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Regio- and stereoisomeric composition of the product mixture in the Diels–Alder reaction of dicyclopentadiene with bicyclononadiene: a NMR and DFT quantum chemical investigation

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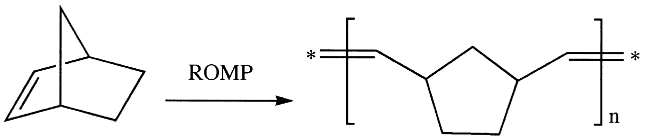
Abstract—The regio- and stereoisomeric composition of the product mixture in the Diels–Alder reaction between dicyclopentadiene and bicyclononadiene is determined by 2D $^{1}H-^{13}C$ HMQC and HMBC and ^{1}H 2D DQF COSY and NOESY NMR techniques. The absence in the experimental mixture of one of the expected products is explained by high-level quantum chemical density functional theory calculations. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Bicycloalkenes, e.g. norbornene (=bicyclo[2.2.1]hept-2-ene) and substituted norbornenes are widely used in ring opening metathesis polymerization (ROMP) (Scheme 1) which is a well-understood process.[1]

The reaction proceeds via a metal-carbene and a metallacyclobutane intermediate observable by NMR.[2–4] The generated polymers display three kinds of molecular features: (i) the C=C bond may be *cis* or *trans*; (ii) the substituents in dyads may be oriented head–head (HH), head–tail (HT) or tail–tail (TT); (iii) the cyclopentane rings in the polymer may have one of two possible configurations; successive rings may have the same configuration (isotactic) or the opposite configuration (syndiotactic).



Scheme 1. The ring opening metathesis polymerization (ROMP) of norbornene.

The relative ease of formation of the intermediate *cis* and *trans* metallacycles determines whether the double bonds eventually formed are *cis* or *trans*. A number of factors appear to be involved e.g. the number of ligands around the metal centre.

Chelating diolefins in particular can have a dramatic effect on the *cis*-content of the polymer. The ROMP of e.g. *endo*-dicyclopentadiene (DCPD) gives high-*cis* polymers as expected if the monomer provides a bidentate chelating ligand. In contrast, *exo*-DCPD, which cannot act as a bidentate ligand, gives high *trans* polymer.[5]

Although 5-substituted and 5,6-disubstituted norbornenes are preferred (co)monomers little is known about the influence of the monomer structure onto the polymer characteristics.[6] For 5,6-disubstituted norbornenes, in which the substituents are part of a ring system, the *endo*-isomers seem to be less reactive than the *exo*-isomers, probably because of the greater degree of steric hindrance in the *endo*-isomer when approaching the propagating complex.[7]

As we are interested in the ROMP of the latter compounds, more particularly of tetrahydroindanylnorbornene (THINB), it appeared as an absolute requirement to investigate first the exact composition and structure of the starting monomers.

In this study, we report on the elucidation by advanced 2D

Keywords: Diels–Alder; dicyclopentadiene; bicyclononadiene; 2D NMR; DFT.

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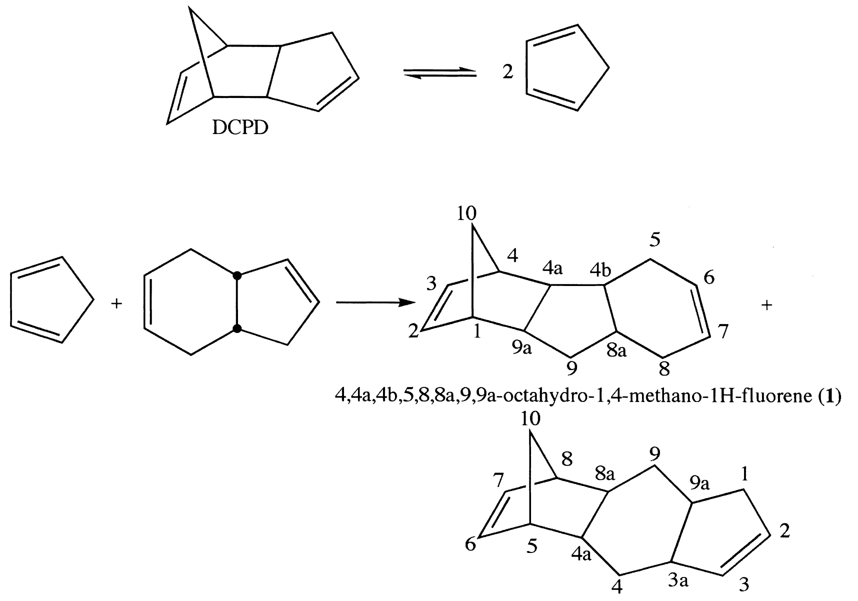


