

Correlation between carbon–carbon bond length and the ease of *retro* Diels–Alder reaction

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Abstract. The bond length between C8–C9 in (1'*R*,4'*S*,4*a*'*R*,8*a*'*S*)-6',7'-dimethyl-1',4',4*a*',8*a*'-tetrahydrospiro[cyclopropane-1,9'-[1,4]methanonaphthalene]-5',8'-dione is 1.571 (2) Å and between C7–C12 is 1.567 (2) Å which are longer than the corresponding bond length for saturated bicyclic systems (1.531–1.535 Å). This paper reports the correlation between bond length and the ease of *retro* Diels–Alder reaction.

Keywords. Crystal structures; *retro* Diels–Alder reaction; spirocyclic dienes.

1. Introduction

The Diels–Alder (DA) reaction is a versatile protocol for C–C bond formation and also compatible with the wide range of functional groups.¹ However, its reverse reaction i.e., *retro* Diels–Alder (rDA), has been relatively less explored owing to the high energy requirement to cross the activation barrier.² Despite existing problems, rDA reaction has evolved as a useful tool and remains to be a preferred method for the preparation of several reactive olefins or metastable molecular entities.^{3,4} The rate of rDA reaction depends on several factors like the geometry of the adducts, hetero atoms, nature of substituents tagged with the adducts, catalysts used, etc. It is well known that trimethylsilyl group on a bicyclic DA adduct exerts a positive effect on the rate of rDA reaction.⁵ Similarly, Kotha and co-workers reported that cyclopropane ring containing norbornane also exerts a positive effect on the rDA reaction due to stabilization of the transition state.⁶ In addition to these factors, studies conducted by White and co-workers on the rDA reaction of bicyclic adducts have pointed out an interesting correlation between the bond distance of the carbon atoms involved in the bond breaking process and the rate of the rDA reaction.^{7,8} To this end, they have examined bond distance between the unsaturated norbornene and its saturated counterpart by x-ray crystallographic data (figure 1). It was observed that the bond length between C1–C10 and C4–C5 has been elongated in unsaturated system **1** as compared to the saturated

system **2**. Therefore, the adduct **1** is more prone to rDA reaction. White and co-workers discussed the effect of orbital interactions on rDA reaction.

In the present manuscript, we examined the crystal structure of (1'*R*,4'*S*,4*a*'*R*,8*a*'*S*)-6',7'-dimethyl-1',4',4*a*',8*a*'-tetrahydrospiro[cyclopropane-1,9'-[1,4]methanonaphthalene]-5',8'-dione and found that the bond length between atoms connecting diene and the dienophile is somewhat longer than the normal C–C bond length. The increased bond length is responsible for the facile rDA reaction of **5**.

2. Experimental

The detailed experimental method for the synthesis of **5** has previously been reported by us.⁶ The product **5** was recrystallized using hexane-ether solvent.

3. Results and Discussion

We have synthesized several cyclopropane containing spirocyclic dienes under mild reaction conditions. The spiro-diene **3** was reacted with 2,3-dimethylbenzoquinone **4** to deliver spirocyclic adduct **5** (scheme 1). The detailed experimental method has been reported in our earlier manuscript.⁶ The *retro* Diels–Alder reaction for this bicyclic system **5** has been achieved by refluxing in toluene for 28 h with 35% yield.

After repeated attempts of crystallization from hexane-ether mixture, we were successful in getting the triclinic crystals of the DA adduct **5**, whose structure

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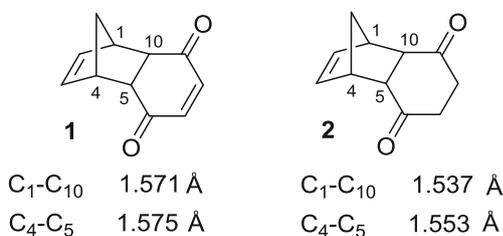
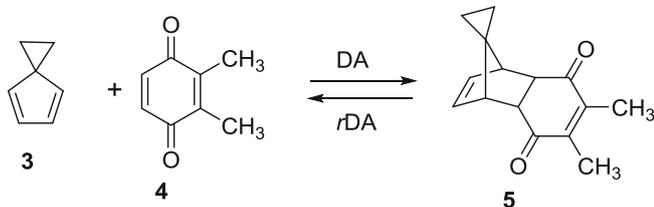


Figure 1. The molecular system examined by White and co-workers^{7,8} for correlation of bond distance with rDA reaction.



