo* isomer is always preferred;

(e) data not available.

calculations were required. *Exo,endo* stereoselectivities found experimentally are successfully predicted by single point energy calculations using the RHF/6-31G* basis set on the RHF/3-21G transition state structures or higher theoretical levels, as summarized in Table IV.

All transition states located correspond to early transition states, as can be deduced from an analysis of geometric parameters and supported by bond order analysis. The explanation for stereochemical preferences was also proposed by electronic and steric interactions in transition states.

Acknowledgements. – We are grateful to Professor Richard V. Williams, Professor Doug Butler and Dr. Scott Fielder for valuable discussions and suggestions during the preparation of this paper. Griffith University Supercomputer Centre in Brisbane for allocation of computer time is also acknowledged.

REFERENCES

1. R. N. Warrener, *Chem. Aust.* **59** (1992) 578–579 and references cited therein.
2. (a) W. Carruthers, *Cycloaddition Reactions in Organic Synthesis*, Pergamon, Oxford, 1990; (b) A. Wasserman, *Diels-Alder Reactions*, Elsevier, New York, 1965; (c) F. Fringuelli and A. Taticchi, *Dienes in the Diels-Alder Reaction*, Wiley, New York, 1990.
3. P. R. Ashton, U. Girreser, D. Giuffrida, F. H. Kohnke, J. P. Mathias, F. U. Raymo, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, *J. Am. Chem. Soc.* **115** (1993) 5422–5429.
4. (a) R. N. Warrener, I. G. Pitt, and D. N. Butler, *J. Chem. Soc., Chem. Commun.* (1983) 1340–1341; (b) R. N. Warrener, P. Groundwater, I. G. Pitt, D. N. Butler, and R. A. Russell, *Tetrahedron Lett.* **32** (1991) 1885–1888.
5. (a) R. N. Warrener, Lj. Maksimović, and D. N. Butler, *J. Chem. Soc., Chem. Commun.* (1994) 1831–1832; (b) D. N. Butler, P. M. Tepperman, R. A. Gau, R. N. Warrener, W. H. Watson, and R. P. Kashyap, *Tetrahedron Lett.* **36** (1995) 6145–6148; (c) R. N. Warrener, S. Wang, Lj. Maksimović, P. M. Tepperman, and D. N. Butler, *Tetrahedron Lett.* **36** (1995) 6141–6144.
6. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.* **107** (1985) 3902–3909.
7. (a) J. J. P. Stewart, *J. Comp. Chem.* **10** (1989) 209–220; (b) J. J. P. Stewart, *J. Comp. Chem.* **10** (1989) 221–264.
8. Spartan v. 4.1.1., Wavefunction Inc., 18401 Von Karman Suite 370, Irvine, California, 92715, 1996.
9. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian 94, Revision B2, Gaussian Inc., Pittsburgh, PA, 1995.
10. C. C. J. Roothan, *Rev. Mod. Phys.* **23** (1951) 69–81.
11. W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. Pople, Ab Initio *Molecular Orbital Theory*, Wiley, New York, 1986.
12. J. W. McIver and A. Komornicki, *J. Am. Chem. Soc.* **94** (1972) 2625–2633.
13. Product numbering system corresponds to their transition structures numbers: **P9**: –496.755210; –499.505034; –499.509087; **P10**: –496.764257; –499.510294; –499.514444; **P1**: –532.367736; –535.320577; **P2**: –532.364047; –535.315121, (3-21G; 6-31G*/3-21G and 6-31G* total energies in Hartrees)
14. For origins and consequences of norbornene π-facial stereoselectivity see: (a) N. G. Rondan, M. N. Paddon-Row, P. Caramella, P. Mareda, P. Mueller, and K. N. Houk, *J. Am. Chem. Soc.* **104** (1982) 4974–4978; (b) J. Spanget-Larsen and R. Gleiter, *Tetrahedron* **39** (1983) 3345–3350; (c) G. Wipff and K. Morokuma, *Tetrahedron Lett.* **21** (1980) 4445–4448; (d) S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.* **98** (1976) 4054–4061.
15. Opposite π-facial selectivity was observed in the bicyclo [2.2.2]octa-14-diene systems (*endo*): R. V. Williams, W. D. Edwards, V. R. Gadgil, M. E. Colvin, E. T. Seidl, D. van der Helm, and M. B. Hossain, *J. Org. Chem.* **63** (1998) 5268–5271.
16. W. R. Hehre, *Practical Strategies for Electronic Structure Calculations*, Wavefunction Inc., Irvine, California, 1995.
17. A. P. Marchand, B. Ganguly, C. I. Malagón, H. Lai, and W. H. Watson, *Tetrahedron* **59** (2003) 1763–1771.
18. (a) R. N. Warrener, S. Wang, R. A. Russell, and M. Gunter, *Synlett* (1997) 47–50; (b) R. N. Warrener, S. Wang, D. N. Butler, and R. A. Russell, *Synlett* (1997) 44–46; (c) R. N. Warrener, S. Wang, and R. A. Russell, *Tetrahedron* **53** (1997) 3975–3990.
19. (a) R. A. Russell, R. W. Longmore, K. D. V. Weerasuria, and R. N. Warrener, *Aust. J. Chem.* **44** (1991) 1341–1345; (b) W. G. Dauben, J. Y. L. Lam, and Z. R. Guo, *J. Org. Chem.* **61** (1996) 4816–4189; (c) K. Mackenzie, E. C. Gravett, J. A. K. Howard, K. B. Astin, and A. M. Tomlins, *J. Chem. Soc., Perkin Trans. 2* (1996) 1233–1242; (d) A. W. McCulloch, D. G. Smith, and A. G. McInnes, *Can. J. Chem.* **51** (1973) 4125–4136; (e) J. D. Slee and E. LeGoff, *J. Org. Chem.* **35** (1970) 3897–3901.