4,4a,4b,5,8,8a,9,9a-octahydro-1,4-methano-1H-fluorene (**1**)

3a,4,4a,5,8,8a,9,9a-octahydro-5,8-methano-1H-benz[f]indene (**2**)

Scheme 2. Diels–Alder reaction of dicyclopentadiene (DCPD) and bicyclononadiene(BCND).

NMR investigations of the structure of THINB, that was obtained as a mixture of tetracyclo[9.2.1.0^{2,10}.0^{3,8}]tetradeca-5,12-diene or 4,4a,4b,5,8,8a,9,9a-octahydro-1,4-methano-1*H*-fluorene **1** (CAS no [36806-69-6]) and tetracyclo[9.2.1.0^{2,10}.0^{4,8}]tetradeca-5,12-diene or 3a,4,4a,4b,5,8,8a,9,9a-octahydro-5,8-methano-1*H*-benz[*f*]indene **2** (CAS no [36806-68-5]), by reaction of bicyclononadiene (BCND) and dicyclopentadiene (DCPD) (Scheme 2). Furthermore the stereospecificity of the reaction was explained by high level quantum chemical calculations of the Hartree–Fock and density functional theory type.[8,9]

2. Results and discussion

2.1. Synthesis

A Diels–Alder reaction is performed according to Scheme 2. DCPD and BCND are mixed in a ratio 4:1, put under nitrogen and autoclaved in a Parr reactor for 6–8 h.

Theoretically, eight isomers can be expected from this reaction since bicyclononadiene (BCND) (or *cis*-3a,4,7,7a-tetrahydroindene) can react either with its double bond in the six-membered ring or in the five-membered ring, with respectively the other ring 'up' or 'down' and forming either an *exo*- or *endo*-norbornene derivative.

An exhaustive literature survey revealed only very few publications dating back to the 1970's on this type of Diels–Alder reaction.[10–13] One of these articles[13] describes the reaction of cyclopentadiene with *cis*-3a,4,7,7a-tetrahydroindene (200°C, 3 h) with formation of three products, a major one resulting from the addition to the cyclopentene ring and two minor ones from the cyclohexene ring. An assignment of all isomers and conformers was proposed solely from 1D ^{13}C NMR spectra.

The latter reaction (starting with dicyclopentadiene) resulted in our hands likewise in a mixture of several compounds, with a composition comparable to the one described, but where also very minor species are detected owing to the better sensitivity of recent NMR equipment and methods. Although the covalent structure proposed by these authors is in accordance with our findings, the stereochemistry we determined is however different for two of the three compounds. This paper revisits and completes the stereochemical characterization of the three major isomers observed, using 2D NMR techniques not available at the time the previous researchers performed their investigations.

2.2. NMR data and structure

As already stated before,[10–13] a mixture of structures of types **1** and **2** (Scheme 2) can be expected.

From the 1D ^{13}C spectrum, it is obvious that three major isomers (A–C) and three minor isomers are present. This is particularly clear in the 125–140 ppm region characteristic for the sp$_2$ carbon atoms (Fig. 1) where three times four major resonances and a comparable set of minor resonances are observed. Together the major isomers integrate for 94%, leaving 6% for the minor ones, each about 2%. The relative amounts of the major isomers are 52% for A, 28% for B and 20% for C.

The structure of the isomers was determined by a combination of several 1D and 2D ^{1}H and ^{13}C NMR techniques. Their constitutional structure was determined from ^{13}C DEPT,[14] 2D ^{1}H homonuclear DQF COSY,[15] 2D heteronuclear ^{1}H–^{13}C HMQC[16] and HMBC[17] NMR spectra, while the stereochemistry was investigated with 2D ^{1}H NOESY[18] NMR.