Scheme 1. The Diels–Alder and the retro Diels–Alder approaches to the norbornene system **5**.

was refined to an R factor of 4.24%. The crystal data and the details of refinement are collected in table 1. The adduct **5** has *endo* conformation with two methyl

groups flanked away from the norbornane ring, cf. figure 2. It was observed for compound **5** that the distance for C8-C9 bond is 1.571 (2) Å and that for C7-C12 bond is 1.567 (2) Å (figure 2). The bond distances observed for the carbon atoms of **5** involved in the bond breaking process are greater than the average C–C bond distance generally found in a saturated bicyclic systems which is 1.531–1.535 Å. The cyclopropane bond, (C13-C14) is aligned in a near anti-periplanar conformation to the C8-C9 bond, which undergoes cleavage during the rDA reaction. The angles between C6-C7-C12 and C1-C8-C9 were found to be 112.81 (13)° and 113.03 (13)°, respectively; clearly, the deviation from the normal angle of 109° is significant. The greater bond lengths and strained conformation in the adduct **5** are possible reasons for the facile nature of the adduct to undergo rDA reaction.

We have also prepared a spirocyclic dione **6** and found no rDA reaction under the above mentioned conditions. It clearly indicates the role of cyclopropane ring in rDA reaction (scheme 2).⁹ Unfortunately, our unsuccessful efforts thus far in obtaining crystals of the adduct **6** for x-ray structure determination preclude correlation, analogous to that of compound **5** of the bond lengths with reactivity.

Table 1. Crystal data and structure refinement details for compound **5**.

Empirical formula	C ₁₅ H ₁₆ O ₂
Formula weight	228.28
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	
a = 7.1512(9) Å	alpha = 64.04(3) deg.
b = 9.114(2) Å	beta = 88.829(16) deg
c = 10.183(3) Å	gamma = 80.669(16) deg
V/Å ³	587.9(2)
Z, Calculated density	2, 1.290 Mg/m ³
Absorption coefficient (mm ⁻¹)	0.084
F(000)	244
Crystal size	0.34 × 0.26 × 0.21 mm
Theta range for data collection	3.50 to 24.99 deg
Limiting indices	-8 ≤ h ≤ 8, -10 ≤ k ≤ 10, -11 ≤ l ≤ 12
Reflections collected/unique	4962/2058 [R(int) = 0.0188]
Completeness to theta = 24.99	99.5%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9825 and 0.9719
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	2058/0/156
Goodness-of-fit on F ²	1.091
Final R indices [I > 2sigma(I)]	R1 = 0.0424, wR2 = 0.1054
R indices (all data)	R1 = 0.0491, wR2 = 0.1098
Largest diff. peak and hole	0.273 and -0.225 e.Å ⁻³

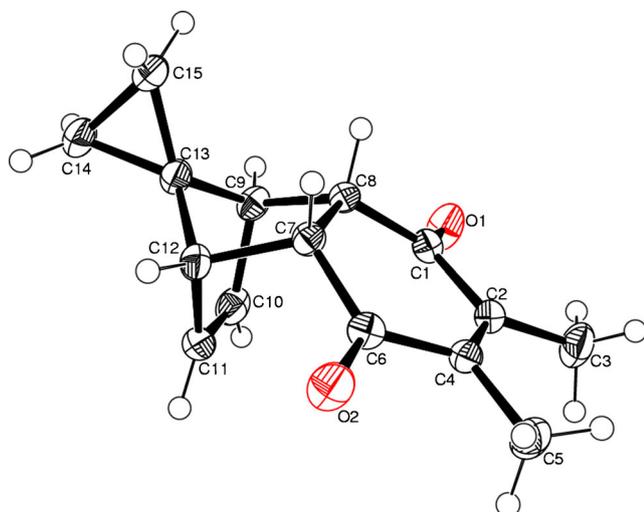
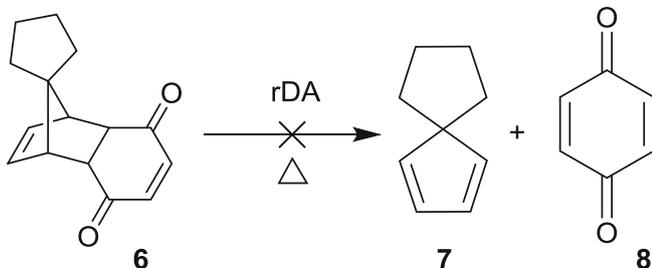


Figure 2. ORTEP perspective diagram of the structure of compound **5**.



Scheme 2. Attempted retro Diels–Alder reaction of the norbornene system **6**.

4. Conclusion

While the occurrence of Diels–Alder reactions are generally reconciled based on overlap of the frontier molecular orbitals, experimental results of *retro* Diels–Alder reactions have rarely been examined from the point of structural considerations. We have shown that the increase in the bond lengths of pertinent C–C bonds, as revealed by X-ray crystal structure analysis, is responsible for the observed facile *retro* Diels–Alder reaction of compound **5**.

Supplementary Information

X-ray diffraction data were collected on an OXFORD XCALIBUR-S CCD single-crystal X-ray diffractometer. The structure was solved and refined by full-matrix least-squares techniques on F² using the SHELX-97 program (Sheldrick, 1997). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Compound **5** CCDC 958630. Copies of available material can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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