20. (a) D. Margetić, R. N. Warrener, and J. R. Malpass, *Internet J. Chem.*, Vol **2**, Article 6, (1999), http://www.ijc.com/; (b) D. Margetić, M. R. Johnston, and R. N. Warrener, *Molecules* **5** (2000) 1417–1428.
21. (a) R. J. Loncharich, F. K. Brown, and K. N. Houk, *J. Org. Chem.* **54** (1989) 1129–1134; (b) D. M. Birney and K. N. Houk, *J. Am. Chem. Soc.* **112** (1990) 4127–4133.
22. P. D. Bartlett, G. L. Combs Jr, A. X. T. Lee, W. H. Watson, J. Galloy, and M. Kimura, *J. Am. Chem. Soc.* **104** (1982) 3131–3138.
23. (a) S. B. Soloway, *J. Am. Chem. Soc.* **74** (1952) 1027–1029; (b) J. K. Stille and D. A. Frey*, J. Am. Chem. Soc.* **81** (1959) 4273–4275, the only exception of this experimental observation is reaction of cyclopentadiene to 1,2,3,4,7,7-hexachloronorbornadiene, where *endo,exo* adduct forms.[17]
24. This reaction was also investigated using DFT methods. It was found that all DFT methods employed incorrectly predict that activation energy for linear isomer **TS9** is smaller than for **TS10** by 0.88; 2.68; 0.85 and 2.27 kJ mol^{-1}, as estimated by B3LYP/6-31G*; SVWN/6-31G*; B3P86/6-31G* and BLYP/6-31G* methods, respectively.

SAŽETAK

Ab initio i semiempirijsko modeliranje stereoselektivnosti Diels-Alderovih cikloadicija furana i ciklopentadiena s norbornenima

Davor Margetić i Ronald N. Warrener

Kvantno kemijski računi rabljeni su za studiranje Diels-Alderove reakcije furana i ciklopentadiena s norbornenima. Locirana su prijelazna stanja i izračunane aktivacijske energije za ove reakcije. Isključiva *exo* π-selektivnost se mogla lako predvidjeti uporabom semiempirijskih ili *ab initio* metoda. Za predviđanje točnih stereokemijskih rezultata adicija koje slijede nakon što je definirano s koje strane alkena dolazi do reakcije diena, bilo je potrebno rabiti *ab initio* račune. Eksperimentalno dobivene *exo,endo* stereoselektivnosti uspješno su predviđene na RHF/6-31G*//3-21G ili višim računskim razinama.