First, the ^{13}C chemical shifts belonging to a same specific (major) isomer were determined from the intensity of the signals in an inverse gated ^{13}C 1D spectrum and their nature

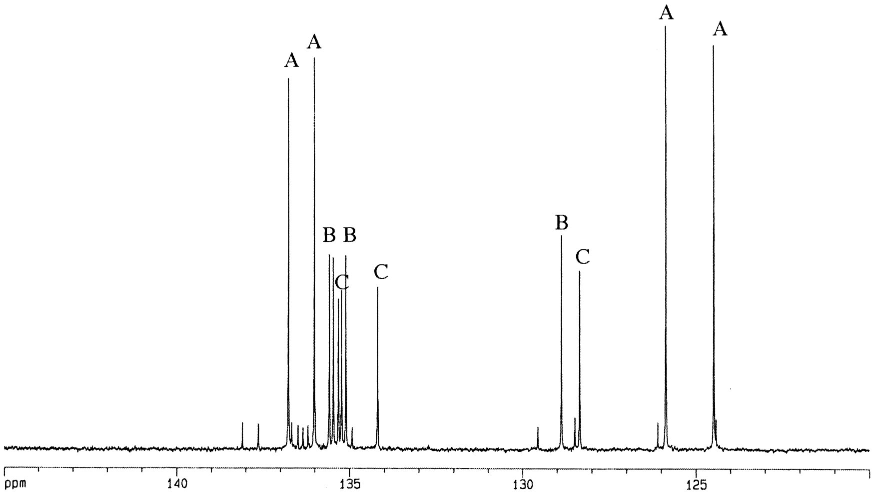


Figure 1. The high frequency region of the 1D ^{13}C spectrum of the tetrahydroindanylnorbornene mixture, showing the resonances of three major isomers A, B and C, together with minor resonances of comparable relative intensities.

was determined from the DEPT spectrum. The corresponding proton chemical shifts in the very crowded ^{1}H spectrum were found via the ^{1}H–^{13}C HMQC experiment, displaying the one bond ^{1}H–^{13}C connectivities. Neighbouring protons were found from the DQF COSY and confirmed or completed by unravelling the ^{1}H–^{13}C HMBC spectrum.

Isomer A turned out to be an octahydro-fluorene (**1**) derivative, whereas B and C are two octahydro-benz[f]-indene (**2**) derivatives. From now on, these particular isomers will be called **1a**, **2a** and **2b**.

The ^{1}H and ^{13}C chemical shifts are summarized in Tables 1 and 2. Once the covalent structure determined, it was possible to assign the relative stereochemistry by interpretation of the 2D NOESY spectrum.

For compound **1a** a cross-peak is observed between one of the H-9 (1.01 ppm) and the H-2 proton signals, which is only possible for *endo*-norbornene. Correlations between the resonances of H-9a and one of the H-8 protons (1.73 ppm) and between H-4a and one of the H-5 protons (1.96 ppm) are conclusive for the 'up' orientation of the cyclohexene ring. This is in accordance with the structure proposed earlier,[10] were however, the assignments of the ^{13}C chemical shifts of 4b and 9a are interchanged.

Table 1. ^{1}H and ^{13}C chemical shifts for **1a**

Atom	δ ^{13}C (ppm)	δ ^{1}H (ppm)
1	45.5	2.73
2	136.0	6.13
3	136.8	6.14
4	44.2	2.73
4a	51.6	2.34
4b	37.8	1.47
5	26.6	1.96, 2.16
6	124.5	5.56
7	125.9	5.64
8	28.3	1.48, 1.73
8a	39.7	2.09
9	35.2	1.01, 1.42
9a	45.1	2.76
10	54.2	1.46, 1.66

For compound **2a** a cross-peak between one of the H-10 proton signals (1.20 ppm) and both H-8a and H-4a resonances unequivocally proofs the *endo*-configuration, in contrast to the *exo*-configuration proposed earlier.[10] No cross-peaks are found between the H-8a or H-4a and the H-9a or H-3a signals respectively suggesting the cyclopentene-ring is 'up'. A cross-peak between the resonances of H-4a and H-3 suggests a conformation with a relatively short distance between these protons, i.e. the cyclohexane ring having a boat conformation. This is confirmed by a cross-peak between one of the H-4 (0.93 ppm) and one of the H-9 (1.00 ppm) proton signals due to a bow-to-stern interaction.

For compound **2b** again the cross-peaks found between one of the H-10 proton signals and the H-4a and H-8a resonances are conclusive for an *endo*-configuration (*exo* in[10]). A cross-peak is found between the H-4a and H-3a signals as well as between H-4a and H-9a and between H-8a and H-3a. These cross-peaks prove the cyclopentene-ring is 'down'. The cross-peak between the signals of one of the H-4 protons (0.49 ppm) and one of the H-9 protons (0.63 ppm) suggests a boat conformation with a bow-to-stern interaction, a fact that is corroborated by the low

Table 2. ^{1}H and ^{13}C chemical shifts for **2a** and **2b**

Atom	2a		2b	
	δ ^{13}C (ppm)	δ ^{1}H (ppm)	δ ^{13}C (ppm)	δ ^{1}H (ppm)
1	39.1	2.24, 2.58	40.3	1.87, 2.59
2	128.9	5.60	128.4	5.55
3	135.6	5.44	134.2	5.46
3a	44.0	2.93	46.4	2.66
4	28.0	0.93, 1.52	30.3	0.49, 1.60
4a	34.4	1.92	39.2	2.01
5	46.6	2.66	45.8	2.73
6	135.1[a]	6.06	135.2[a]	6.05
7	135.5[a]	6.06	135.3[a]	6.05
8	46.6	2.62	46.5	2.60
8a	33.2	1.99	39.0	1.95
9	30.5	1.00, 1.34	32.0	0.63, 1.51
9a	32.3	2.51	35.3	2.26
10	49.1	1.21, 1.39	49.5	1.28, 1.46

[a] Assignment can be interchanged between atoms 6 and 7.

chemical shift of these two protons which results in two well separated first-order multiplets, that are interpreted both as doublets of doublets of doublets, appearing quartet-like because they result from diaxal vicinal proton–proton couplings combined with a geminal one of identical magnitudes.

All the higher mentioned NOESY NMR data are in complete agreement with the spatial structures (Fig. 2), optimised with the aid of the Gaussian 98 set of programs (details are given in Section 4).

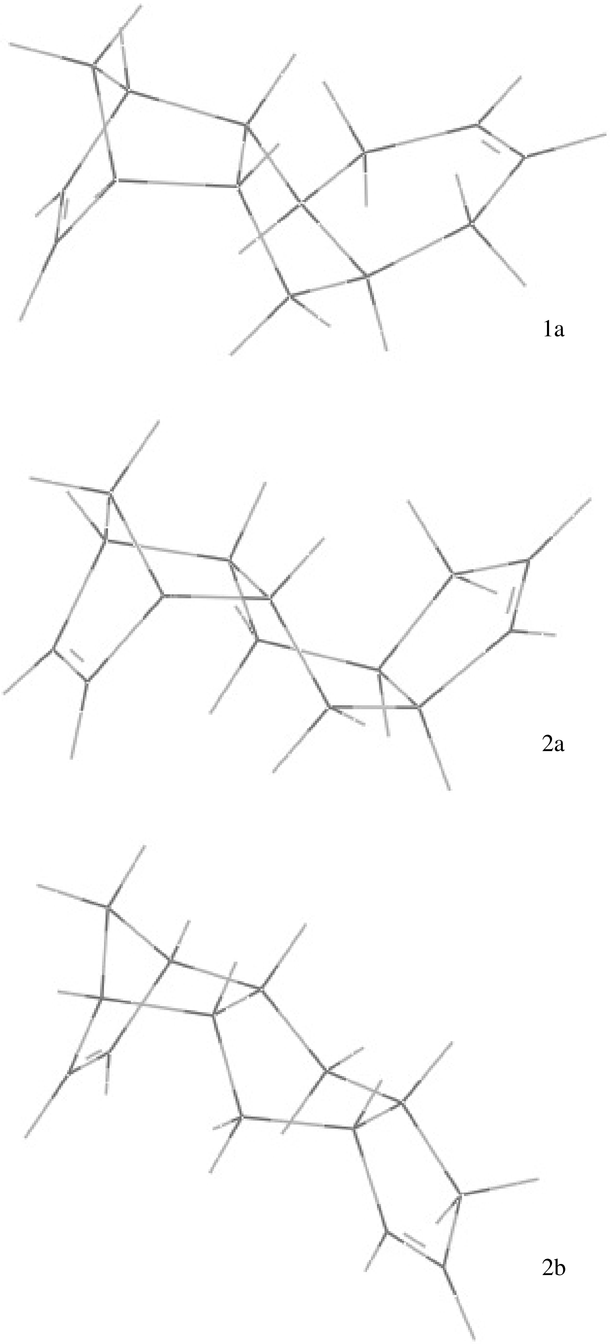


Figure 2. The spatial structures of isomers **1a**, **2a** and **2b**, optimised at the HF/6-31G(d) level followed by re-optimisation at the B3LYP/6-31G(d) level.

From the composition of the reaction mixture, it turns out that there is no preference for the reaction of the double bond of either the cyclopentene or cyclohexene ring since about equal amounts of both are present (52/48). In all cases the *endo*-isomers are formed, as could be expected from the '*endo* rule' in Diels–Alder reactions. Although no analysis of the minor components is made, they can be assumed to be the *exo*-counterparts of the three major isomers **1a**, **2a** and **2b**. However, where reactions with the cyclohexene side proceeds both ways giving an isomer with a cyclopentene up and an isomer with a cyclopentene down, only one isomer is obtained through reaction with the cyclopentene double bond.

2.3. Theoretical investigations

In an attempt to understand the experimentally observed stereospecificities, it was decided to perform quantum chemical calculations in order to investigate the Diels–Alder reaction of bicyclononadiene with dicyclopentadiene.

High level ab initio and B3LYP/6-31G(d) DFT methods have proved to give excellent results for energy barrier estimation of cycloaddition reactions.[19–21] These ab initio and DFT calculations have previously been used to predict stereospecificities of different Diels–Alder reactions of cyclic dienes with cyclic dienophiles.[22,23] Consequently, we have used the HF/6-31G(d) and B3LYP/6-31G(d) levels of theory to investigate the potential energy surface (PES), by means of the location of transition structures and related minima. This will enable us to rationalize and explain the experimental observations as was done in the past by some of the present authors, for example, on the [2+1] cycloadditions of hydrogen isocyanide[24] or CO and CS[25,26] to alkynes.

The total energies of the calculated molecules and their associated transition states are shown in Fig. 3. The formation of a reactant complex at lower energy than the reactants is similar to the both experimentally and theoretically well-documented cases of gas phase S_N2 reactions[27–29] or radical abstraction reactions.[30–32]

B3LYP transition state structures are depicted in Fig. 4. All located transition state structures correspond to the concerted synchronous mechanism. Four final products **1a**, **1b**, **2a** and **2b** can be formed via the corresponding transition states **TS1a**, **TS1b**, **TS2a** and **TS2b** respectively. A B3LYP/6-31G(d) exploration of the PES along the four reactive channels (see Fig. 3) points out that the most reactive channels correspond to the final cycloadduct **1a**, **2a** and **2b** via their corresponding **TS1a**, **TS2a** and **TS2b**, respectively, whereas the most unfavourable reactive channel corresponding to **1b** requires higher energy. It is interesting to note that the PES difference between the **1a** and **1b** isomers (15.7 kJ/mol) is higher than for **2a** and **2b** isomers (1.8 kJ/mol). Therefore, these results give a theoretical ab initio basis to the experimental data.

Calculating the activation energies by taking the energy differences between the transition states (TS) and reactant complexes (Comp) for each product reveals the sequence **1b** (131.2 kJ/mol)$\gg$**1a** (114.6 kJ/mol)$>$**2a** (109.0 kJ/mol)$\approx$**2b**

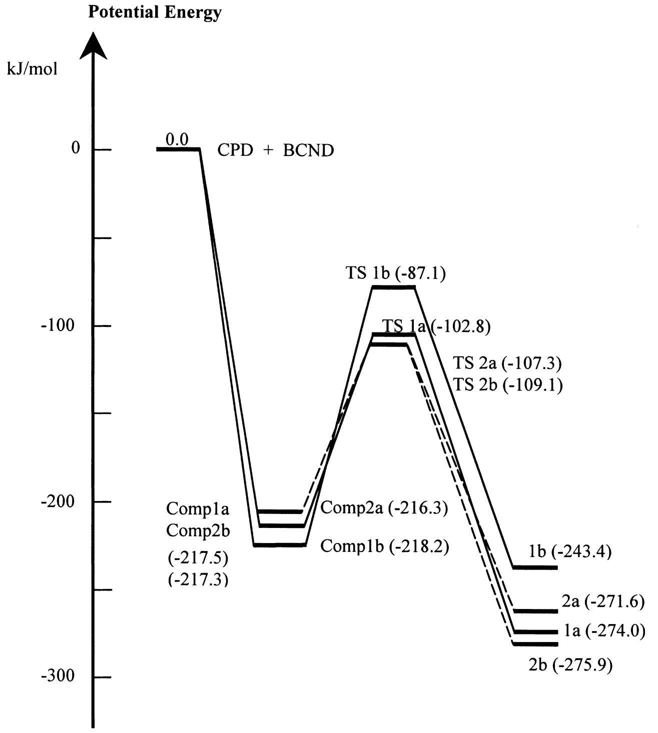
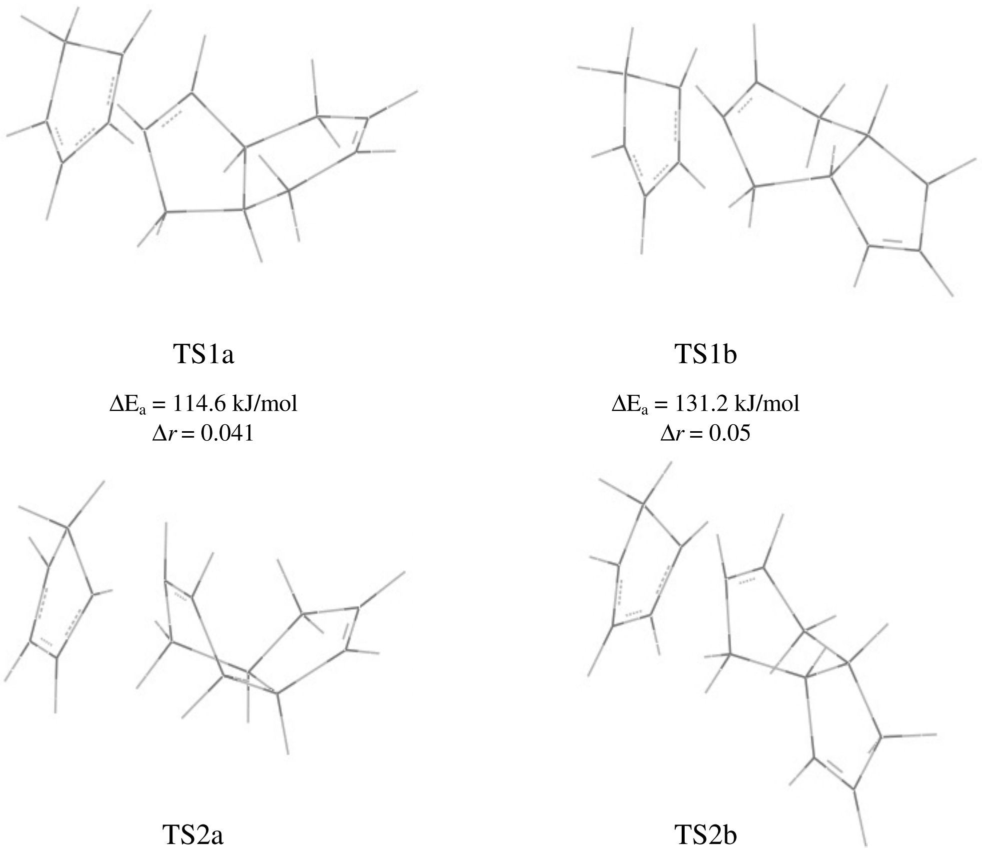


Figure 3. The relative energies of the reactant complexes ('comp'), transition states ('TS') and products with respect to the isolated CPD and BCND reactants calculated at the B3LYP/6-31G(d) level.

(108.2 kJ/mol). The same sequence is also found in the reaction energies calculated as the difference in energy between the reactant complex and the final product, e.g. **1b** (−25.1 kJ/mol)≫**1a** (−56.5 kJ/mol)≈**2a** (−55.3 kJ/mol)≈**2b** (−58.6 kJ/mol). These sequences are in line with the main directions of the experiments indicating the absence of **1b**, and comparable amounts of **1a**, **2a**, and **2b**. Finer details of the sequence **1a**, **2a**, and **2b** are hard to explain within the few kJ range of both the activation energies and reaction energies.

For the transition state **TS1a**, the lengths of the C4–C4a and C1–C9a forming bonds are 2.270 and 2.229 Å, respectively. This transition state corresponds to a concerted cyclo-addition process where the two σ-bonds are asynchronously formed. The extent of the asynchronicity can be measured by means of the difference between the lengths of the two σ-bonds that are being formed in the cyclo-addition process, i.e. $\Delta r = l(\mathrm{C4{-}C4a}) - l(\mathrm{C1{-}C9a})$. For **TS1a**, this value is $\Delta r=0.041$. However, a different behavior is found for **TS2a** and **TS2b**, where negative values of Δr for the C8–C8a and C5–C4a forming bonds, are observed. For all transition states there is a correlation between the asynchronicity of the bond formation process and the corresponding relative energies: an increase of the asynchronicity (Δr) is accompanied by an increase of PES.



TS1a

$\Delta E_a = 114.6$ kJ/mol
$\Delta r = 0.041$

TS1b

$\Delta E_a = 131.2$ kJ/mol
$\Delta r = 0.05$

TS2a

$\Delta E_a = 109.0$ kJ/mol
$\Delta r = -0.015$

TS2b

$\Delta E_a = 108.2$ kJ/mol
$\Delta r = -0.021$

Figure 4. B3LYP/6-31(d) structures of the transition states TS for the concerted pathway of the Diels–Alder reaction of CPD with BCND; ΔE_a and Δr are the activation energies and the extent of asynchronicity (see text) respectively.

3. Conclusion

The Diels–Alder reaction between dicyclopentadiene and bicyclononadiene gives rise to three major reaction products out of eight possible structures. These three major reaction products are fully characterized by advanced 2D NMR techniques. They are all three *endo*-isomers. No preference is observed for the reaction of the double bond of either the cyclopentene or cyclohexene ring of the starting bicyclononadiene. However, where reactions with the cyclohexene side proceeds both ways giving an isomer with the cyclopentene ring 'up' and one with the ring 'down', only one isomer is obtained for the reaction with the cyclopentene double bond. This experimental outcome is confirmed by quantum chemical calculations investigating the potential energy surface along the reactive channels for four final products and indicating an unfavourable energy profile for the fourth isomer that is indeed not obtained experimentally.

4. Experimental

4.1. Monomer preparation

The monomers are obtained as a mixture from the Diels–Alder reaction of dicyclopentadiene (DCPD) with bicyclononadiene (BCND) performed in an autoclave at 180°C for 6–8 h under 1 bar of starting nitrogen pressure with a BCND/DCPD ratio of 4:1. Purification is achieved by distillation in vacuo (boiling point: 117.2–118.5°C at 10 mbar).

4.2. NMR experiments

The ^{1}H and ^{13}C NMR spectra were recorded at 303 K in $CDCl_3$ on a Bruker AMX500 spectrometer. Chemical shifts were referenced to the residual solvent peak and converted to the standard Me_4Si scale by adding 7.23 and 77.0 ppm for ^{1}H and ^{13}C respectively. The 1D ^{13}C DEPT and gradient pulsed proton detected 2D $^{1}H-^{13}C$ HMQC and HMBC correlation spectra as well as the 2D ^{1}H NOESY and DQF COSY spectra were acquired using the pulse sequences of the Bruker program library.

4.3. Computational methodology

All quantum chemical calculations were carried out with the aid of the Gaussian 98 set of programs.[33] Geometrical parameters of the relevant structures were initially optimised at the HF/6-31G(d) level followed by re-optimisation at the B3LYP/6-31G(d) level. Analytical harmonic vibrational wave numbers of these stationary points have again been computed at the same B3LYP level in order to verify further their identity and to estimate the zero-point energies (ZPEs), which then were scaled down by a factor of 0.9806.[34] Throughout this paper, bond distances are given in Å, bond angles in degrees, total energies in hartrees, and zero-point and relative energies, unless otherwise noted, in kJ/mol.

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